NORTHWESTERN UNIVERSITY

Cage Structure Materials for n-type Transparent Conducting Oxides

A DISSERTATION

SUBMITTED TO THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

for the degree

DOCTOR OF PHILOSOPHY

Field of Materials Science and Engineering

By

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EVANSTON, ILLINOIS

June 2007

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ABSTRACT

Cage Structure Materials for n-type Transparent Conducting Oxides

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The transport properties of may enite-based materials, Ca₁₂Al₁₄O₃₃, were investigated. Systems studied included H-doped/UV-irradiated Ca₁₂Al₁₄O₃₃, Ca_(12-x)Mg_xAl₁₄O₃₃ (x = 0.1, 0.3, 0.5, 0.8, 1) and Ca₁₂Al_(14-x)Si_xO_(33+ $\frac{x}{2}) (x = 1, 2, 3, 4). The as-prepared Ca₁₂Al₁₄O₃₃ exhibited a room temperature electronic conductivity on the order of 10⁻¹⁰ S/cm, and a high temperature (600 °C) ionic conductivity approximately an order of magnitude less than that of yttria-stabilized zirconia. After H-doping/UV-irradiation Ca₁₂Al₁₄O₃₃ displayed an electronic conductivity of 0.3 S/cm at room temperature rising reversibly to 1 S/cm at ~130°. Beyond this temperature hydrogen loss is evident and with it the carrier concentration decreases. Below room temperature the system exhibits a variable range hopping and a small polaron hopping above room temperature. H-treated/UV-irradiated Mg-substituted compounds present inferior electrical properties compared to Ca₁₂Al₁₄O₃₃, with conductivities in the range of 0.15 - 0.28 S/cm at room temperature. Magnesium is suggested to be responsible for the overall decrease in conductivity, as theoretical calculations suggest that it acts as a blocking agent. On the other</sub>$ hand, the proton-implanted/UV-irradiated $\operatorname{Ca}_{12}\operatorname{Al}_{(14-x)}\operatorname{Si}_{x}\operatorname{O}_{(33+\frac{x}{2})}$ shows an increase in conductivity, consistent with the aliovalent substitution. Conductivities of 0.68 S/cm were found for the higher Si-substitution level (in H-implanted specimens) suggesting that the amount of free oxygen ions inside the structural cavities plays a significant role in determining the electrical properties of the compound. Results are in good agreement with density functional calculations performed on all these systems.

The highly reduced $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system presents a wide range of conductivities dependent on the reduction time. The maximum value obtained was 1400 S/cm for $Ca_{12}Al_{14}O_{33}$ reduced in the presence of titanium shot for 4 days of treatment. A reversal in the sign of the thermopower was observed for the high conductivity samples. The temperature dependance of the conductivity shows degenerate behavior above room temperature, and a linear relation between the resistivity and temperature below room temperature. This degenerate behavior suggests an insulator-to-metal conversion, however, it can also be explained by the small polaron mechanism observed for the H-treated/UV-activated mayenite-based samples. Ultimately, mobility data will define the type of mechanism governing this compound's behavior.

Approved:

Prof. Thomas O. Mason

Department of Materials Science and Engineering Northwestern University, Evanston, IL Jan. 10th, 2007

Acknowledgements

I would like to thank my two advisors, I wouldn't have made it here without their guidance and support. Prof. Thomas Mason, your patience is admirable and your passion for teaching is really contagious, thank you for sharing it with me. Prof. Ken Poeppelmeier, thanks for always pointing me in the right direction even if that meant to read the same paper for the 10th time. You showed me I can enjoy Chemistry almost as much as skiing.

I am infinitely grateful to Prof. Julia Medvedeva, a great physicist and friend; I will always be indebted for her help. Thanks for walking me through the mysteries of physics, and for always finding the time to teach me some more. I want to specially acknowledge Prof. Art Freeman, I greatly benefited from his knowledge and challenging ideas.

I am grateful to the Fulbright program and the Materials Research Science and Engineering Center at Northwestern University for providing the funding for my project.

I want to thank present and former members of my two groups for insightful discussions and good times. Dr. Brian Ingram, no words are enough to express my gratitude for mentoring me in the ups and downs of this process, I owe you more than one beer. Dr. "Ni" Wansom, I couldn't have have a better IS teacher, thanks for being your wonderful self. Dr. Neil Kidner, if there is anyone with infinite patience that's you Neil, thanks for always finding some time for my questions and for sharing with me the passion for the beautiful game. Dr. Leta Woo, all that I know about American politics I learned from you, thanks for teaching me it's good to disagree. "Lance" Harvey, you did teach me that there is "clean" and there is "Lance clean", I think we hold the all time record for the biggest clean in the Mason's lab. I'll miss talking to you through the window glass every morning. Courtney Lanier, thanks for your friendship all these years, I'm going to miss you. Dr. Ian Saratovsky and Dr. Jared Smit, you taught me life should be taken a little bit more lightly ... thanks guys!. Evan Stampler, your bitter sense of humor made me laugh all these years, don't lose it. Jake Haag, thanks for always having a smile and a good story, I'll miss laughing with you. I know I'm forgetting people, my apologies and thanks to all of you.

My deep gratitude to Peggy Adamson and Tracy Bruhn, you are amazing and I wouldn't have survived graduate school bureaucracy without your help. Marko Seniw, thanks for always being there "ching-ching".

Very special thanks to Nasim Alem, Norma Cortes, Steve May and "Lance" for your hard effort in helping me run some experiments, I owe you one.

Thanks to all my friends, close and far away, you make life a wonderful experience and a reason to smile every morning, I love you all.

Infinite thanks to my family in Argentina. Mama y Papa, you have more faith in me than my own self, I have no words to express my love for you. To my Abuelos, my biggest fans, thanks for the wisdom and unconditional support. Ivana y Marcela, my sisters and best friends, thanks for always having a sympathetic ear, the right word to cheer me up and being my tether to earth. Los quiero muchisimo !

I'm extremely grateful to my family here, thanks for your support and love, you definitely changed my life. Special thanks to my husband, Arno, for sharing with me the laughs, detours and oddities along the road. You are the best and I love you deeply.

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CHAPTER 1

Introduction

1.1. Transparent conducting oxides overview

Transparent conducting oxides (TCOs) are materials that exhibit high transparency in the visible range of the electromagnetic spectrum as well as high electrical conductivity. Thin films of these materials find applications as the transparent electrodes of a wide range of devices including flat-panel displays, electrochromic windows, photovoltaic systems, deicers and emerging applications such as flexible and invisible electronics [7, 8, 9, 10, 11].

The common way of achieving the two mutually exclusive characteristics of transparency and conductivity is by degenerately doping a wide band gap oxide, pushing the Fermi levels well into the conduction band. Figure 1.1 shows a schematic band structure from Hamberg and Granqvist that display the fundamental electronic structure required for n-type behavior [12].

As derived from Ohm's law the conductivity (σ) is the proportionality constant relating the current density to an applied electric field, and it is given by:

(1.1)
$$\sigma = \frac{nq^2\tau}{m^*} = nq\mu$$

where q is the fundamental unit of charge, m^* is the effective mass, τ is the relaxation time, n is the carrier concentration and μ is the mobility. Enhancement in the conductivity can be obtained by increasing the carrier concentration or the mobility. The later can



Figure 1.1. Schematic from Hamberg and Granqvist showing a degenerately doped wide band gap oxide.

be increased by increasing the relaxation time or decreasing the effective mass. A long relaxation time implies a low defect population (assuming ionized impurity scattering) and hence long times between scattering events. A small effective mass implies low inertia carriers that are easily moved by an applied force.

TCOs transmit light in the visible region and in the near infrared (NIR). As a consequence of their high free carrier density, TCO materials tend to reflect a substantial portion of the incident radiation at longer wavelengths, just like metals, and therefore are ideal for coatings on energy efficient-windows. This transition happens at the plasma frequency, (ω_p) that can be calculated using the Drude theory of free electrons [13, 14].

(1.2)
$$\omega_p^2 = \frac{e^2 N}{m_e^* \varepsilon_0 \varepsilon_\infty}$$

where e is the charge of an electron, m_e^* is the effective mass, N is the carrier concentration, ε_0 is the permittivity of free space and ε_∞ is the high frequency permitivity. At high frequencies (short wavelengths) the incident light has enough energy to excite an electron from the valence to the conduction band. In the case of an insulating oxide this would be equal to the fundamental band gap. However, as TCOs have their Fermi levels inside the conduction band, the energy needed to promote an electron from the valence to the conduction band is significantly larger than the fundamental band gap. This effect was first described by Burstein and Moss [15, 16] and is commonly known as the Burstein-Moss shift, as seen in Fig. 1.1. Hence, for applications as transparent electrodes, the usable optical window extends from the plasma frequency to the frequency related to the effective band gap. Also note from Eq. 1.2 that a large carrier concentration can shift the plasma edge into the visible range and limit the transparency. This effect was first seen and reported by Hamberg and Granqvist on ITO [12, 17].

The co-existance of transparency and conductivity in oxides was first observed in 1931 in SnO₂ [18] and a decade later the first SnO₂-based films on glass were patented [19] and employed as windshield de-icers in World War II. The following decades saw the development of In_2O_3 : Sn (ITO) with conductivities on the order of $1 \cdot 10^4$ S/cm and excellent optical properties [20, 21]. ITO along with SnO₂: F and ZnO : Al are still the most used and widely studied transparent conductors among the oxides. However, a large number of alternative ternary oxides have been under exploration for the last couple of decades, including Cd₂SnO₄, Zn₂SnO₄, MgIn₂O₄, ZnSnO₃, GaInO₃, Zn₂In₂O₅ and In₄Sn₃O₁₂ [9, 7, 22, 23, 24]. The families of all these new potential TCOs have been summarized by T. J. Coutts et. al. in the phase space of binary oxides shown on Fig. 1.2 [13]. Many of these materials have shown some improvement in their properties over



Figure 1.2. T. Coutts phase space representation of binary, ternary and quaternary oxides under study for TCO applications.

the established commercial ones, although none of them has yet had sufficient overall properties to clearly replace them [7].

1.2. Motivation for this study

In the past few years, the perception that ZnO- and InSnO-based materials were sufficient for TCO applications has begun to change. The acknowledgments of the limitations of the existing materials coupled with the fast growing need for larger-area display devices with greater signal speeds is opening the way to new and improved materials. In addition to the need of finding a more conducting TCO, there is a need to reduce the dependence on the element Indium as the main component of the commercial TCOs. At present, the flat panel display (FPD) industry utilizes more tin doped indium oxide than any other industry requiring TCOs [7, 13, 24]. The worldwide market for FPD went from \$ 24.6 billion in 2000 to \$ 37.7 billion in 2003. By 2006, the FPD industry is expected to reach \$ 65.5 billion, according to DisplaySearch, a market information firm. The compound annual growth rate (CAGR) of FPD over the entire period 2000 to 2006 is just under 18 percent, more than four to six times the estimates of the gross domestic product (GDP) growth rate of the world's leading economies. Currently, the main driver for FPD industry growth is the accelerating substitution of FPD for cathode ray tube displays in desktop monitors. By 2006, nearly 80 % of desktop monitor units shipped are expected to be FPD. In addition to this fast growing market we should consider the photovoltaic industry that continues to grow at a steady pace of 25-30% year. It is expected that the demand of these two combined markets will increase far beyond the production of indium in the next ten years. Moreover, the Earth is estimated to only contain about 0.1 ppm of indium which means it is about as abundant as silver, although indium is in fact nearly three times more expensive by weight. Fig. 1.3 shows the evolution through the years of the market price of the five metals whose oxides show TCO properties, plus aluminum for the purpose of comparison.

Clearly In and Ga are in a different range of price due principally to their scarcity, however, after the FPD industry had its boom the prices have decreased considerably mainly governed by the demand. Of the rest of the cations, Cd has been the one to show great promise, however, its potential role in human carcinogenesis prevents wide scale acceptance [13].

On the other hand there are not many options if we consider that most of the useful oxide-based materials are n-type conductors that ideally have a wide band-gap (> 3 eV), the ability to be doped to degeneracy, and a conduction band shape (governing its effective mass) that ensures the plasma absorption edge lies in the infrared range. Alternatives are



Figure 1.3. Prices of the most commonly used TCO materials from United States Department of Interior, geological survey.

still being studied in these same systems, based on new and more advanced deposition techniques as well as the idea of using amorphous phases instead of crystalline ones.

This study was based on the need for inexpensive and environmentally benign TCO alternatives. The idea of rendering oxides of the main-group metals conducting by alternative processes was the main focus of this work. A report in 2002, where a well-known insulating oxide widely used in high-alumina cements was rendered conductive triggered this research [25]. The objective of this study was to understand this new activation

technique and the opto-electronic properties imparted to the host material in order to formulate a new criterion to obtain high electrical conductivity and complete transparency from oxides that were never considered an alternative before.

1.3. Approach

In 2002, the insulating oxide 12CaO-7Al₂O₃ (or Ca₁₂Al₁₄O₃₃) was reported to be rendered conductive by hydrogen doping and subsequent UV light irradiation [25]. This new discovery opened the possibility of reconsidering main-group metals for designing TCO materials. In striking contrast to the conventional process for designing TCOs, this approach requires the host material to be an insulator with a band gap > 6.2 eV and a concentration of impurities (e.g. H⁻, OH⁻, Cl⁻) large enough so the overlap of their electronic wave functions will form an impurity band inside the gap. The impurity band leads to a high carrier mobility due to the extended nature of these states, resulting in a relatively low scattering. Furthermore, if the impurity band is narrow enough (< 1.8 eV) the intraband transitions will be kept below the visible range, as well as the plasma frequency. Contrary to the commonly used materials for TCO applications, where due to the interband-transitions from the partially occupied band at the top of the conduction band, 100% transparency can never be achieved, this approach suggests that the combination of 100% optical transparency and high electrical conductivity may be feasible [26].

CHAPTER 2

Literature Review and Background

2.1. Donor doping of existing TCO materials

All well-known TCOs share similar chemical, structural and electronic properties as well as carrier generation mechanisms. These oxides come from post-transition or transition metals and have a generally closed-packed structures with four- or six-fold coordinated metal ions. Upon introduction of native or substitutional dopants, they show high transparency in the visible range and high electrical conductivity. Common to all TCOs, a highly dispersed band at the bottom of the conduction band is the most important feature of the host electronic band structure. It is responsible for the high mobility of the carriers (electrons) owing to their small effective masses and the low optical absorption plus a pronounced Burstein-Moss shift, which helps to keep intense interband transitions out of the visible range [15, 16]. It is widely accepted that n-type TCO materials should contain a metal with a $(n-1)d^{10}ns^0$ electronic configuration, that the valence band is formed by $O^{2-}:2p$ bonding states and the $3d^{10}$ state of the metal lies well below the valence band edge. Also that the conduction band is constituted by 5s antibonding states [27, 14]. When a donor is introduced or an impurity band that overlaps the edge of the conduction band is formed, a degenerate semiconductor is produced. If the concentration of the donor or the impurities is low, the Fermi energy (E_F) appears right below the conduction band edge, but for high concentrations the E_F rises above the conduction band



Figure 2.1. Fan and Goodenough schematic representation of energy band model for ITO for small and large donor levels and/or impurity concentration.

edge. Figure 2.1 taken from Fan and Goodenough exemplifies this for the case of In_2O_3 , where the impurity band is formed by oxygen vacancies and/or Tin 5s donor levels [27].

2.2. Main group metal-oxides in TCOs

In 1977 Shannon et. al. introduced a new group of ternary oxides and speculated that continuous edge sharing of Cd^{2+} , In^{3+} and Sn^{4+} octahedra were a necessary criterion for the formation of a transparent conductor [28]. Following these early studies, a number of research groups have studied complex oxides as TCO materials [29, 22, 30, 9]. A recent studied evaluated why this octahedral coordination about the cation is such a dominant feature and whether electronically inert cations can be effectively used for TCO applications. Mizoguchi and Woodward were the first ones to explore the use of divalent and monovalent main-group cations (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Na⁺, K⁺, Ag⁺, Cd²⁺, Zn²⁺) for applications in the design of TCOs materials. Their work considered degenerately doping a ternary oxide with main group cations. They reported studies in perovskites and pyroclore structures [31], extended later to rutile (SnO_2) , trirutile, PbSb₂O₆-type and ilmenite [32].

Their studies on the structural and compositional features that favor the occurrence of transparent conductivity showed that the coordination of the anion, rather that the cation plays the pivotal role dictating the the dispersion of the conduction band. If the anion coordination environment is symmetric (referring to the covalent bonding interactions with the surrounding cations) and the anion-cation bond is reasonably covalent, the conduction band will be disperse. They showed that the anion coordination is fairly symmetric in many binary oxides (ZnO, CdO, In_2O_3 and SnO_2). Upon going to a ternary compound $A_x M_y O_z$ where M is a main group ion, typically the higher valent M cations will be asymmetrically arranged around oxygen and the lower valent A cations will complete the coordination sphere. If the covalency of the A-O and M-O interactions are not too different, as they would be when the A cation has an $(n-1)d^{10}ns^0$ electron configuration, the bonding at oxygen is likely to remain reasonably symmetric and a dispersed conduction band will result. While the conduction band will not be as dispersed as a binary oxide, the extra freedom to manipulate the composition and structure allow the possibility to tailor the electronic energy levels in complex TCO materials needs. So the approach of degenerately doping a ternary oxide with a main-group metal should be discounted, with the exception of the perovskite $BaSnO_3$, where a symmetric arrangement of M-cations can be obtained around the oxygen, but it has not been proven to reach doping levels to become highly conductive. A totally different approach has to be considered to use main-group metals for TCO applications.

2.3. Mayenite materials

2.3.1. Structure

Mayenite, $Ca_{12}Al_{14}O_{33}$, is an insulating material with a band gap of 4.8 eV. It is a bodycentered cubic crystal that belongs to the space group I43d with a lattice parameter equal to 11.989 Å[1]. The unit cell posses 118 atoms and contains two molecules of $Ca_{12}Al_{14}O_{33}$. It is a cage-like structure with 12 cages per unit cell as shown in Fig. 2.2. Table 2.1 shows the atomic parameters as reported by Bartl and Scheller [1]. The cages are approximately 5 Åin diameter and have openings between cages of 3.5 Å. These entrances are believed to control the mass transport between the inside and outside of the cages. The chemical formula may be represented by $[Ca_{24}Al_{28}O_{62}]^{+4}+2O^{-2}$, where the former denotes the lattice framework and the latter are the free oxygen ions that give charge neutrality to the lattice. If we divide the charge of the framework by the total number of cages, $(\frac{4}{12})$, we see that each cages has a mean effective charge of $+\frac{1}{3}$. The free oxygen ion is accommodated into the cage to compensate the positive charge of the framework and is coordinated to six Ca^{2+} that form part of the walls of the cage. The spacing in between the free oxygen ion and the closest Ca^{2+} cation is 3/2 times bigger than the sum of their effective ionic radii, suggesting that the O^{-2} ion is loosely bound to the framework. Figure 2.2 shows the structure of a $Ca_{12}Al_{14}O_{33}$ cage and the complete unit cell.

2.3.2. Ionic conductivity

The first report regarding the electrical properties of the $Ca_{12}Al_{14}O_{33}$ crystal dates from 1988, when Lacerda et al.. found that as prepared mayenite exhibit oxide ion conductivity within an order of magnitude smaller than that of yttria-stabilized zirconia (YSZ)



Figure 2.2. (a) Cage of $Ca_{12}Al_{14}O_{33}$ (b) Unit cell of $Ca_{12}Al_{14}O_{33}$ containing 12 cages.

Table 2.1. Atomic parameters and symmetry dependance from Bartl and Scheller [1].

	Ca	Al(1)	Al(2)	O(1)	O(2)	O(3)
x/a ₀	0	0.0187(4)	-0.125	0.151(1)	-0.064(1)	0.337(15)
y/a_0	0.25	0.0187(4)	0	-0.037(1)	-0.064(1)	0
z/a_0	0.1397(4)	0.0187(4)	0.25	0.057(1)	-0.064(1)	0.25
β_{11}	0.0015(2)	0.0010(2)	0.0006(4)	0.0018(6)	0.0013(5)	0.003(9)
β_{22}	0.0015(2)	0.0010(2)	0.0007(3)	0.0017(6)	0.0013(5)	0.001(7)
β_{33}	0.0019(3)	0.0010(2)	0.0007(3)	0.0014(6)	0.0013(5)	0.002(9)
β_{12}	0.0001(2)	0.0000(1)	0	0.0009(6)	0.0000(5)	0
β_{13}	0	0.0000(1)	0	0.0003(5)	0.0000(5)	0
β_{23}	0	0.0000(1)	0	0.0004(5)	0.0000(5)	0.001(9)
[33, 34]. In their report conductivity measurements were performed by impedance spectroscopy and subsequently the conducting species were confirmed using a concentration cell, where opposite pellet surfaces are exposed to different atmospheres and the cell voltage is measured as a function of temperature.

2.4. Hydrogen treatment

Two main activation processes have been discovered to render the insulating $Ca_{12}Al_{14}O_{33}$ oxide conductive:

1) Hydrogen-doping (or hydrogen-implantation) followed by ultra violet (UV) light irradiation

2) Removal of the free O^{-2} species through severe reduction

The first process was reported in 2002 by Hayashi et al. [25], when it was discovered that $Ca_{12}Al_{14}O_{33}$ could incorporate hydrogen at elevated temperatures through the following chemical reaction:

(2.1)
$$O^{-2} + H_2 \rightarrow OH^- + H^-$$

The treatment was undertaken at 1300 °C for 2 h in a mixed atmosphere of 20% H_2 / 80% N₂ followed by a rapid quenching to room temperature. The rapid quenching prevents diffusion inside the structure of atmospheric species and outside the structure of extra framework species. In a later work Hayashi reported that high treatment temperatures enhance the formation of H⁻ [35]. After hydrogen incorporation the unit cell contains two cages occupied by OH₋, another two occupied by H₋ and the remaining 8 cages of the unit cell are empty. Nuclear Magnetic Resonance (NMR) verified the presence of H⁻

species in the hydrogenated sample at a concentration comparable to that of OH⁻ anions [25].

Hydrogen annealing results in no apparent change in the optical and electrical properties of the material. However, upon ultraviolet (UV) irradiation two optical absorption bands are induced, giving rise to a persistent color change from white to green together with a considerable conductivity increase from 10^{-10} S/cm to 0.3 S/cm at room temperature. A detectable signal in electron paramagnetic resonance (EPR) was suggested to indicate the presence of paramagnetic ions or defect centers. The negative shift of the g-factor ($\Delta_g = g - g_e$) indicates also that the center responsible for the signal is associated with a trapped electron. The lack of hyperfine splitting showed that this trapped-electron center has to be coordinated to Ca²⁺, whose natural abundance in the nonmagnetic form is 99.9%. The report suggested that the electron originated from ultraviolet irradiation according to:

$$(2.2) H^- + Energy \to H^0 + e^- + phonon$$

Hayashi et al. proposed also that an empty cage, with a net positive charge of $+\frac{1}{3}$, electrostatically captures this electron and forms an F^+ -like center and that electron migration is due to variable range hopping from cage to cage.

A subsequent study by Hayashi [35] showed that if the conductivity is governed by a hoping from cage to cage, there has to be a high potential barrier to prevent the inversion process and stabilize the conductive state. This stabilization was ascribed to the reaction of H^0 with extra framework O^{-2} ions according to:

(2.3) Emptycage₍₁₎ +
$$H_{(2)}^-$$
 + $O_{(3)}^{-2} \rightarrow OH_{(3)}^-$ + $e_{(1)}^-$ + $e_{(2)}^-$

where the subscripts identify different cages.

2.4.1. F / F^+ -centers

F-centers have been known for a long time as color centers in alkali halides. Evidence of the existence of *F*-centers in the alkaline earth oxides was first reported by Wertz et al. (1957) in MgO [36]. Since then the de Boer model of an *F*-center as an anion vacancy with a single trapped electron has been confirmed for CaO, SrO and BaO by electron spin resonance studies on single crystals. Through the years the nomenclature used for defects in alkali halides has been extended to oxides, with only one apparent complication. The charge state of a particular defect in the oxides may be different from the analogous defect in the halides. For example, an oxygen vacancy with a single trapped electron does have magnetic properties similar to the alkali halide *F*-center and has been named after it [36, 37]. However, this center in the oxide is positively charge and it is more appropriate to refer to it as an *F*⁺-center. Thus, the term *F*-center indicates the electrically neutral defects in the oxides which have symmetry properties similar to the counterpart defect in the alkali halides [38]. The most convincing evidence for the correctness of the de Boer model is given by the electron spin resonance measurement of the interaction of the unpaired electron with neighboring nuclei, but these hyperfine interactions can only be observed with nuclei possessing a nuclear spin. Reported values indicate that the F^+ center electron in all the alkaline earth oxides is much more localized within the vacancy
than its counterpart in the alkali halides, as expected from the deeper potential well in a
divalent lattice. Moreover, the electron is less localized in the vacancy and more on the
cations as the atomic number increases [38].

Different mechanisms operate in the thermal diffusion of F^+ -centers depending upon temperature range. Montojo et al. [39] reported that below 900 °C the jump from the center to the nearest anion vacancy is the most feasible mechanism. Thus, the movement is related to the temperature by

$$(2.4) x = \mu_F E t_t$$

where μ_F is the F^+ center mobility, E is the applied electric field and t_t is the transit time for the movement inside the crystal a distance x. The center mobility depends on the temperature following

(2.5)
$$\mu_F = \mu_0 \exp\left(\frac{-U}{k\,T}\right)$$

where U is the activation energy for the jump, k is the Bolztman constant and μ_0 is the pre-exponential factor

Over the years, values for the diffusion of the center have only been reported for alkali halide crystals and typical parameters are $\mu_F = 0.06$ and U = 0.55-0.8 [40, 39]

2.4.2. Reported electrical and optical properties

Table 2.2 lists the room temperature transport properties reported by Hosono's group for hydrogen treated crystal, ion beam treated, H⁺-implanted treated crystal and thin films [25, 41, 42]. The conductivity enhancement after UV irradiation is on the order of 10 orders of magnitude and it was measured by complex impedance spectroscopy using In-Ga alloy as electrodes. The light-induced conductivity remains unchanged even after irradiation stops.

As mentioned before two optical absorption bands are induced after UV irradiation. Hayashi et al. related them to the persistent color change from white to green and the dramatic change in conductivity after observing that the relative change of the intensity of these bands and the increase of conductivity were each proportional to the photon doses. It should be mentioned that even thought the relative intensities of the absorption bands seem to remain the same the absolute absorbance and conductivity are a function of the irradiation flux and the effectiveness of the hydrogen treatment [25]. The carrier content data for the hydrogen treated single crystal was determined by electron paramagnetic resonance (EPR), considering that each F^+ -like centers was a free electron involved in the conduction. On the other hand, the carrier content of the proton-implanted thin films was obtained using the oscillation strength of one of the optical absorption band.

Hayashi et al. showed that for the single crystal specimen, the light induced conduction was persistent up to 320 °C and recombination of hydrogen rarely occurs below this temperature. According to their data it was not until 550 °C that the sample releases the

	Conductivity	Absorption		Carrier Content	Seebeck Coefficient
Sample	(300 K)	band	Color	(cm^{-3})	(300 K)
As prepared					
$Ca_{12}Al_{14}O_{33}$	$< 10^{-10} { m S/cm}$	$\sim 5~{\rm eV}$	Colorless		
$Ca_{12}Al_{14}O_{33}$					
: H-treated	$< 10^{-10} { m S/cm}$	$\sim 4 \text{ eV}$	Colorless		
Single crystal					
$Ca_{12}Al_{14}O_{33}$	$0.3~\mathrm{S/cm}$	2.8 eV	Green	$2 \cdot 10^{19} *$	-360 mV/K
: H-treated		0.4 eV			
: UV-irradiated					
Thin film					
$Ca_{12}Al_{14}O_{33}$	$0.62~\mathrm{S/cm}$	2.9 eV	Colorless		
: H-treated	$1.1 \mathrm{S/cm}$	$0.37 \ \mathrm{eV}$			
: UV-irradiated					
Single crystal					
$Ca_{12}Al_{14}O_{33}$	$10 \mathrm{S/cm}$	2.8 eV	Colorless	$7.6 \cdot 10^{20} **$	
: H^+ -implant.		0.44 eV			
: UV-irradiated					

Table 2.2. Reported electrical properties of $\rm Ca_{12}Al_{14}O_{33}$, * carrier content obtained by EPR, ** carrier content estimated from absorption coefficient.

absorbed hydrogen by the following process [35, 43]

$$(2.6) H_{(cage)}^{-} + H_2O_{(gas)} \rightarrow OH_{(cage)}^{-} + H_2 (cage)$$

This suggested that in the range of 320° C - 550° C the insulator to conductor conversion is reversible. This same report showed that when temperature was lowered from room temperature to 10 K the conductivity decreased proportional to $T^{-1/4}$ suggesting a variable range hoping mechanism at that temperature. Fig 2.3 shows the optical absorption and the conductivity at low temperatures from Hayashi et al. [25].

Toda et al. grew pollycrystaline thin films of $Ca_{12}Al_{14}O_{33}$ by pulsed laser deposition (PLD) that presented excellent optical transmission in the visible range, >85%, and



Figure 2.3. $Ca_{12}Al_{14}O_{33}$ single crystals (0.3 mm thick) (a) Absorption spectra before (black line) and after(green line) Hydrogen doping and UV irradiation with a Xe lamp (b) Conductivity (σ) vs. temperature (K), for T <Room temperature.

nearly 100% in the NIR [42]. Is worth noting that all these films were grown on MgO substrates and were amorphous below 800°C, consistent with the transition temperature of $Ca_{12}Al_{14}O_{33}$ glasses. In this work Toda et al. suggested that the electronic conduction is governed by a polaron mechanism based on the conductivity dependence to T^{-1} . In a different report Hayashi et al. demonstrated that electron beam-irradiation activates also the insulating hydrogen doped mayenite with a carrier electron formation yield of ~30 for a 25 keV incident electron. The interesting feature of this study is the posibility of obtaining a fine conductive patterning directly on the surface of the hydrogenated mayenite without photomask and electron beam resist [44].

Finally, proton implantation was undertaken by Miyakawa et al. on similar thin film specimens; they showed that films implanted at 600 °C and a fluence of $1 \cdot 10^{18} \ cm^{-2}$

presented a conductivity of 10 S/cm, optical transmission > 85% and a mobility of ~0.1 $cm^2/(V.s)$ [41]. As a

2.5. Reduction by a base metal

The second activation process that renders the $Ca_{12}Al_{14}O_{33}$ crystal conductive was reported a year after the initial discovery of persistent light activated conductivity in Htreated mayenite. Matsuishi et al. found that the $Ca_{12}Al_{14}O_{33}$ system could become a persistent conductor by exhaustive reduction in vacuum using calcium metal [45]. Large single crystals were vacuum sealed in silica glass tubes in the presence of Ca shot and heated to 700 °C for several days. Once out of the silica tubes, the samples presented a surface layer of crystalline CaO that was mechanically removed to expose the now reduced $Ca_{12}Al_{14}O_{33}$ crystal. The reaction can be written as

$$\left[Ca_{24}Al_{28}O_{64}\right]^{4+} + 2O^{2-} + Ca \rightarrow CaO + \left[Ca_{24}Al_{28}O_{64}\right]^{4+} + (2-x)O^{2-} + (2x)e^{-}$$

where x is a function of the treatment time. Matsuishi et al. obtained five specimens by treating the single crystals for 4, 12, 18, 40 and 240 hours. X-ray measurements revealed that the treatment did not change the basic structure of the framework, however the samples changed color from colorless to green and finally to black with increased duration of the treatment. A noticeable shift of the absorption edge from 5 eV to 4 eV was observed along with two induced absorption bands at 2.8 eV and 0.4 eV. The shape and position of the bands were shown to agree well with the ones found for the hydrogenated samples and in both cases the one at 2.8 eV was related to the coloration. They also related this similarity to the same defect center, an F^+ -like center. Furthermore, they suggested that if the $[Ca_{24}Al_{28}O_{62}]^{+4}$ framework is viewed as a large cation and the four localized electrons that accompany the lattice distortion as anions, the $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻ material can be considered a thermally stable electride.

2.5.1. Electrides

As mentioned in the previous section, when a low concentration of electrons is trapped at anion vacancies, F^+ centers are generated. Crystalline electrides can be seen as stoichiometric F-centers in which all ionic sites contain trapped electrons [46, 47, 48]. J. Dye defined these materials as compounds where the electrons behave as anions populating sites normally occupied by Cl^- and OH^- . According to his definition they are neither delocalized as in a metal, nor localized on specific atoms or molecules. Electrides are strongly reducing materials where the electrons are localized in cavities at separate sites from the cations. They are well defined crystalline salts, whose crystal structure can be determined. The mobility of the trapped electrons depends on the structure and is apparently influenced by the size and length of the cavities or channels that connect the different anionic sites. Prior to the work on mayenite, all electrides made to date are organic and the key to their synthesis is the capture of the cation in an alkali metal solution by a non-reducible complexant, usually a crown ether, a cryptand or their nitrogenous analogs. The thermal instability combined with the difficulty to grow large samples of these compounds has been the major impediment to study their properties. Little is know about their electrical properties and the relationship to the crystal structure [46].

$[Ca_{24}Al_{28}O_{62}]^{+4}$				
$+(2-x)O^{2-}+(2x)e^{-}$				Seebeck
$0 \le x \le 1$	Conductivity		Carrier Content	Coefficient
f(treatment time)	(300 K)	Color	(from EPR)	(300 K)
4 hours	$8.73 \cdot 10^{-4} \text{ S/cm}$	Yellowish	$7.22 \cdot 10^{16} \text{ cm-}3$	-780 $\mu V/K$
12 hours	$2.20 \cdot 10^{-2} \text{ S/cm}$	Green	$1.29 \cdot 10^{18} \text{ cm-}3$	-540 $\mu V/K$
18 hours	$0.15~\mathrm{S/cm}$	Green	$4.53 \cdot 10^{18} \text{ cm-}3$	-420 $\mu V/K$
40 hours	$8.16 \mathrm{~S/cm}$	Black	$1.82 \cdot 10^{19} \text{ cm-}3$	-109 $\mu V/K$
240 hours	$97.77~\mathrm{S/cm}$	Black	$5.11 \cdot 10^{19} \text{ cm-}3$	-44.6 $\mu V/K$

Table 2.3. Reported electrical properties of $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$.

2.5.2. Reported electrical and optical properties

Table 2.3 summarizes the transport properties for the Ca-reduced system obtained by Matsuishi et al. No other group apart from the author reported on this system, probably due to the complexity of the processes. Similar to the hydrogenated samples, two absorption bands appeared in the optical spectra after Ca treatment, the shape and position of which are consistent with the ones obtained for the hydrogen-treated specimens, which Matsuishi et al. interpreted as arising from the same defect center (F^+ -like center) responsible for both conduction and coloration.

The carrier concentrations listed above were obtained from spin concentration by EPR, considering that every F^+ -like center acts as a free carrier. Matsuishi et al. noted that for the samples treated the longest, these values differed from the carrier content obtained from the absorption coefficients of the bands at 0.4 eV and 2.8 eV [3]. The discrepancy suggested that the antiparallel spin coupling takes place, forming diamagnetic

electron pairs or a bipolaron above a critical concentration of F^+ -like centers. Based on the absorption coefficients, Matsuishi et al. obtained a maximum value of carrier concentration of $2 \cdot 10^{21} \ cm^{-3}$ for the 240 h sample, and a mobility of $\sim 0.1 \ cm^2/(V.s)$. This carrier concentration agrees well with the maximum of $2.33 \cdot 10^{21} \ cm^{-3}$, assuming all the O^{-2} in the unit cell are replaced by $4e^-$, and is consistent with XRD refinements suggesting that almost all of the free O^{-2} are extracted from the cages for the 240 h sample. The reported optical absorption spectra are shown in Fig 2.4, where samples treated 0, 4 and 12 hours were evaluated by common spectrophotometry. Meanwhile the diffuse reflectance spectra of powdered samples treated 18, 40 and 240 hours are shown in Fig. 2.4(b). The temperature dependence of the conductivity, in the range of 15K to 300K, is shown on Fig 2.4 (c), where it can be seen that for the low conductive samples (4 h, 12 h) the conductivity is proportional to T^{-1} , consistent with the simple polaron conduction model. For the samples treated 18 h and 40 h, conductivity is proportional to $T^{-1/4}$ suggesting a variable range hopping mechanism at these temperatures. And for the 240 h the sample conductivity is nearly temperature-independent.

2.6. Theory and calculations - the origin of the photoconductivity

In collaboration with Hosono's group, Sushko et al. performed theoretical calculations to go along with the promising results obtained for the crystalline $Ca_{12}Al_{14}O_{33}\dot{A}$ part from Sushko et al. and Medvedeva et al. (Northwestern University), only one other author commented on the controversial origin of the conductivity [49].

Sushko et al. considered the case of the hydrogenated and calcium-treated samples to be the same in the dilute doping region where, according to their previous reports, the



Figure 2.4. $Ca_{12}Al_{14}O_{33}$ Ca-treated single crystals from Matsuishi et al. (a) optical absorption spectra for samples with different treatment times (b) diffuse reflectance spectra for powder samples with different treatment times and (c) conductivity (σ) vs. temperature (K), for T <room temperature [3].

instertitial oxygen ions are substituted by electrons confined in inner lattice cages [50, 51]. They showed that the electrons substituting anions form deep electron states localized in the positively charged cages, differentiating this material from all the known organic electrides.

In the dilute limit, electrons are thought to be localized and undergo variable range hopping at low temperature and at high concentrations the electrons tend to pair and demonstrate antiferromagnetism [25, 45]. Their ab initio calculations show that the cage electrons are coupled to a strong lattice deformation and provide an explanation for conductivity and optical absorption in this system. They used an embedded cluster technique to study the theoretical behavior of the cages. A cluster with a defect treated quantum mechanically is embedded in the rest of the polarizable crystal treated classically as show in Fig. 2.5. They suggest that this accounts for both ionic and electronic contributions to the polarization of the defect environment.



Figure 2.5. Schematics of the embedded cluster calculations by Sushko et al.

Two adjacent cages placed at the center of the nanocluster are treated quantum mechanically and surrounded by spherical region I with a radius of approximately 13 Å. The remaining part, region II, is represented by classical nonpolarizable ions. The two neighboring cages are not equivalent. One of them has a classical neighboring cage with an O^{-2} in it, and the other one does not have an extra framework oxygen ion in the neighboring cage. Their calculations show that the electron density has predominantly *s* character and is localized at the center of a cage in the same way that a single electron is localized in an anion vacancy, just like an F^+ -like center. They also mentioned that extra framework oxygen ions tend to minimize their electrostatic repulsion but do not form an ordered sublattice [51, 50]. After comparison of the local atomic structures obtained for the electron localized in two different cages, Sushko et al. proposed a characteristic lattice distortion for this crystal, with the strongest relaxation of two Ca ions in each cage located on the opposite side of the walls with the center of the cage in between them. Unlike other



Figure 2.6. Schematic of the distortion generated by the O^{-2} ion inside the cage, view from side and top of the cage respectively, by Sushko et al.

ions, the ones exposed to the electron density localized inside the cage displace towards the center by approximately 0.4 Å (see Fig. 2.6). Most of the other ions displace away from the center and the relaxation reaches 10 Å from the center of the cage. They also mentioned that the elasticity of the cage walls and their large displacements is due to a strong electron-phonon interaction.

Subsequently, Sushko et al.examined cage-to-cage hopping using a simple linear interpolation approach, to examine the energy barrier for the electron intercage migration. If R_1 and R_2 are the coordinates of all atoms for the two different configurations of the electron, when localized in cage 1 and cage 2 respectively, the coordinates of the all the lattice atoms along the hoping path can be calculated as:

$$(2.8) R = t \otimes R_1 + (1-t) \otimes R_2$$

where t is a parameter varied from 0 to 1 to calculate all the points along the adiabatic path. In this approach all the points obtained represent the upper limit of the "true" hopping barrier. The barrier for hopping between cages obtained by this approximation was quite small, 0.1 eV for the jump from cage 1 to cage 2, and 0.17 eV from cage 2 to cage 1. These numbers suggest a high conductivity, mainly due to the small distance between cages and the flexible structure. To complete their work, they calculated the optical absorption energies and the transition matrix elements for the lowest excited states along the hopping path. Fig. 2.7 shows a schematic of the energy levels of the system, where the occupied state of the electron localized in the cage lies 4 eV above the top of the valence band and the lowest optical excitation corresponds to the electron transfer between adjacent cages (0.6-1.1 eV), which is predominantly s-type in character.

Finally, the different higher optical transitions correspond to $s \rightarrow p$ excitations within the cage (2.3-2.7 eV). These excited states lie very close to the bottom of the framework conduction band suggesting that excitation in this band can lead to ionization of the electron into the conduction band and thus photoconductivity. Sushko et al. concluded that the formation of these deep electron states in the positively charged cages gives rise to the conductivity and the two absorption bands reported by Hayashi et al. [25] are related to the intracage and intercage transitions discussed above.

In a completely different work Li et al. addressed the validity of the electride model for $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ by using a plane-wave pseudo potential to study the geometrical and electronic structure of the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system [49]. They mentioned that the embedded cluster model used by Sushko et al. is only suitable for the dilute electron limit and the results obtained with it should not be extrapolated to the $Ca_{12}Al_{14}O_{33}$ system



Figure 2.7. Schematic of the energy levels of the system showing the optical transitions by Sushko et al.

with high electron concentrations. They emphasized that the two quantum mechanical cages are geometrically different on account of different classical neighboring cages, and that this artificial difference between the cages is the reason why highly localized electrons occur in only one of the two cages.

In order to analyze the electride model, they calculated the charge density in a 1.5 eV window around the Fermi level, which gives the spatial distribution of the extra electrons. They found that the density was equally distributed in the twelve cages and that most of the charge density was located inside the cages. By integrating the charge density inside the cages, using the ionic radii of all the atoms involved (Ca, Al and O), Li et al. evaluated quantitatively the degree of localization. They found that 75 % of the extra electron density is distributed in the twelve cages, which supports only partially

the electride model for $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$. To complete this work Li et al. performed topological analysis of the electron localization functions (ELF) to analyze the chemical bonds involved in this sytem. For F/F^+ centers, which are usually chemically bonded (ionically) to the host lattice as a quatum-mechanical subsystem, the ELF topology posses a localization attractor at the vacancy site [52]. Although they found a local maxima at the center of the cage similar to the ELF topology for F/F^+ centers, Li et al. concluded that the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system it is very different from the electride model originally suggested by Sushko, Hayashi and Matsuishi [50, 51, 45, 25], based on the delocalization of the electrons. They also suggested to consider this material a nonstoichiometric electride.

The work performed by Medvedeva et al. will be presented in detail later in this dissertation. From density functional calculation they demonstrated that electron trapping on a vacancy does not occur and that the conduction mechanism has a fundamentally different nature than the F^+ -center original proposed by Hayashi et al [25, 3, 51]. The differences arise from the two distinct models used and the simplifications made by Sushko et al. in their calculations. Their embedded cluster technique does not take into account all the "defects" present in the H-doped UV-irradiated Ca₁₂Al₁₄O₃₃ systems, H⁰, e⁻, H⁻ and OH⁻ neither does it include the neighboring cages (even if they are empty) to provide the right distribution of charge on the cage walls, what leads to complete different results and interpretations. For the case of the [Ca₂₄Al₂₈O₆₂]⁺⁴+4e⁻ system, Medvedeva et al. predicted a change in conduction mechanism from hopping to metallic-like behavior for the highly reduced samples. Meanwhile, Sushko et al. uses the same model and interprets the reduction as an increase in the number of F^+ -centers to the limit of obtaining an "electride". As Li et al. mentioned in their work the embedded cluster technique should only be used in the dilute limit of carrier concentration, thus extrapolation of the results from the H-doped UV-irradiated $Ca_{12}Al_{14}O_{33}$ system to the $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻ should not be made based on this approach.

CHAPTER 3

Experimental Procedure

3.1. Sample preparation

3.1.1. Bulk samples

Conventional high temperature solid state synthesis was used to produce solid bulk ceramic pellets of mayenite and Mg-substituted mayenite. The phase diagrams for the binary CaO-Al₂O₃ system and for the ternary CaO-Al₂O₃-MgO system are shown in Fig. 3.1 and 3.2 respectively, where the two extremes of the prepared samples of Ca_(12-x)Mg_xAl₁₄O₃₃ (x = 0.1 and 1) are highlighted [53, 54]. The component oxides CaCO₃, Al₂O₃, MgO (> 99.99%, Alfa Aesar) were mixed stoichiometrically in agate mortar and pestle under acetone. Once a homogeneous mixture was achieved, specimens were produced by pressing $\frac{1}{2}$ " pellets at 100-200 MPa with a Carver hydrahulic press. The pressed samples were then placed in Al₂O₃ crucibles (Coors Inc.) surrounded by a bed of their constituent powders to prevent reaction with the crucible walls. They were fired in air at 1300 °C for 24 hours (Carbolite RHF 1400, UK) and air quenched on a refractory brick. Once the specimens were at room temperature they were reground and repressed to improve the mixing of the oxides. The final firing was at 1300 °C for 24 hours. After characterization, the single-phases specimens were kept in desiccators.



Figure 3.1. Binary phase diagram for the system $CaO - Al_2O_3$.



Figure 3.2. Ternary phase diagram for the system $CaO - MgO - Al_2O_3$ showing the samples of $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x = 0.1 to 1) prepared.

3.1.2. Hydrothermal synthesis

Hydrothermal synthesis is a low temperature (< 215 °C) low pressure (< 10 atm) technique [55] useful for accessing some phases that otherwise would not form by solid state reaction. This is the case of the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ system, when trying to achieve substitution levels falling outside the equilibrium composition (see Fig. 3.3) [56]. It was shown by Fujita et al. that hydrothermal synthesis of the Si-substituted mayenite can be achieved through a garnet precursor [57, 58]. Garnet is a general name applied to a group of specific silicate minerals that crystallize in the cubic system (or pseudo cubic). The hydrous component of the garnet named grossular, $Ca_3Al_2(SiO_4)_3$, is the hydrogarnet precursor for this synthesis where (OH⁻) groups substitute some (SiO₄)-tetrahedra [59].

Some changes to the original reported synthesis by Fujita et al. were made in order to account for the lack of stirring in our system. High purity $Ca(OH)_2$, amorphous-SiO₂ and γ -Al₂O₃ (> 99.99%, Alfa Aesar) were mixed in an agate mortar in the presence of acetone. Once the acetone was evaporated the stoichiometric amounts of starting powders were placed in a 125 mL PTFE (Teflon)-lined autoclave (Parr Inst. Co) with 12mL of H₂O per gram of powder. Fig. 3.4 shows an schematic of the system.

The autoclave was then sealed and ramped to 200 °C in 2 hours, the system was held at that temperature for 13-15 hours, and then cooled down to room temperature. The reaction under these conditions is

$$(3.1) \qquad 3\operatorname{Ca}(\operatorname{OH})_2 + \gamma - \operatorname{Al}_2\operatorname{O}_3 + (3 - y)\operatorname{SiO}_2 \xrightarrow{\operatorname{H}_2\operatorname{O}} \operatorname{Ca}_3\operatorname{Al}_2(\operatorname{SiO}_4)_{(3-y)}(\operatorname{OH})_{4y}$$



Figure 3.3. Phase diagram for the system $SiO_2 - CaO - Al_2O_3$ showing $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ (x = 1 to 4) falling outside the equilibrium region.



Figure 3.4. Illustration of the vessels use for hydrothermal synthesis of $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$, (a) Teflon liner (b) pressure vessel (c) loaded pressure vessel.

for y = 3, 2.8, 2.6, 2.4, 2.2, where $Ca_3Al_2(SiO_4)_{(3-y)}(OH)_{4y}$ is a hydrogarnet phase use as the precursor to obtain the desired $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ phase. The stability of the hydrogarnet decreases with increasing silica content in the bulk composition and with increasing reaction time, so it is very important to let the autoclave cool as quickly as it can in order to not hold the reaction much longer than 13-15 hours. The product of the hydrothermal synthesis was filtered and rinsed with water and ethyl alcohol to prevent carbonization of the material [60]. Subsequently, it was dried out overnight at 120 °C and X-rayed. Once the phase purity was confirmed, the hydrogarnet precursor was calcined at 800 °C for 15-24 hours to obtained $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ by the following reaction

$$(3.2) \quad (7 - \frac{x}{2}) \operatorname{Ca_3Al_2}(\operatorname{SiO_4})_{(3-y)}(\operatorname{OH})_{4y} \rightarrow \operatorname{Ca_{12}Al_{14-x}Si_xO_{33+\frac{x}{2}}} \\ + (9 - \frac{3x}{2}) \operatorname{CaO} + (14y - xy) \operatorname{H_2O} \\ + (21 - 7y - \frac{x}{2}(1+y)) \operatorname{SiO_2}$$

for y= 3, 2.8, 2.6, 2.4, 2.2 and x = 0, 1, 2, 3, 4 respectively. As can be seen from Eq. 3.3, lime is a by-product of the reaction and the higher the Si content in the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ phase, the less CaO in the system. Common methods to eliminate the lime phase from the system include complexing it with (Ethylenediaminetetraacetic acid) EDTA or by direct reaction with dilute acetic acid. Both of these options were tried, but unfortunately the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ is not stable enough to withstand the treatments. Fig. 3.5 summarizes the procedure to obtain the Si-subtituted mayenite phase.

3.1.3. Single crystal growth

The $Ca_{12}Al_{14}O_{33}$ system melts congruently at 1415°C, as it can be seen in the phase diagram of Fig. 3.1. However, it is highly reactive and often oxidizes crucible materials



4 Wash (Water and Ethyl alcohol) and dry 120°C overnight 5 Calcine 800°C, 15-24 hrs (7-x/2)Ca₃Al₂(SiO₄)_{3-y}(OH)_{4y} → Ca₁₂Al_(14-x)Si_xO_(33+x/2)+(9-3x/2)CaO + (2y)H₂O

Figure 3.5. Schematic of the heating profile and steps to synthesize $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$.

such as Pt or Ir, when grow by the commonly used Czochralski method [61, 62]. Crystal growth by the floating zone method was tried and reported by different authors, with one notorious commonality. In spite of being a congruent melting compound, all the authors found the growth of mayenite very difficult, with the formation of many bubbles and cracks, as well as a very unstable molten zone [63, 64, 65]. The reason for the bubbles seems to be the facility of this specimen to absorb gases from the air (e.g. O_2 , CO_2). Meanwhile the transparency of the material seems to be responsible for the instability of the molten zone, which causes the infrared light to penetrate too easy into the material and heat the center of the crystal more than the surface, giving a concave solid-liquid interface [63]. In this study, stoichiometric mixtures of CaCO₃ and Al₂O₃ (>99.99%, Alfa Aesar) where mixed in an agate mortar and fired at 1300 °C in alumina crucibles under ambient conditions to obtain the starting powder of Ca₁₂Al₁₄O₃₃ for crystal growth.

The starting powder was then mixed with 10 vol % aqueous poly vinyl alcohol(PVA) (Alfa Aesar 98-99%, hydrolyzed low molecular weight) as a binder to facilitate compaction. Two $Ca_{12}Al_{14}O_{33}$ rods, support rod and feed rod, where prepared by placing and compacting the powder in a cylindrical rubber sleeve of ~ 6 mm diameter and 7 - 9 mm of length. After compacting all the powder the rubber sleeve was evacuated and hydrostatically pressed at 70 kPa. The obtained feed and support rods were then sintered in vacuum at 1300 °C for 48 hours. Before finding these optimal preparation steps for the rods, a couple of crystals were grown without PVA binder and sintered in dry air at 1300 °C for 24 hours, but as it will be seen in Fig. 3.7, significantly more bubbles and cracks were found in these crystals. The feed rod was suspended from the upper shaft of the floating zone furnace using a platinum wire, while the support rod was rigidly affixed to the bottom shaft using steel wire, as shown on Fig. 3.6. The rods were rotated at 18 rpm in opposite directions to facilitate the homogenization of the molten zone.

Growth was carried out in an optical image furnace (CSI FZ-T-10000-H-VI-VP, Crystal Systems, Inc., Japan) equipped with four 1000 Watt tungsten halide lamps focused by four polished elliptical mirrors. The four mirror stages are the moving portion of this system, and their speed sets the growth rate. For the present work the rate was 3 mm/hr. To minimize the formation of bubbles, the growth was carried out under flowing N₂. In each case, the quality of the grown crystal was evaluated by X-ray diffraction and optical microscopy. Fig. 3.7 shows one of the crystals obtained and some of its cross sections. As mentioned above, there is a visible difference between the crystals pre-sintered in vacuum with PVA binder and in dry air without PVA.



Figure 3.6. Schematic of the crystal growth in a floating zone furnace.

3.2. Activation process

3.2.1. Hydrogen treatment in high temperature furnace

Samples of $Ca_{12}Al_{14}O_{33}$ and $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ were placed in Al_2O_3 crucibles inside a tightly sealed closed one-end 18" quartz tube (Quartz scientific, OH). The quartz tube was sealed with a water-cooled brass end cap under a constant forming gas (4-5 % H₂, N₂ balance) flow. Subsequently it was placed inside an Al_2O_3 tube already inside a high temperature furnace (Carbolite, UK), where the samples were taken to 1300 °C for 2 hours and then rapidly cooled to room temperature by rapid extraction of the quartz tube from the furnace. Fig. 3.8 shows the experimental setup used to incorporate hydrogen in the $Ca_{12}Al_{14}O_{33}$ crystal.



Figure 3.7. Crystals of $Ca_{12}Al_{14}O_{33}$ (a) No binder and pre-sintered in dry air for 24 hrs (b) poly vinyl alcohol (PVA) as binder and pre-sintered in vacuum for 48 hrs.



Figure 3.8. Hydrogen treatment setup.



Figure 3.9. Samples of $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ (a) before and (b) after high temperature hydrogen treatment with Pt foil cover.

The instability of the $\operatorname{Ca}_{12}\operatorname{Al}_{(14-x)}\operatorname{Si}_x\operatorname{O}_{(33+\frac{x}{2})}$ samples made the hydrogen treatment in the high temperature furnace almost impossible. Initially shorter periods of times (~5 min) at 1300 °C were tried, but the samples decomposed into the equilibrium oxides shown on the phase diagrams of 3.3. Reduction of the temperature to 800-900 °C resulted in no detectable incorporation of hydrogen (after UV irradiation). Finally, Pt was used as a catalyst for hydrogen reaction [66]; the surface of the pellets were covered with a piece of Pt foil, and the specimens were taken to 800-900 °C. The samples showed some incorporation of hydrogen after UV irradiation (see Fig. 3.9), but not high enough to get quantitate measurements out of the samples.

3.2.2. Proton implantation

The fact that the samples did change color after hydrogen treatment in the presence of Pt was promising, and led to consideration of proton implantation as an alternative. Samples of $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ (x = 0, 2, 3, 4) were received by Dr. Yonquiang Wang at Los Alamos National Laboratory, where a 200 kV ion implanter is capable of producing many ion species from gases, transition metals, and rare earth metals, with a



Figure 3.10. Samples of $Ca_{12}Al_{14}O_{33}$ before and after activation process (a) pellets specimens (b) surface layer under optical microscope.

beam current ranging from microamperes to hundreds of microamperes. The implantation can be conducted at different temperatures ranging from liquid N₂ to 1100 °C. Typical implantation fluence is from 10^{14} to 10^{17} atoms/cm². The working parameters found for these samples were 57.5 keV of H⁺ dose, a fluence of $1 \cdot 10^{14}$ atoms/cm² at 300 °C. It should be noted that the first implantation was carried out at 600 °C but the specimens decomposed. The final implantations were therefore carried out at 300 °C.

3.2.3. Ultraviolet light irradiation

After hydrogenation, all the samples were exposed to UV light in a clean room. The source was a mercury short arc lamp (Model HAS-200 D.C.) of total radiation 52.3 Watts in the window of 275 to 650 nm, commonly used for photolithography. Exposure time ranged from 50 to 70 min, after which a colored layer is induced on the suface of the samples. Fig. 3.10 shows the effects on the $Ca_{12}Al_{14}O_{33}$ and $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ samples. On the other hand, Fig. 3.11 shows the effects on the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ samples, where the thickness of the colored layer is much smaller owing to the limited penetration of the ions during implantation.



Figure 3.11. Samples of $\operatorname{Ca}_{12}\operatorname{Al}_{(14-x)}\operatorname{Si}_x\operatorname{O}_{(33+\frac{x}{2})}$ before and after activation process.

3.2.4. Reduction by a base metal

Following Matsuishi's procedure [45], single crystal samples were reduced in the presence of Ca shot (99.99 %, Alfa Aesar). Disks of $Ca_{12}Al_{14}O_{33}$ single crystals were cut with an Isomet slow speed saw (Buehler Ltd., IL) and sealed by torch under vacuum inside quartz tubes of 15 mm diameter and ~10 cm length (Quartz scientific, OH). The samples were placed in a tube furnace at 800 °C for various periods of time. As Matsuishi's results were hard to reproduce a similar procedure was used with Ti granules (99.99 %, Alfa Aesar). This time the temperature was raised to ~1000 °C to improve the kinetics of the reaction. It is important not to cool down the samples inside the tube furnace, it was found that the quartz tubes would often break in this process, allowing oxygen to react with the samples. Instead, the quartz tubes were taken out of the hot furnace and placed on a refractory brick.

During the reduction treatment a mirrored surface forms on the walls of the quartz tube (see Fig. 3.12(a) and surface layers of Ca – CaO or Ti – TiO_{2- δ} deposit on the surface of the samples. According to Matsuishi et al. the process consists of the sublimation of the metal under the reaction conditions and the formation of metal deposits on



Figure 3.12. Reduction with a base metal (a) mirror-like surface on the quartz tube after treatment (b) samples surface layer and its thickness right after treatment.

the surface of the Ca₁₂Al₁₄O₃₃ crystal. The metal in intimate contact with the surface extracts the free oxygen inside the crystallographic cages and a reacts with it, forming an oxide layer on the surface. This layer has to be removed by mechanical polishing. Fig. 3.12(b) shows the appearance of the surface and the thickness of the layer deposited immediately after treatment. Figure 3.13 shows the crystal after mechanical polishing and x-ray verification. The polishing was done in a manual polisher (Buehler Ltd., IL) with SiC films ranging from 600 grit to 1200 grit. To acquire a smother surface, diamond lapping films of 20 μ m, 10 μ m and 1 μ were employed (Buehler Ltd., IL).

Similar reduction treatment with Ca metal was attempted on $Ca_{12}Al_{14}O_{33}$ polycrystalline samples, but after polishing and x-ray analysis a CaO phase was found in the bulk as well as visible spots of the intermetallic compound, Al_2Ca (see Fig. 3.14).



Figure 3.13. $Ca_{12}Al_{14}O_{33}$ crystals (a) before treatment (b) after reduction treatment and mechanical polish.



Figure 3.14. Ca₁₂Al₁₄O₃₃ polycrystalline specimen after Ca metal reduction.

3.3. Structural characterization

3.3.1. Phase analysis

The phase purity of the samples was confirmed by powder x-ray diffraction (XRD) using $CuK\alpha$ radiation (Rigaku, MA). Ground powders were hand pressed into a rectangular cavity on a 5 x 3 cm glass sample holder (Rigaku, MA) or, in certain cases, entire pellets

were attached to the holder using modeling clay, making sure their exposed surfaces were parallel to the holder surface. The tube was operated at 40 kV and 20 mA and a nickel filter was used to remove the CuK β contribution from the diffraction pattern. For routine phase analysis, powders were scanned between 10° and 80° in 2 θ with a step size of 0.05° and a dwell time of 1s. Diffraction patterns obtained were analyzed using Jade 7.0 (Materials Data Inc., CA), where they were compared to existent JCPDS cards (Joint Committee on Powder Diffraction Standards) in order to identify the phases present.

3.3.2. Lattice constant measurements

Laticce parameters were determined for the Ca₁₂Al_(14-x)Si_xO_(33+ $\frac{x}{2}) samples using Rietveld$ analysis of the x-ray diffraction data [67, 68, 69]. This method refines various parameters,including lattice parameters, peak width and shape, and preferred orientation to derive anew diffraction pattern. Once the derived pattern is nearly identical to the original data,various properties pertaining to the sample can be obtained (e.g., crystallite size and siteoccupancy factors). One advantage of the Rietveld technique is that it does not requiresthe use of standards. Instead, it calculates how the diffraction profiles are affected bythe different crystal parameters. It continues to refine its estimates of the new diffractionprofiles and computes a difference pattern. As this difference becomes smaller, the derivedpattern begins to look more like the original data. At some point there is no improvement,and the refined pattern's parameters are used to calculate results. The software packageused to perform Rietveld refinement was GSAS (General Structure Analysis System),which is a comprehensive system developed by Los Alamos National Laboratory scientistsfor refinement of structural models to both x-ray and neutron diffraction data. The</sub> package can be used with both single-crystal and powder diffraction data [70, 71]. Within GSAS, the program GENLES is the one responsible for the least squares refinement that constructs a single full least square matrix using multiple data sets.

For structural refinement, XRD patterns were collected using a Scintag XDS 2000 4circle diffractometer with a resolution of 100 μ m and 0.02° and a GeLi solid state detector. The step size was lowered to 0.02° and the dwell time increased to 2s to improve the statistical distribution of points. Silicon was used as an internal standard to correct for any systematic shift due to goniometer error and sample displacement. Peaks were fit with a pseudo-Voigt function, which weights Lorentzian and Gaussian profiles related to the Full Width Half Maximum (FWHM) of the diffraction pattern. The background was subtracted using a 7th-order polynomial.

3.4. Composition analysis

3.4.1. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was performed on the Ca₁₂Al₁₄O₃₃ samples in air and flowing N₂ to study the desorption of gases and thermal decomposition. Measurements were made on a TA Instruments TGA 2950 thermogravimetric analyzer. The heating profile was a linear ramp from room temperature to 800 °C at 5 °C/min. The sample was held isothermally at 800 °C for 12 h and then allowed to cool down. TGA analysis was also performed on the hydrogarnet precursor Ca₃Al₂ (SiO₄)_(3-y) (OH)_{4y} to study the loss of H₂O in the transformation to Ca₁₂Al_(14-x)Si_xO_(33+ $\frac{x}{2}$). The same ramp of 5 °C/min was used for this case as well as the same holding time at 800 °C.

3.4.2. Time of flight secondary ion mass spectroscopy (ToF-SIMS)

Secondary Ion Mass Spectrometry (SIMS) is based on the analysis of the ionized particles emitted from the surface when energetic primary particles bombard the surface. A schematic of the mechanism is shown on Fig. 3.15. The pulse of primary ions with an energy of 1-25keV, bombard the sample surface causing the secondary ions or clusters of ions to be ejected from the surface. The secondary ions are then electrostatically accelerated into a field-free drift region with a nominal kinetic energy of

$$(3.3) E_k = e.V_o = \frac{m.v^2}{2}$$

where V_o is the accelerating voltage, m the mass of the ion involved, v the flight velocity of the ion and e its charge. From Eq. 3.3 it is evident that the ion with the lowest mass has highest flight velocity. Thus they will reach the secondary-ion detector earlier. As a result, the mass separation is obtained from the different time of flight, t, required for each ion to reach the detector.

(3.4)
$$t = \frac{L}{\sqrt{\frac{2.e.V_o}{m}}}$$

Where L is the effective length of the mass spectrometer. A variety of masses (ions) are recorded by the detector with the time sequence to give the SIMS spectrum.

SIMS is the most sensitive technique for elemental analysis, which allows the detection of trace impurity levels. SIMS is used to analyze not only the elemental composition but also the chemical structure of the surface [72]. Samples of $Ca_{12}Al_{14}O_{33}$ and $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ where studied using this technique, the primary pulse was set to



Figure 3.15. Schematics of the Time of Flight Secondary ion Mass Spectrometer (ToF-SIMS).

20keV and was composed of Ga⁺ ions. The primary ion dose was changed from $\leq 10^{12}$ ions/cm² for mass analysis to $\leq 10^{13}$ ions/cm² for imaging, at the operators discretion. The resulting ion emission was detected by a mass spectrometer equipped with appropriate ion collection optics and registered on Wincadence software. For this experiment the samples were annealed in deuterium gas (5% Deuterium / N₂ balanced) instead of hydrogen for a more precise data collection. The mass spectrometer is indeed sensitive to hydrogen but when looking at such small amounts the hydrogen due to contamination of the sample plays a very important role.

3.4.3. Raman spectroscopy

Raman spectroscopy is one of the most powerful techniques for the characterization of solids and surfaces of technological importance. When light is scattered from a molecule most photons do so elastically. Most scattered photons have the same energy, frequency and wavelength, as the incident photons (ν_o). This effect is called Rayleigh scattering. However, a small fraction of light (1/1000 of the scattered light) is usually scattered at
optical frequencies different from the frequency of the incident photons (ν_i), such that $\Delta E = h |\nu_0 - \nu_i|$ corresponds to energies absorbed by the sample. The process that leads to this inelastic scattering is called the Raman effect. Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. When referring to the Raman effect, chemists are really referring to the vibrational contribution. The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule. A plot of intensity of scattered light versus energy difference is commonly called a Raman spectrum [73, 74].

Raman studies of the $\operatorname{Ca}_{12}\operatorname{Al}_{(14-x)}\operatorname{Si}_x\operatorname{O}_{(33+\frac{x}{2})}$ specimens were conducted on a Raman instrument built at Northwestern University by Prof. Stair's group [75, 76, 77]. The spectra were collected on a Triax 550 single-grating spectrograph with a UV-enhanced CCD detector. A UV edge filter (Barr Associates) was used to block Rayleigh scattering. The 244-nm excitation is produced by a Lexel 95 SHG (second harmonic generation) laser equipped with an intracavity nonlinear crystal, BBO (beta barium borate, BaB₂O₄), which frequency-doubles visible radiation into the mid-ultraviolet region. Raman spectra were collected under ambient conditions. The laser power and spot size at the sample position were 2 mW and 50 μ m respectively. Data collection times varied from 60 s to 20 min, depending on the signal level. The Raman shift was calibrated by measuring several liquid standards, including cyclohexane, acetonitrile, acetone, chloroform, ethyl acetate, toluene, and benzene. A mathematical procedure involving a quadratic fit of the observed to the actual wavenumbers of the standards was used for the calibration. The band positions in the Raman spectra were determined using the program PeakFit v4.11.

3.4.4. Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) was used primarily to look at the morphology and particle size distribution of all the ceramic powders used in the powder solution composite (PSC) technique for determining the conductivity. Data were collected on a Hitachi S-3500 SEM at Northwestern University. Sample preparation included the suspension of the powders in drops of acetone and subsequently pipeting the mix onto carbon tape attached to an SEM metal stub. The crystals of $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻ were also examined under the SEM and analyzed by Energy Dispersive Spectroscopy (EDS) on a Hitachi, Pioneer S-4500 SEM. The samples for this case were well polished, washed with acetone, and then attached to carbon tape on the SEM stub.

3.5. Electrical characterization

3.5.1. Room temperature conductivity of bulk ceramics

4-point DC conductivity measurements were conducted using a 4-point probe head (C4S-44-1S) with 4 aligned tips and a spacing between them of 1.016 mm (Cascade Microtech, Beaverton, OR). The probe was lowered to contact the surface and current was passed through the outer two tips using a Keithly 224 constant current supply (Cleveland, OH) and the potential drop across the inner two tips was measured by a Keithly 195A digital multimeter (cleveland, OH). The conductivity was then calculated by

(3.5)
$$\sigma = \frac{1}{\rho} = \frac{1}{\frac{V}{I} \cdot w \cdot C\left(\frac{d}{s}\right) \cdot F\left(\frac{w}{s}\right)}$$

where σ is the conductivity, ρ is the resistivity, s is the probe tips spacing, V is the voltage drop and I is the current passing through the sample. $C(\frac{d}{s})$ and $F(\frac{w}{s})$ are geometric correction factors considering that the sample has a finite diameter and thickness, and wand d are the sample thickness and diameter respectively [78].

3.5.2. Room temperature conductivity of powdered ceramics

Conventional four-point conductivity measurements on sintered specimens is not possible every time. In some cases, the powders are unstable at sintering temperatures, e.g., they are obtained by low temperature techniques or they are just nano-size crystals and it is not desirable to heat them leading to grain growth. Instead, the electrical conductivity of these kind of specimens can be studied by the powder solution composite technique (PSC), allowing for the measurements to be performed directly on the ceramic powders [79]. The PSC technique is based on impedance spectroscopy (IS) and effective medium theory; it uses slurries formed by the ceramic powder in question and electrolytic solutions of varying conductivity to establish the true bulk conductivity of the powder. The method requires proper combination of variable particle conductivity that falls within an achievable range of matrix conductivity, and the establishment of a relatively high impedance interface between the particles and the matrix. This can be due to a second phase on the surface of the particles, a Schottky barrier, or merely the ionic double layer that forms on the surface of an electronic conductor in an electrolytic matrix. Any non-reactive aqueous electrolyte solution spanning a range of conductivity may be used in this method with the sole consideration that the powdered sample conductivity falls within that range. The common electrolyte used in this technique is NaCl, but owing to reaction with some

specimens AgNO₃ was employed as an alternative. For this work aqueous solutions of NaCl were prepared ranging usually from 0.002 M ($\sim 10^{-4}$ S/cm) to 5 M (~ 0.28 S/cm). Each of the solutions was measured by itself in order to aquire a reference line. Afterwards each of the solutions was mixed with a calculated amount of powder to produce a slurry of 0.2-0.3 volume fraction. The measuring device consists of a polyethylene tube (4.75 mm ID x 20 mm) and two stainless steel plugs. The composite slurry was allowed to settle and then carefully pressed to the desire volume fraction. A Solartron 1260 Impedance Response Analyzer was employed with Z-60 personal computer software for data collection (Schlumberger, Houston, TX, USA). Alligator clips at the end of coaxial cables were used to make electrical contact to the stainless steel plugs. The excitation voltage was 1V and the scans were performed from 10 MHz to 1 Hz, with data collected at 10 steps per frequency decade.

Typical impedance results are represented in Nyquist plots (negative imaginary impedance vs. real impedance) with frequency increasing from right to left. Such plots show semicircular arcs that are related to the different elements of the composite system. Figure 3.16 shows the PSC setup and typical Nyquist plots obtained in this technique, comparing data for a NaCl solution by itself and that of a "composite" of the identical NaCl solution with 0.3 volume fraction of a ceramic powder. The single arc in the case of the plain solution corresponds to the electrode response and the intercept agrees well with the DC resistance of the solution. Nyquist plots obtained when analyzing composite slurries present different behaviors depending on the solution conductivity; examples covering the whole range of electrolyte conductivity can be found in Ingram et al. [79]. For the case shown in Fig. 3.16, we observe a dual-arc behavior when the powder is added



Figure 3.16. Powder Solution Composite set up and their typical impedance response in Nyquist plots.

to the solution. In this regime the particles are more conductive than the homogeneous electrolyte and the behavior can be described by the frequency-switchable interface model [79, 80, 81]

Many mixing laws and effective media theories have been used to describe the electrical behavior of composites, depending upon particle shape and size distribution [81, 82, 83, 84, 85, 86, 87, 88]. The electrical response of the PSC slurries is clearly affected by these variables and a noticeable change in the ratio between particle and matrix conductivity can be observed. Hence, in order to properly fit the PSC data it is necessary to previously gather microscopic information of the powders under study.

Although the conductivity of the particles can be directly calculated from a single datum using effective media equations, the experimental error introduced by this individual calculation can lead to large errors in the calculation of the particle conductivity. In order to address this error several measurements are taken over a range of electrolyte solution conductivities, which is the basis of the PSC technique [79]. Fig. 3.17 shows a typical



Figure 3.17. Typical PSC plot; where the grey circles correspond to the sample under study, the dashed line is the fit using effective media and equivalent circuit and the thicker line is the reference obtained by analyzing each of the plain solutions.

PSC plot, where the conductivity of the composite is plotted versus the conductivity of the solution. The phase under study is represented with grey circles, the calculated fit is a dashed line and the reference line made by measuring the plain solution is the thicker line.

3.5.3. High and low temperature in-situ conductivity

Conductivity measurements between room temperature and 500°C were taken using the Van der Pauw technique, where a 4-point spring-loaded probe touches the sample in four different points close to the edges [89]. Four probing tips where mounted on an Al_2O_3 tube and wired to the current source (Keithley 705, Cleveland, OH) and a digital multimeter (Keithley 195A, Cleveland, OH). The Al_2O_3 tube with the probes was inserted into a quartz tube as a sample holder. Fig. 3.18 show the schematic of the setup.



Figure 3.18. Schematics of the van der Pauw setup

A resistance $R_{AB,CD}$ is defined as the potential difference $(V_D - V_C)$ between the contacts D and C per unit current flowing through the contacts A and B. Similarly a resistance $R_{BC,DA}$ can be defined and the following relation holds for a specimen of arbitrary shape:

(3.6)
$$\exp\left(-\pi R_{AB,CD}\frac{d}{\rho}\right) + \exp\left(-\pi R_{BC,DA}\frac{d}{\rho}\right) = 1$$

where ρ is the resistivity of the material and d is the thickness of the UV-activated slab. Corrections were made for layer thickness and sample diameter in every case.

In order to estimate the magnitude of the error introduced when the contacts are not right at the circumference of the sample, van der Pauw derived an approximation formula given by

(3.7)
$$\frac{\Delta\rho}{\rho} = -\frac{d^2}{2D^2\ln 2}$$

where D is the distance from the edge of the sample and d has the same meaning as before. It should be mentioned that corrections for porosity were not performed on any of the UV irradiated mayenite samples owing to the uncertainty in the properties of the irradiated layer. However, conductivity measurements on powder specimens using a powder solution composite technique (PSC) showed a very good agreement with the conductivity values obtained by the four point probe method without the porosity correction [79].

Conductivity measurements at low temperatures (Room temperature - 75 K) were taken using the same technique. This time the 4 Van der Pauw probes were solder with indium to the surface of the $Ca_{12}Al_{14}O_{33}$ sample. The sample was placed in a holder cooled with liquid nitrogen and the probes were then wired to a current source (Keithley 705, Cleveland, OH) and a digital multimeter (Keithley 195A, Cleveland, OH).

3.5.4. Magnetoresistance

Measurements of the magnetoresistance is a common tool in semiconductor physics as its dependence on the magnetic field show characteristics features of the conduction mechanism. Measurements of magnetoresistance are based on the same principle as Hall effect measurements, which is the Lorentz force acting on an electron that moves along a direction perpendicular to an applied magnetic field deviating the electron from its linear trajectory.

$$(3.8) F = q\bar{v} \otimes B$$

However, when measuring magnetoresistance we are interested in the drop of the applied electric field due to the Lorentz force (MR) and when measuring hall effect we are interested in the voltage generated across the sample by the Lorentz force (V_H). It is important to note that for magnetoresistance measurements the magnetic field can adopt



Figure 3.19. Schematic of the Hall effect and magnetoresistance set up

any angle with respect to the electric field especially when studying anisotropic materials. Fig. 3.19 illustrates the idea of the set up.

Magnetoresistance was measured on UV-irradiated H-doped $Ca_{12}Al_{14}O_{33}$ samples using the Van der Pauw configuration. The sample was placed in a holder, where the probes were solder with indium. The wires from the holder were connected to a current source (Keithley 705, Cleveland, OH) and a digital multimeter (Keithley 195A, Cleveland, OH). The entire holder was then placed in between a magnet, which filed ranged from 0 to 5000 Gauss. The temperature was varied from room temperature to 75K by adding liquid N₂. Hall data was collected on the $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻ samples using a Bio-rad 5500 Hall system (Cambridge, MA). Probes were place in the van der Pauw configuration and a magnetic field of 0.31 Tesla was applied. Measurements were done at room temperature with an excitation voltage ranging between 1-10 mA.

3.5.5. Impedance spectroscopy

Impedance spectroscopy was used to gather information about the high oxide ion conductivity of the mayenite samples. Pressed pellets were sintered in air by firing them at 1300-1350 °C for 24 h. Once the porosity was significantly reduced, platinum paste (Heraeus) was painted on the opposite pellet surfaces and bonded by firing at 900 °C for a couple of minutes. Leads to the impedance analyzer where attached with dots of sticky silver paint (Heraeus) and dried at 120°C for an hour. The sample was then placed inside a tube furnace, whose temperature was controlled and measured within 2°C. An HP 4192A impedance response analyzer interfaced to a lab view program used to obtain the respective Nyquist plots. The excitation voltage was 1V and the scans were performed from 10 MHz to 1 Hz, with data collected at 10 steps per frequency decade.

3.5.6. Conductive atomic force microscopy (c-AFM)

Conductive AFM is a powerful current sensing technique for characterizing conductivity variations in resistive samples. Samples of $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^-$ were studied using this technique to correlate conductivity to the microstructure. Conductive AFM can simultaneously map the topography and current distribution of a sample. The module consists of a specially designed cantilever holder that includes a transimpedance amplifier. The gain of the amplifier can be chosen by the user, standard values range from $5 \cdot 10^7$ to $5\dot{1}0^9$ volts/amp. The easiest imaging mode for measuring the localized conductivity of a sample is to combine the current measurements with contact mode AFM imaging. All images in this work were acquired by Norma Cortes in Mark Hersam's group using contact mode with a conductive diamond cantilever, with a nominal spring constant of 1-2N/m

and good wear characteristics. The contact tip was scanned through the ground sample surface at a bias of -3 to -7 V. All experiments were performed at room temperature in a humidity controlled glove box filled with N_2 and at room temperature.

3.5.7. Thermopower (room temperature - $100 \,^{\circ}C$)

Room temperature thermopower data were collected on bar-shaped samples cut from the pellets with an Isomet slow speed saw (Buehler Ltd., IL). The bars of approximately 10 mm x 3 mm x 3 mm were sandwiched lengthwise between two gold foil contacts. In some cases, when measuring the thermopower of UV-irradiated specimens, the bars were painted on the contact faces with a silver colloidal suspension to improve the electrical and thermal contact between the small UV-activated layer and the two gold electrodes. One gold contact was in thermal equilibrium with a 23 W heating element and the other was in thermal equilibrium with a cylindrical steel slug that rested on an insulating ceramic brick. A type S (Pt-Pt/10 % Rh) thermocouple bead was welded to both gold contacts. A thermal gradient was created by switching on the heating element and allowing it to reach 100 °C, at which point, the heating element was switched off, letting the system thermally relax. The temperature difference (ΔT) and the voltage difference (ΔV) were measured at regular intervals (3 sec) using a programmable scanner (Keithley 705, Cleveland, OH) and a digital multimeter (Keithley 195A, Cleveland, OH) connected through an IEEE port to a personal computer. Thermopower was calculated by fitting the temperature and voltage gradient data with a least-squares fit as the sample approached equilibrium using the concept presented by Hong et al. [90]

(3.9)
$$Q = -\lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T}$$

A correction for the contribution of the Pt thermocouple to the overall thermopower has to be made using the following equation [91].

$$(3.10) Q_{actual} = Q_{measured} + Q_{Pt}$$

The thermopower at temperatures slightly above 100° was obtained using the same technique, with the only difference being that the heat sink (the ceramic brick where the steel slug rests) was exchanged for a hot plate. With the hot plate the whole system can be taken to a higher base temperature and from there the procedure with the heating element can be repeated. It should be noted that the temperature range is somewhat limited (< 150 °C) and to perform high temperature thermopower measurements one should visit the work by Hong et al. [90].

3.6. Optical characterization

3.6.1. Diffuse reflectance

The optical properties of the bulk specimens were estimated from diffuse reflectance measurements, since thin films of these materials were unavailable for direct transmission data. The radiation reflected by a medium can be separated into two components (See Fig. 3.20). The first one, called specular reflection, is the reflection at the surface of the



Figure 3.20. Representation of the reflected radiation by a diffusing media. medium and obeys the Fresnel equation

(3.11)
$$R = \frac{(n-1)^2 + k_0^2}{(n+1)^2 + k_0^2}$$

where R is the fraction of the incident beam being specularly reflected, n is the relative refractive index of the sample, and k_0 is the absorption index defined by Lambert's law.

$$(3.12) I = I_0 \exp\left(-\alpha d\right)$$

where I and I_0 are the final and incident radiation respectively, d is the distance traveled inside the material and α is the absorption coefficient characteristic of the material.

The second component, called diffuse reflection, is generated by the radiation that penetrates the surface and undergoes multiple scattering within the specimen (e.g. from pore / grain surfaces). A portion of this scattered radiation is returned to the surface emerging as the diffuse reflection component. This component also contains valuable absorption information as the radiation passes through particles. The attenuation of the incident radiation has a similar form to Eq. 3.12 with the difference that α is now the mean absorption coefficient and d is the mean penetrated layer. Both of these components can be used to determine the absorption properties of a given medium, however, most materials reflect a combination of these components in an unknown proportion and absorption affects the two of them in different ways. For these reasons, one should minimize either one of the components when performing spectrophotometric measurements [92]. For the resent work, the specular reflection was the one minimized.

The spectra for the specimens were collected on a Cary 500 UV-VIS-NIR spectrophotometer (Varian Instruments Inc., Palo Alto, CA) using a Diffuse Reflectance Accessory (DRA) between 250 and 800 nm with a lead sulfide detector. The system switches lamps from a tungsten (visible range) to a deuterium (UV range) at ~350 nm [93]. The DRA accessory has the ability to collect most reflected radiation, remove any directional preferences, and present an integrated signal to the detector. This accessory gives the possibility of choosing which reflection component is to be analyzed. The apparatus has two different settings, "S" for specular reflection and "D" for diffuse reflection. Fig. ?? shows how the DRA sphere cancels the other component for each setting. The data were corrected with a spectrum obtained from a polytetrafluoroethylene (PTFE) reference specimen. The optical gap was estimated from the absorption edge that was determined by the intersection of a line drawn through the sloped portion of the transition region between high and low transmission and the baseline of the low-transmission portion of each spectrum [94, 95].

3.7. Theoretical calculations

First-principles all-electron density functional electronic structure calculations for pure and H-doped $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x=0, 1 and 2) were performed by Prof. Julia Medvedeva



Figure 3.21. DRA sphere (a) "D" mode (b) "S" mode

using DMol3 method [96]. A Perdew-Wang exchange-correlation functional was used [97] and a doubled numeric basis set [96] with local basis cutoffs of 11.0 a.u. Summations over the Brillouin zone were carried out using 24 special k points in the irreducible wedge. The structures were modeled within the cell of mayenite with one formula unit (i.e., 59 atoms per cell which combine into six cages) with periodic boundary conditions. We used the linear muffin-tin orbital (LMTO) method within the atomic sphere approximation [98] for the cell of $Ca_{12}Al_{14}O_{33}$ with one formula unit, i.e. a total of 59 atoms per cell which combine into six cages; 85 empty spheres were included to fill out the open space. The equilibrium relaxed geometry of the structures was determined via total energy and atomic force minimization; during the optimization, all atoms were allowed to move in x, y and z directions, while the volume of the unit cell was fixed to the experimental value of the mayenite crystal [1].

CHAPTER 4

The $Ca_{12}Al_{14}O_{33}$ phase

4.1. Phase analysis

Bulk mayenite ($Ca_{12}Al_{14}O_{33}$) samples were prepared by solid state reaction using the technique described in section 3.1.1. Activation by hydrogen treatment and UV irradiation was performed following the steps mentioned in section 3.2.1 and 3.2.3, promoting the following reactions (Eq. 2.1 and 2.2)

Hydrogen treatment:

(4.1)
$$O^{-2} + H_2 \rightarrow OH^- + H^-$$

UV-irradiation:

(4.2)
$$H^- + Energy \rightarrow H^0 + e^- + phonon$$

Phase analysis of the samples after each of the treatments was verified by powder x-ray diffraction as mentioned in section 3.3.1. The result powder patterns are shown in Fig. 4.1, where a good match with the corresponding JCPD card for mayenite (00-009-0413) is observed and no structural differences between the as-prepared mayenite, the hydrogen-doped mayenite and the UV-irradiated / hydrogen-treated mayenite can be observed.



Figure 4.1. Powder x-ray diffraction pattern of $Ca_{12}Al_{14}O_{33}$, H: $Ca_{12}Al_{14}O_{33}$ and UV:H: $Ca_{12}Al_{14}O_{33}$ compared to may entre JCPDS card [4]. Labels indicate Miller indices for diffracting planes.

4.2. Excess oxygen

Thermogravimetric studies were conducted on portions of pellets of as-prepared $Ca_{12}Al_{14}O_{33}$ with a relative density of ~80%, in order to observe the uptake of gases from the atmosphere. Fig. 4.2 shows the excess weight over the stoichiometric composition for the $Ca_{12}Al_{14}O_{33}$ specimen heated in air. A maximum of 1.23 % weight increased is observed at ~280 °C.

When the as-prepared samples were heated in a N_2 atmosphere, no change in weight was observed, but if the sample previously heated in air (Fig. 4.2) was heated in a N_2 atmosphere, 1.03% weight loss is observed at around 800 °C (see Fig. 4.3).

This finding is consistent with the observation by Hayashi et al., where a similar behavior in a comparable study was related to the absorption and desorption of water



Figure 4.2. Thermogravimetric analysis of $Ca_{12}Al_{14}O_{33}$ polycrystal heated to 800 °C in air.

and oxygen gas from the atmosphere [99, 100]. Oxygen is desorbed at ~800°C, meanwhile water is desorbed over 1000°C. Owing to the temperature limit of our thermogravimetric analyzer, we can not observe the corresponding weight loss. The driving force for this process is the instability of the free oxide ions in the cage, which is suggested to have an intermediate state between the O^{-2} ion in the gas phase and that in an ordinary metal-oxide lattice. Further studies related these uptakes of gases to the formation of the various oxygenated species, O_2^{-2} , O^- , O_2^- , OH^- via the following reactions [101, 102, 103, 104, 3]

Oxygen absorption:

$$(4.3) O_{2 \, (gas)} \rightleftharpoons O_{2 \, (cage)}$$



Figure 4.3. Thermogravimetric analysis of $Ca_{12}Al_{14}O_{33}$ polycrystal heated to 815 °C in N₂.

(4.4)
$$O_{(cage)}^{2-} + O_{2(cage)} \rightleftharpoons O_{(cage)}^{-} + O_{2(cage)}^{-}$$

(4.5)
$$2O_{(cage)}^{2-} + O_{2(cage)} \rightleftharpoons 2O_{2(cage)}^{2-}$$

$$(4.6) 2O^-_{(cage)} \rightleftharpoons O^{2-}_{2(cage)}$$

Water absorption:

(4.7)
$$O_{(cage)}^{2-} + H_2 O_{(surface)} \rightleftharpoons 2OH_{(cage)}^{-}$$

Active oxygen radicals such as, $O_2^- O^-$, O_3^- are very important chemical species for catalytic applications, but are beyond the scope of this work. For the purpose of this study, the thermogravimetric results give us important information on the optimal way of preparing mayenite samples and how to minimize the bubbles formed during crystal growth (see section 3.1.3).

4.3. Electrical properties

4.3.1. Ionic conductivity

As mentioned in section 3.5.5, the first report regarding the electrical transport of cystalline $Ca_{12}Al_{14}O_{33}$ was related to its ionic conductivity. We reproduced that first work by Lacerda et al. [33] using a similar setup and impedance spectroscopy (IS) following the description from section 3.5.5. Typical Nyquist plots from this study are shown in Fig. 4.4, where the open circles represent the experimental data and the dashed line is the fit obtained using an (RQ)(RQ) equivalent circuit model in the program developed by Boukamp B. [105]. The circuit description code (CDC) developed by Boukamp is based on the assumption that every element can be considered as a black box connected to two terminals. It is in essence the translation of an equivalent circuit into a representation that can be interpreted by the program. Each symbol represents a specific type of element, e.g. R for resistance and Q for constant phase elements (CPE), and the parenthesis are a reminder for the program that the response of a complex element should be calculated first. So the code (RQ)(RQ) translate as the series combination of two parallel resistor and non-ideal capacitor.



Figure 4.4. Typical Nyquist plot for as-prepared $Ca_{12}Al_{14}O_{33}$ at two different temperatures. Open circles correspond to experimental data and the dashed line a calculated fit using an equivalent circuit model (RQ)(RQ).

At low temperatures (~ 390 °C) two semicircles are obtained, where the low frequency arc (to the right of the graph) has an associated capacitance of ~ 1 nF/cm and was related to the grain boundary response and a high frequency arc (to the left of the graph), showing a capacitance of ~ 5 pF/cm, that was associated with the bulk response of the sample. The resistance of the bulk (R_b) and the grain boundary (R_{gb}) are given by the intersection of the corresponding arcs with the real (Re(Z)) axis. When heating the sample around 720 °C only the grain boundary arc is observed and the bulk data can be obtained from the modeling with and (RQ)(RQ) circuit using the equivalent circuit software and estimating the Q from the bulk response (as shown in Fig. 4.4).

Figure 4.5 shows the results obtained for the bulk conductivity of the as-prepared mayenite pellet, over the temperature range 210 - 720 °C, compared to the data of Lacerda et al. [33], together with data for the widely studied yttria-stabilized zirconia. The asprepared $Ca_{12}Al_{14}O_{33}$ pellets exhibit a conductivity 8-10 times less than yttria-stabilized, zirconia consistent with the Lacerda et al. results [106, 33, 34]. It should be mentioned that we did not reproduce the measurements using a concentration cell, but Lacerda et al. [33] confirmed by that method that the conducting species were oxide ions. The activation energy for the diffusion of charge carriers in the bulk of the $Ca_{12}Al_{14}O_{33}$ crystal can be derived from Fig. 4.5 and the temperature dependence of the conductivity given by:

(4.8)
$$\sigma = A \exp\left(\frac{-E_{diff}}{RT}\right)$$

where A is a constant, E_{diff} is the diffusion activation energy, of carriers and R is the gas constant. From the slope of Fig. 4.5, an activation energy of ~ 71 KJ/mol was obtained for the carriers diffusion. The slight shift of the data to smaller conductivity values is probably due to a different concentration of oxygen radicals. As shown in the previous section, the behavior of the Ca₁₂Al₁₄O₃₃ system is sensitive to the sample history; according to various studies oxygenous species like O_2^{-2} O_2^- and OH⁻ are less mobile and might significantly reduce the conductivity [100, 99, 102, 103, 104].

4.3.2. Results by the powder solution composite (PSC) technique

As described in Section 3.5.2 the conductivity of a UV-irradiated / H-doped Ca₁₂Al₁₄O₃₃ sample was analyzed using the powder solution composite technique. To complement this technique, SEM images were acquired to gather information on the morphology and particle size distribution of the Ca₁₂Al₁₄O₃₃ phase under study. Fig. 4.6 shows a typical SEM image of the UV-irradiated / H-treated Ca₁₂Al₁₄O₃₃ powder; the particles present a broad distribution of sizes, from 10 μ m to agglomerates of 80 μ m and the morphology can be seen and modeled as spherical, even though the particles may have sharp edges.



Figure 4.5. Ionic conductivity results for as-prepared $Ca_{12}Al_{14}O_{33}$ sample.



Figure 4.6. SEM image of UV-irradiated H-doped $Ca_{12}Al_{14}O_{33}$ powder used for PSC measurements.

According to the particle size and distribution we found that the effective medium equation found that gave the best fit to the composite data is the Bruggeman asymmetric model [86, 82, 79], given by:

(4.9)
$$(1-f) = \frac{K_c - K_p}{K_c^{1/3} \cdot (1-K_p)}$$

where K_c is the conductivity ratio between the composite and the solution (σ_c/σ_s) , K_p is the conductivity ratio between the particles and the solution (σ_p/σ_s) , and f is the volume fraction of the suspended phase, calculated as:

$$(4.10) f = \frac{w/\rho}{\pi . r^2 . L}$$

here w is the weight of the amount of powder used, ρ is its theoretical density, and $(\pi.r^2.L)$ is the volume of the PSC chamber. Figure 4.7 shows the resulting PSC plot for the UV-irradiated / H-doped mayenite sample, where the conductivity of the composite is plotted versus the conductivity of the solution. The experimental data points for the activated Ca₁₂Al₁₄O₃₃ phase are represented with red markers, the calculated fit with the Brugemman asymetric equation is the red line and the reference line given by the plain solution is the black line. For this case the cross-over point between the fitted data and the plain solution gives the true bulk conductivity of the particles (0.17 S/cm). Individual error bars reflect uncertainty in measuring interelectrode spacing and in evaluating resistance from the corresponding cusp in the impedance plots. By passing the fit through the lower and upper limit of the error bars we can estimate the overall error in the bulk conductivity, 0.17 ±0.02 S/cm.



Figure 4.7. Powder Solution Composite (PSC) results for UV-irradiated H-doped $Ca_{12}Al_{14}O_{33}$ powder.

4.3.3. Conductivity vs. temperature

The conductivity result from PSC measurements reported in the previous section (0.17 ± 0.02 S/cm) agrees well with the value obtained by 4-point DC measurements at room temperature on a UV-irradiated H-doped Ca₁₂Al₁₄O₃₃ pellet (0.15 S/cm). It should be mentioned that this sample was hydrogen treated and UV irradiated in the same batch with the powder used for PSC. As will be evident in later figures and in agreement with reports by Hayashi et al. [25], the conductivity depends on how much hydrogen the sample incorporates and the intensity / duration of the UV light exposure, so it is important to be consistent in the preparation before comparing results. Figure 4.8 shows the temperature dependence of the conductivity above room temperature. The systematic error, which is constant for all the data points is on the order of 10 % (owing principally to uncertainty



Figure 4.8. Temperature dependence of the conductivity for UV-iluminated H-doped $Ca_{12}Al_{14}O_{33}$ pellet (300K - 400K).

in the thickness of the irradiated layer). The random error is much smaller and not bigger that the symbol size. The data from Fig. 4.8 (a) is re-ploted in Arrhenius form in Fig. 4.8 (b) showing the thermally activated conductivity with an activation energy, $E_H = 0.13$ eV. Note that this value is typical of small polaron conductors (0.11 - 0.23 eV) [107, 108, 109, 110, 111].

Below room temperature the conductivity decreases to a value of $2 \cdot 10^{-4}$ S/cm at 77.8 K. The natural logarithm of the conductivity appears to be proportional to T^{-1/4} for the whole range of temperature (77 - 300 K) as shown in Fig. 4.9, however, this same figure shows a small discontinuity at ~150 K and the data points below that temperature can also be plotted versus T^{-1/2} showing a similar linear behavior. These results indicate that at high temperatures the conductivity has an activated nature and below room temperature the conductivity follows the Mott behavior for variable range hopping [112]. It could be argued from Fig. 4.9 that a third regime (< 150K) also exists, where conductivity



Figure 4.9. Temperature dependence of the conductivity for UV-iluminated H-doped $Ca_{12}Al_{14}O_{33}$ pellet (77K - 300K).

follows Efros-Shklovskii behavior [113] but the changeover is difficult to distinguish within experimental error.

4.3.4. Thermopower measurements

Thermopower measurements on UV-irradiated / H-doped Ca₁₂Al₁₄O₃₃ samples (Fig. 4.10) show that the Seebeck coefficient is roughly temperature independent in the range of 25-120 °C. The average value for the coefficient in that range is ~200 ±10 μ V/K, where the negative sign indicates that the carriers are electrons (n-type). The fact that the conductivity is thermally activated while the Seebeck coefficient is roughly temperature



Figure 4.10. Thermopower measurements of UV-irradiated H-doped $Ca_{12}Al_{14}O_{33}$ cut in 10 x 3 x 3 mm bars.

independent establish as the existence of an activated mobility and suggests that the electronic transport mechanism is by small polaron hopping. The discussion in Appendix A treats the small polaron conduction in detail.

4.4. Magnetoresistance

A characteristic feature of the hopping nature of the electric transport is a gigantic positive magnetoresistance which depends exponentially on the strength of the magnetic field [113]. Results of the magnetic field dependence of the resistivity are shown in Fig. 4.11. The left most graph shows the temperature dependence of the resistivity for two different magnetic fields. Note that only at low temperatures it is possible to observe a slight change in resistivity with an applied field of 5000 Gauss. Even though Fig. 4.11(a) does not give much input on the behavior of this material, Fig. 4.11 (b) shows a marked difference between the sample at room temperature and under liquid nitrogen. At 300 K no difference in the magnetoresistance is perceptible, but at 77 K and over



Figure 4.11. a) Temperature dependence of the resistivity in UV-irradiated H-doped $Ca_{12}Al_{14}O_{33}$ for two values of magnetic field (0 and 5000 G) (b) Magnetic field dependence of the magnetoresistance (%) for two temperatures (Liquid nitrogen and room temperature). The magnetic field was applied in and out of plane with the electric field and no difference was observed.

4000 Gauss the magnetoresistance seems to increase exponentially. This suggest that the conduction mechanism is the product of carrier hopping, however to be conclusive, more data should be gather at lower temperatures and stronger magnetic fields. This behavior has been observed in many semiconductors but the comparison to well tabulated data [114] is somewhat complicated owing to the small range of our measurements. On the other hand, it is important to mention that even with the possibility of going to liquid helium temperature (~ 2 K) the conductivity of this material will drop to $1 \cdot 10^{-8}$ S/cm in the absence of a magnetic field, making the measurements extremely difficult.

4.5. Reversibility of the activation process

Conductivity measurements during heating-cooling cycles were conducted on UVirradiated / deuterium-doped mayenite specimens to study the reversibility of the activation process. The reason for using deuterium was that some of these same samples were simultaneously studied by Secondary Ion Mass Spectroscopy (SIMS) as mentioned in Section 3.4.2. The first cycle run is shown in Fig. 4.12, where in order to look at theoretical predictions, the newly UV-irradiated / D-doped sample was heated to 140 °C following the A \rightarrow B path and then cooled down. The path upon cooling does not match the original A \rightarrow B line. Instead it lies a little higher in conductivity following the B \rightarrow C path in Fig. 4.12. This behavior was found to occur only the first time the sample was heated, as subsequent temperature cycling resulted in no changes from the B \rightarrow C path. Theoretical calculations relate this to the realization of the optimal arrangement of the hopping centers and it will be discussed later in this chapter (see Section 4.9). Even though the finding is consistent with theoretical calculations, it should be noted that the difference between the two paths becomes very small when considering the systematic error of ~ 10% on each marker (see Fig. 4.12).

The second heating-cooling cycle is shown in Fig. 4.13 (a), where the arrows indicate the evolution of the experiment. The sample was heated from room temperature to 180 °C inside a tube furnace, while conductivity measurements were taken using the Van der Pauw technique described in section 3.5.3. From room temperature to \sim 130 °C the conductivity increases reversibly with temperature along the upper line. Once temperature exceeds 135 °C, conductivity drops irreversibly and on cooling, the conductivity decreases along the lower line. Upon reaching room temperature, the sample was re-irradiated in



Figure 4.12. Conductivity vs. Temperature of the UV-irradiated D-doped $Ca_{12}Al_{14}O_{33}$ when heating-cooling specimens for the first time.

an attempt to recover the original state, but the original values could not be reproduced and the sample followed the same lower line upon re-heating. The irreversibility above 135 °C suggests that the amount of hydrogen trapped inside the sample decreases, and with it the amount of carriers. Hereafter we will refer to this maximum temperature as the decomposition temperature.

4.6. Hydrogen content

To confirm the hypothesis that the decrease in carrier content is related to hydrogen loss above the decomposition temperature, SIMS investigations on the surface of the UVirradiated / D-treated $Ca_{12}Al_{14}O_{33}$ sample were carried out. The same sample utilized in the previous section for the heating-cooling cycle was analyzed at room temperature before and after the cycle. Data collected by SIMS show the presence of deuterium inside the specimens, as can be seen from the spectra and the maps in Fig. 4.14. A significant



Figure 4.13. (a) Conductivity vs. temperature for a heating (red arrow) and cooling (blue arrow) cycle of UV:D: $Ca_{12}Al_{14}O_{33}$ (b) Re-plot of the heating-cooling cycle using Eq. A.8 for small polaron conductors.

loss of deuterium was also detected in the samples after heating. Table 4.1 shows the relative values of deuterium-to-calcium and the percentage loss.



Figure 4.14. Composition spectra image from SIMS for a UV-irradiated D-doped $\rm Ca_{12}Al_{14}O_{33}$ specimen.

Table 4.1. SIMS results for deuterium loss in UV-irradiated / D-treated $\rm Ca_{12}Al_{14}O_{33}$.

Relative ratio	Sample before cycle	Sample after cycle	Deuterium loss
D_2/Ca	0.000733	0.000455	38%

This is conclusive evidence that above the decomposition temperature, $Ca_{12}Al_{14}O_{33}$, releases hydrogen (deuterium) and that the conductivity is a function of the hydrogen content.

4.7. Transport mechanism

So far evidence has been presented that hydrogen is responsible for the unusual insulator-to-conductor conversion of $Ca_{12}Al_{14}O_{33}$ in agreement with Hayashi's findings [25]. It was also found that activated mayenite exhibits a thermally activated conductivity and mobility, suggesting that the conduction mechanism for this material follows small polaron conduction in contrast with Sushko and Hayashi idea of an F^+ -like center (see section 2.4).

To take this analysis a step further, the conductivity values from Fig. 4.13 (a) were re-plotted in an Arrhenius form as shown in Fig. 4.13 (b) using the functional form of the conductivity for the small polaron conduction model, as described by Eq. A.8 from Appendix A:

(4.11)
$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E_H}{k.T}\right)$$

From the slopes of the lines in Fig. 4.13(b) we can calculate the hopping energy (E_H) , of ~ 0.13 eV, and from the intercept with the y-axis we can determine the σ_0 coefficients (17039 S.K/cm for the heating path and 11058 S.K/cm for the cooling path). Again, the value of hopping energy falls inside the range of well known small polaron conductors [107, 108, 109, 110, 111] and the variation in the pre-exponential factor is equal to ~35 %, which agrees well with the percent deuterium loss found by SIMS. Furthermore, If we look at the parameters that make up the pre-exponential factor, σ_0 , from Eq. A.9:

(4.12)
$$\sigma_0 = \frac{g.c.N.(1-c).e^2.a^2.\nu}{k}$$

where g is a geometrical factor on the order of unity related to the coordination number of equivalent sites, a is the jump distance between equivalent sites, ν is the lattice vibrational frequency, N is the total available number of sites for hopping, c is the fraction of occupied sites and (1 - c) is the probability that the adjacent site has the appropriate valence for a jump to occur. We can relate the 35 % decreased in σ_0 (owing to deuterium loss) to a decrease in the number of available sites (N) and/or the fraction of occupied sites (c), if all the rest other parameters are assumed to remain constant.

To further develop this idea, thermopower measurements were performed on the same system described in the previous section, 4.5. Before the sample was heated, the value for the Seebeck coefficient was -193 μ V/K and after heating beyond the decomposition temperature it became -209 μ V/K. If we use the equation for the Seebeck coefficient of small polaron conductors described in Appendix A (section A.10):

(4.13)
$$Q = \pm \frac{k}{e} \left(\ln \frac{2(1-c)}{c} \right)$$

where k/e is 86.14 μ V/K, c is the fraction of occupied sites and 2 accounts for the spin degeneracy, we obtain a value of c= 0.175 before heating and 0.150 after heating beyond the decomposition temperature. This agrees well with all the previous observations that the number of carrier decreases once the decomposition temperature is crossed. But the change from 0.175 to 0.150 in the fraction of occupied sites is only 14.4% insufficient to explain the ~35% decrease in the pre-exponential factor. This suggests that the number of available sites (N) must also change, and that hydrogen is part of the path for the small polaron hopping. These findings correlate well with the proposed hopping path obtained from density functional calculations, discussed later in this chapter (section 4.9), where the free electrons hop through a path formed by 12 atoms per unit cell, 2 of which are hydrogenous species (OH⁻ and H⁰), see Fig. 4.19.

Moreover, if we consider that after hydrogen treatment there are two H⁻ per unit cell, and that each of them releases one electron according to Eq. 8.2, the calculated fraction of occupied sites is given by 2/12 = 0.166. This value agrees well with the experimental fraction of occupied sites, c = 0.164, given when applying Eq. 4.13 to the average value of thermopower found on section 4.3.4 for a range of temperatures (-200 μ V/K).

Finally, the carrier content and the mobility can be calculated from

$$(4.14) n = N.c$$

(4.15)
$$\mu = \frac{n.e}{\sigma}$$
where $N = 12/(\text{volume unit cell}) = 6.9 \cdot 10^{21}$, c = 0.164. The carrier content $\sim 1 \cdot 10^{21} \text{ cm}^{-3}$ and the mobility is $\sim 1.4 \cdot 10^{-3} \text{ cm}^2/\text{Vs}$, consistent with mobility values typical for small polaron conduction [110].

4.8. Diffuse reflectance

Diffuse reflectance spectra collected for the Ca₁₂Al₁₄O₃₃ specimens are shown in Fig. 4.15. The absorption edge, is estimated at the intersection of a line drawn through the slope where the transmission drops abruptly as marked with an arrow on Fig. 4.15. This can be used to obtain an estimative of the band-gap as it was mentioned on section 3.6.1. The as-prepared and hydrogen-treated $Ca_{12}Al_{14}O_{33}$ samples present similar optical transmission at 600 nm of >90%. However, a new optical band is induced in the hydrogenated samples and the band gap shifts from $E_g \sim 5 \text{ eV}$ for the as-prepared sample to $\sim 4 \text{ eV}$. The UV-irradiated / H-doped sample showed a strong green coloration, along with a transmission of 28% at 600 nm and a band gap ~ 2.58 eV, consistent with previous reports [25]. Once the sample was heated beyond the decomposition temperature and cooled back to room temperature (following the heating cycle of section 4.5), the transmission increased to 60% at 600 nm and a significant loss of its bright green color was observed, consistent with the drop in carrier population. An attempt to recover the original state by re-irradiating the sample gave exactly the same diffuse reflectance spectra, confirming that the original state cannot be recovered once the decomposition temperature was surpassed.



Figure 4.15. Diffuse reflectance results for $Ca_{12}Al_{14}O_{33}$ samples; the marker shows how the estimations of the band gap were taken.

4.9. Electronic structure and first ab initio study of hopping transport

The electronic structure of $Ca_{12}Al_{14}O_{33}$ was calculated in collaboration with Medvedeva and Freeman [115]. As mentioned in section 2.3.1, the framework of $Ca_{12}Al_{14}O_{33}$ includes 64 oxygen ions; the remaining two oxygen ions which provide charge neutrality are located inside the cages (see Fig. 2.2) These two O^{-2} are distributed between 24 sites that produce a structural disorder. From full-potential linearized augmented plane-wave (FLAPW) total energy calculations [116] of seven structures with different distances between these two oxygen ions (ranging from 5.1 to 10.4 Å), it was found that the O^{-2} ions tend to maximize the distance between them by forming a bcc lattice, with the crystallographic basis oriented randomly with respect to that of the whole crystal. The calculated electronic density of states (DOS), using the linear muffin-tin orbital (LMTO) method before hydrogen doping is shown in Fig. 4.16, where oxygen 2p states form the top of the valence band between 6 and 2 eV (the Fermi level is taken as zero), while the bottom of the conduction band is formed from Ca 3d states. Located inside one of the six cages, O^{-2} gives a fully occupied impurity peak below E_F . The calculated band gap, 4.8 eV, underestimates the experimental absorption edge by 4%.

The incorporation of hydrogen results in the appearance of new bands as shown in Fig. 4.17. Since hydrogen shares its electron with O^{-2} (forming a hydroxide ion), filled σ and nonbonding π bands and unoccupied σ' band are introduced. Also the 1s states of H⁻ form a fully occupied impurity band below E_F . After hydrogen doping, the energy of the transitions from O 2p states to Ca 3d states is decreased by 0.7 eV (from 5.9 to 5.2 eV), in agreement with experimental results. The maximum efficiency of the UV activation of the H⁻, which corresponds to transitions from H⁻ 1s states to the 3d states of its closest Ca neighbors, occurs at about the same photon energy, Fig. 4.17. These results are in contrast with the conclusion of Hayashi et al. [25] that hydrogen controls the absorption edge.

For UV-irradiated / hydrogen-doped mayenite, we calculated the model system where the electron released from H^- is transferred equally to the d states of six Ca neighbors.



Figure 4.16. Total and partial DOS of $Ca_{12}Al_{14}O_{33}$ E_F is at 0 eV and the Al 3d states form the band centered at ~2.8 eV.

It should be mentioned that we have no way of distinguishing by density functional calculations if H⁻ releases one electron as suggested by Eq. 2.2 or two electrons as mentioned in Eq. 2.3. For the purpose of these calculations we will refer to H^{*} as the hydrogenous species resulting from UV irradiation. The self-consistent DOS shows the formation of a new band (Fig. 4.18) with the same total number of states, m, as in the band gap of the system before UV irradiation. However, since m is now 2 times larger than the number of available electrons, E_F passes through the middle of the band and the system becomes conducting. The calculated positions of the characteristic absorption bands [0.38 and 3.5 eV, Fig. 4.18 agree well with experimental results (0.4 and 2.8 eV),



Figure 4.17. Total DOS of H-doped $Ca_{12}Al_{14}O_{33}$. The band gap, E_g is between O 2p and Ca 3d states. The DOS of the OH⁻ and H⁻ is enlarged by a factor of 5. The UV activation corresponds to the transition from H⁻ 1s to the 3d states of its closest Ca (dashed line), with energy E_e .



Figure 4.18. (a) Total DOS of UV-irradiated H-doped $Ca_{12}Al_{14}O_{33}$ and the join DOS calculated using the optical selection rules and nearest neighbor transitions (b) enlarge total DOS of of UV-irradiated H-doped $Ca_{12}Al_{14}O_{33}$ showing a soft Coulomb gap.

as is the intense charge transfer transition from oxygen 2p states to Ca 3d states, which occurs at ~4.8 eV.

The nonzero DOS at E_F ; $g(E_F)$ is found to be determined mainly by H^{*}, O^{*}, and Ca states, atoms that are spatially well separated from each other, which points to the hopping nature of the conductivity. It is striking that the arrangement of the atoms corresponds to the shortest electron hopping path: only the closest Ca neighbors of O^{*}, Ca(2) and Ca(3) (at distances of 3.3 and 2.4 Å, respectively), and the closest Ca neighbors of H^{*}, Ca(1) and Ca(4) (both at 2.8 Å), give significant contributions to $g(E_F)$. Fig. 4.19 shows the proposed hopping path and the relative contributions per atom to the DOS at the Fermi energy are shown in Table 4.2 and Fig. 4.20. The longest segment on the hopping path corresponds to the distance between Ca(1), Ca(2), and O^* , which explains the higher probability to find the electron on Ca(1) and Ca(2). With the information of the distances between hopping centers we can recall the equation for the pre-exponential factor (Eq. A.9) and calculate the optical phonon frequencies responsible for the hopping. By assuming that a is equal to the average of the distances given above, using $\sigma_0 = 17039$ S.K/cm, $N=6.9\cdot10^{21}$, c=0.164 and estimating g to be z/6, where z is the number of hopping sites surrounding a site, the frequency (ν) appears to be $3 \cdot 10^{13} \text{ s}^{-1}$ which is in perfect agreement with other polaron systems [117, 118, 119]

Finally, the charge density distribution calculated in the energy window of 25 meV below E_F clearly shows the connected electron density maxima along the hopping path, see Fig. 4.21(a). The charge density in the empty cages is insignificant, Fig. 4.21(b), demonstrating that trapping of the electron on the vacancy does not occur.

Hopping transport in systems with localized electronic states has been studied analytically, numerically, and experimentally [112, 113, 120, 121, 122]. At high temperatures, the hopping occurs between nearest neighbors and has an activated nature. At lower



Figure 4.19. Proposed hopping path for electron migration. The cube represent the unit cell and only atoms that give dominant contribution to the non zero DOS at E_F .

Atoms	%	Atoms	%	Atoms	%
Ca(1)	7.6	Ca(4)	4.2	rest Ca	~ 1.0
Ca(2)	8.4	H^*	6.9	rest O	~ 0.7
O* Centers of	7.6	Ca(3)	3.8	Al	0.1
empty cages	0.3				

Table 4.2. The relative contributions per atom to the DOS at $E_{\rm F}$.

temperatures, the activation energy for hops between localized centers can be reduced by enlarging the hopping distance, which leads to the variable range hopping described by Mott and Davis [112]. At yet lower T, the electron-electron repulsive interaction between charge carriers may result in the formation of a Coulomb gap [113] centered at E_F . The



Figure 4.20. The relative contributions per atom to the DOS at E_F .



Figure 4.21. Contour map of the charge density distribution within a slice passing through the center of (a) a cage with H^0 and (b) an empty cage (vacancy).

value of the gap can be estimated as

(4.16)
$$E_{CG} = \frac{e^2}{4.\pi.\epsilon_0.\epsilon.r_{ch}}$$

where e is the elementary charge, ϵ_0 is the permittivity constant, ϵ is the relative dielectric constant, and r_{ch} is the characteristic distance between interacting electrons. In the present case, r_{ch} is equal to the cube root of the unit cell volume divided by 2. Using $\epsilon = 2.56$ from Zhmoidin et al. [123] yields 0.3 eV for the gap value which agrees with the observed absorption peak at 0.4 eV reported by Hayashi et al. [25]. Similar to the above qualitative picture, the behavior of the conductivity at finite temperature can be predicted based on the calculated DOS in the vicinity of E_F for irradiated H-doped mayenite. Clearly, this exhibits a soft Coulomb gap (see Fig. 4.18(b)) near E_F and, similar to Fig.10.1 in Shklovskii and Efros [113], has two peaks. Moreover, the splitting of the hybrid band, 0.38 eV, agrees well with the value of the gap estimated above on the basis of the strong electron repulsion. These results indicate Efros-Shklovskii (ES) behavior [113] of the conductivity At low T:

(4.17)
$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_{ES}}{T}\right)^{\frac{1}{2}}\right] \quad with \quad T_{ES} = \frac{\beta_{ES}.e^2}{k_B.k.\xi}$$

where ξ is the localization length, k_B is the Boltzmann constant, and $k = \epsilon_0 \cdot \epsilon$. When T increases, the Coulomb gap fills. A substantial DOS should be observed already at T~0.05 $\Delta \epsilon$, where $\Delta \epsilon$ is the gap width [124]. At this T, the changeover to the Mott behavior should occur [112]

(4.18)
$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_M}{T}\right)^{\frac{1}{4}}\right] \quad with \quad T_M = \frac{\beta_M}{k_B \cdot g_0 \cdot \xi^3}$$

The double peak structure completely disappears at T~0.4 $\Delta\varepsilon$. Using $\Delta\varepsilon\simeq$ 0.38 eV from Fig. 4.18(b), we obtain the crossover T between Mott and ES behavior to be T_c~170 K. Indeed, for H-doped UV-irradiated mayenite, the T^{-1/4} dependence of log(σ) was found experimentally for 50 < T < 300 K, as mention in section 4.3. The H^{*} species may also occupy cages farther away from the the OH⁻ occupied cages, however, we found this arrangement to be less favorable energetically, by 96 meV. It is feasible that under rapid cooling of the sample annealed at 1300°C, some hydrogen becomes frozen into these positions. After UV irradiation, the corresponding hopping path involves a long segment between two Ca atoms (now increased from 3.7 to 6.5 Å), so that $g(E_F)$ becomes zero and the hopping has an activated behavior. If temperature is now increased to a level sufficient for hydrogen migration, these atoms will be able to diffuse into the energetically favorable positions, which facilitates the hopping and leads to an increase of σ . These predictions were confirmed experimentally and were shown in Fig. 4.12.

Finally, the observations on proton implantation made by Miyakawa et al. [41] agree with our model and its predictions: the calculations show that along with the increased concentration of the excess electrons, the proton implantation will result in the appearance of new unoccupied states in the band gap, making H^+ one of the hopping centers that creates a conductivity path and so enhances the transport.

4.10. Summary

The $Ca_{12}Al_{14}O_{33}$ structure was found to be render conducting by hydrogen treatment and subsequent UV-light irradiation. The free oxygen ions inside the crystallographic cages of mayenite react when expose to different environments absorbing a variety of species, i.e., water, oxygen, etc. The as-prepared system also presents an ionic conductivity an order of magnitude smaller than YSZ. Meanwhile, the electronic conductivity of the H-doped UV-irradiated mayenite at room temperature is approximately 0.3 S/cm. The conductivity rises reversibly with temperature until the decomposition temperature is surpassed and beyond this decomposition temperature the conductivity drops irreversibly owing to hydrogen loss. Thermopower measurements are consistent with the decrease of carriers generated by the hydrogen loss. Temperature dependence of the conductivity suggest that the transport mechanism follows a hopping model, in particular a small polaron conduction model, which was also corroborated by magnetoresistance measurements. Analysis based on the small polaron mechanism suggest hydrogenous species are part of the conducting path, which agrees with density functional calculations.

The strong dependence of the conductivity on the particular atoms participating in the hopping suggests the possibility of varying the conductivity by proper doping. For example, we expect that Mg substitution can lead to a decrease in σ once Mg substitutes one of the Ca atoms involved in the hopping, since its 3*d* states will lie much higher in energy than that of Ca, while Sr substitution may not result in any significant changes in σ . Instead, one way to possibly improve the electronic transport consists in increasing the concentration of hopping centers by substituting Si⁴⁺ for Al³⁺.

CHAPTER 5

The $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ phase

5.1. Phase analysis

Bulk magnesium substituted mayenite $(Ca_{(12-x)}Mg_xAl_{14}O_{33})$ samples were prepared by solid state reaction using the technique described in section 3.1.1. Subsequent hydrogen doping and UV irradiation were performed following the steps mentioned in section 3.2.1 and 3.2.3. Phase analysis of the as-prepared $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x = 0.1, 0.3, 0.5, 0.8, 1) samples is shown in Fig. 5.1, a good match in every instance with the corresponding JCPD card for mayenite (00-009-0413). Even though Mg^{2+} is smaller than Ca^{2+} when occupying an octahedral site, as shown in table 5.1, the substitution level is very small to perceive any significant shift on the XRD patterns.

Ion	Electron configuration	Coordination number	Effective ionic radii
Ca^{2+}	3p 6	VI	1.00
		VII	1.07
		VIII	1.12
		IX	1.18
		Х	1.28
		XII	1.35
Mg^{2+}	2p 6	IV	0.49
		VI	0.72
		VIII	0.89

Table 5.1. Effective ionic radii from Shannon et al.[2].



Figure 5.1. Powder X-ray diffraction pattern of $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x = 0.1, 0.3, 0.5, 0.8, 1) compared to pure may enite and the intensity map showing no significant lattice shift upon Mg substitution.

XRD analysis was also undertaken comparing the as-prepared samples to the hydrogendoped and the UV-irradiated / hydrogen-treated $Ca_{(12-x)}Mg_xAl_{14}O_{33}\dot{S}$ imilar to the case of the pure mayenite specimens reported in the previous chapter, no structural change seems to be induced by the activation treatment (see Fig. 5.2).



Figure 5.2. Powder X-ray diffraction pattern of $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x = 0.5) compared to may enite JCPDS card [4], H-doped $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ and UV-irradiated H-doped $Ca_{(12-x)}Mg_xAl_{14}O_{33}$.

It is worth mentioning that samples with higher substitution levels fall outside the equilibrium region of this phase, as was shown on the ternary diagram of section 3.2. An example of the X-ray powder pattern for a sample prepared with 4.5% MgO in an attempt to obtain $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ with x = 1.5 is shown in Fig. 5.3, where is clear that there is more than mayenite in the equilibrium.

5.2. Ionic conductivity

Similar to the measurements reported for pure mayenite (see section 4.3.1), ionic conductivity was evaluated for pellets of as-prepared $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ under ambient



Figure 5.3. Powder X-ray diffraction pattern of sample prepared with $\sim 5\%$ MgO looking to obtain Ca_(12-x)Mg_xAl₁₄O₃₃ (x = 1.5).

conditions. Nyquist plots for the magnesium-substituted systems are similar to the ones obtained for the pure mayenite, where a grain boundary arc with an associated capacitance of ~ 1 nF/cm is found at low frequencies and a bulk arc with a capacitance of ~ 5 pF/cm lies at higher frequencies (see Fig. 4.4). An (RQ)(RQ) equivalent circuit model was used to fit the arcs and to obtain the value of the bulk resistance [105]. Figure 5.4 shows the results obtained for the bulk conductivity of the as-prepared $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x = 0.3 and 1) pellets, over the temperature range 300 - 650 °C, compared to previous values obtained for the pure $Ca_{12}Al_{14}O_{33}$ sample and yttria-stabilized zirconia (YSZ).

As mentioned in the previous chapter the as-prepared $Ca_{12}Al_{14}O_{33}$ pellets showed a conductivity ~10 times less than yttria-stabilized zirconia, consistent with previous findings. Meanwhile, the magnesium substituted specimens showed an even bigger difference



Figure 5.4. Ionic conductivity results for as-prepared $Ca_{12}Al_{14}O_{33}$ sample.

in conductivity with YSZ, which increased with the substitution level. For x = 0.3 the conductivity is 20 times smaller than YSZ and for x = 1 the conductivity drops to 45 times less than YSZ. This could indicate that the more Mg introduced in the sample, the higher the concentration of less mobile species, e.g. O_2^{-2} , O_2^{-} and OH^{-} . Moreover, the activation energy for the diffusion of charge carriers in the bulk of the $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ crystals seems to increase with the substitution level. Using Eq. 4.8 and the slopes shown in Fig. 5.4, diffusion energies of $E_{diff} = 74$ kJ/mol for x=0.3 and $E_{diff} = 80$ kJ/mol for x=1 are obtained. This also supports the idea that magnesium favors the formation of less mobile oxygenous species, i.e., more energy is require for the carriers to diffuse. It is important to mention that this should not affect the behavior of the samples after hydrogen treatment and UV-irradiation. It has been reported in the literature that hydrogen is still incorporated into samples through an exchange reaction between O_2^- and H^- and/or between O_2^{-2} and $2H^-$, owing to the inability to avoid the incorporation of oxygen radicals during high temperature annealing, even in N₂ atmosphere.

5.3. Oxygen species

Raman spectroscopy was undertaken in order to characterize the oxygen radicals present in the $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ samples. Figure 5.5 shows the resulting spectra where the pure mayenite sample is compared to $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x = 0.3, 0.5 and 1). For all the samples the band at 540 cm⁻¹ relates to the fundamental vibration of a cubic crystalline lattice, and the band at 776 cm⁻¹ corresponds to the stretching vibrations of the AlO₄ tetrahedra. It is evident in the $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ specimens, that a small band exists around 880 cm⁻¹; this band is commonly assigned to O_2^{-2} species [57, 58, 125]. Thus, the idea that less mobile species exist in the Mg-substituted system is corroborated by this technique.

5.4. Conductivity vs. temperature

The temperature dependence of the conductivity for the hydrogen-doped/UV-irradiated $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x = 0.1; 0.3; 0.5; 0.8; 1.0) is shown in Fig. 5.6. Again the systematic error is on the order of 10%, mainly due to uncertainty in the geometric factors and the random error is on the order of the symbol size or less. As shown in Fig. 5.6, the conductivity is strongly dependent on the substitution level and rises reversibly from room temperature to approximately 130 °C. Similar to the findings mentioned in section 4.5 on the non-substituted $Ca_{12}Al_{14}O_{33}$ samples, once the temperature exceeds ~135 °C the



Figure 5.5. Raman spectra for the ${\rm Ca}_{(12-x)}{\rm Mg}_x{\rm Al}_{14}{\rm O}_{33}$ (x = 0.1, 0.3, 0.5, 0.8, 1) vs. ${\rm Ca}_{12}{\rm Al}_{14}{\rm O}_{33}$.



Figure 5.6. Temperature dependence of the conductivity for UVilluminated / H-doped $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x = 0, 0.1, 0.3, 0.5, 0.8,1) pellets (300K - 400K).

conductivity drops irreversibly. This drop was related to the amount of hydrogen released when the temperature exceeds the decomposition temperature. Figure 5.6 also shows a slight shift of the decomposition temperature to higher values as the substitution level increases.

The gradual shift of the decomposition temperature for the Mg-substituted mayenite results from two factors. First, the magnitude and resulting slope of conductivity vs. temperature in the reversible conductivity regime (up to the decomposition temperature) decrease monotonically with increasing Mg-content. Secondly the post-peak is virtually the same for all the Mg-substituted specimens, which is noticeably different than for the non-substituted mayenite. These two factors will be discuss separately in the sections below.

5.5. Magnesium - hydrogen affinity

The fact that the post-peak behavior is virtually the same for all the Mg-substituted samples and significantly different from the pure mayenite specimen's indicates that the kinetics of decomposition are different for the Mg-substituted materials and the host material. This is not attributable to changes in microstructure; the grain sizes (5-10 μ m) were very similar for all the specimens, as shown in Fig. 5.7. Also, there was no systematic change in specimen density with the Mg-level .

A possible explanation can be obtained from density functional calculations for the H-doped $Ca_{(12-x)}Mg_xAl_{14}O_{33}$. From a comparison of the total energies of the 12 fully relaxed structures with different Mg site locations, it was found that the H⁻ relaxes toward the Mg atom and demonstrates a strong Mg-H bonding, cf. Fig. 3. This fact, combined with the tendency for Mg atoms to cluster, could account for the sluggish decomposition kinetics in the Mg-substituted samples.

5.6. Thermopower measurements

Thermopower measurements on UV-irradiated/H-doped $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ samples were undertaken at room temperature for the different substitution levels (x = 0.1, 0.3, 0.5, 0.8, 1). Figure 5.8 shows the coefficients obtained vs. the substitution level compared to the value presented in section 4.3.4 for the pure mayenite specimen. As it can be seen,



Figure 5.7. Optical images of the $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ grain sizes.

thermopower is consistently negative (n type) and, within experimental error, independent of the amount of magnesium substitution and temperature. The average value of the coefficient is 206 $\pm 12 \ \mu V/K$, indicated in Fig. 5.8 as a solid line.

The fact that the conductivity is thermally activated, while the Seebeck coefficient is temperature independent, confirms that an activated mobility exists in the $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ system. Again, this is indicative of a small polaron conduction mechanism. Based on the experimental result of the thermopower, -206 μ V/K \pm 12 μ V/K (see Fig. 5.8), and using Eq. A.10 from Appendix A

(5.1)
$$Q = \pm \frac{k}{e} \left(\ln \frac{2(1-c)}{c} \right)$$



Figure 5.8. Thermopower vs substitution level of $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ at room temperature.

the fraction of conducting species is therefore constant and can be estimated to be 0.155 \pm 0.02, which is consistent with two carriers per unit cell moving along a 12-site hopping path (c = 2/12 = 0.166), as suggested in the previous chapter.

5.7. Conduction mechanism and Mg as a blocking agent

The fact that the magnitude of the conductivity decreases monotonically in the reversible conductivity regime was examined using the expression for the small polaron conductivity from Appendix A (Eq. A.8).

(5.2)
$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E_H}{k.T}\right)$$

Figure 5.6, showing the conductivity of the Mg-substituted samples, was re-ploted in Arrhenius form and is shown in Fig. 5.9, where the hopping energy E_H is found to be



Figure 5.9. Arrhenius plot of electrical properties for $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x = 0, 0.1, 0.3, 0.5, 0.8, 1).

the same for the different values of substitution (x = 0.1; 0.3; 0.5; 0.8; 1.0), including the non-substituted sample, and equal to 0.12 eV. The pre-exponential factor obtained from the different intercepts of Fig. 5.9 drops dramatically with the substitution level, and ranges from 16000 S.K/cm (x = 0) to 2370 S.K/cm (x = 1), as shown in Fig. 5.10.

Analogous to the work presented in the previous chapter, it is assumed that the geometrical factor (g), the jump distance (a) and the lattice vibrational frequency (ν) do not change significantly with doping level. Considering that the value of c is approximately constant as calculated from thermopower measurements, the different values obtained for σ_0 (see Fig. 5.10) have to be related to variations in the total density of conducting sites (N) with the substitution level. This suggests that once Mg substitutes on Ca sites in the cage structure of Ca₁₂Al₁₄O₃₃, the cages occupied by Mg are eliminated from the



Figure 5.10. Pre-exponential factor and normalized pre-exponential factor vs. substitution level.

conduction process, as if Mg were a blocking agent. Indeed, from a comparison of the total energies of the 12 fully relaxed structures with different Mg site locations, it was found by theoretical calculations that the Mg atom prefers to substitute for one of the Ca nearest neighbors of H⁻, i.e., the Ca atom which is involved in the hopping in pure mayenite [115, 126]. This analysis can be taken one step further by considering the pre-exponential factor data normalized by that of the non-substituted sample (cf., Fig. 5.10). Figure 4.19 shown in the previous chapter represents a complete unit cell (two formula units) showing only the atoms which contribute to the conduction mechanism. There are 12 conducting sites (8 Ca atoms, two OH⁻ and two H⁰) in 4 out of 12 cages that are involved in the conduction path. If magnesium ions have a tendency to occupy any of the calcium sites in the 4 conducting cages (as found by the total energy calculations mentioned above), and if each magnesium ion eliminates all of the 12 sites on the conducting path (i.e., it blocks the whole unit cell), we would expect an initial slope of 3 on Fig. 5.10, given by:

(5.3)
$$\frac{N_{(x)}}{N_{(x=0)}} = \frac{\sigma_0}{\sigma_{0(x=0)}} = 1 - \frac{12}{4}x = 1 - 3x$$

As can be seen in Fig. 5.10, only the x=0.1 datum agrees with this slope. The data at higher suggesting that not all magnesium atoms are occupying conducting sites. Indeed, under the rapid cooling of the sample annealed at 1300 °C, some of the Mg atoms can become "frozen" into the positions located far away from the hopping path, since the corresponding total energy is found to be only \sim 57 meV higher than the most energetically favorable structure, in which Mg substitutes one of the hopping centers of the UV-activated system.

Now, to further understand the conductivity behavior versus Mg concentration, the total energy of 11 structures of $Ca_{10}Mg_2Al_{14}O_{33}$ were compared with different site locations for the second Mg atom (the first Mg atom was located at the most energetically favorable position as obtained from the calculations for $Ca_{11}Mg_1Al_{14}O_{33}$). It was found that the second Mg atom prefers to be located in the same cage with the first one, thus demonstrating a tendency for Mg atoms to cluster.

Based on these results, Eq. 5.3 was modified by introducing the factor λ , which represents the fraction of magnesium ions in conducting cages. Moreover, if we consider that a second magnesium atom occupying a calcium site in a conducting cage results in no additional reduction of the conducting sites, the propensity of magnesium ions to cluster in the conducting cages can be accounted for by the term δ in the following equation

(5.4)
$$\frac{N_{(x)}}{N_{(x=0)}} = \frac{\sigma_0}{\sigma_{0(x=0)}} = 1 - 3\lambda x (1 - \delta x)$$

where δ is the fraction of Mg ions in cages with another Mg ion. The best fit to the experimental data in Fig. 5.10 is $\lambda=0.57$ (approximately 43% of the Mg ions occupying nonconducting cages) and $\delta=0.5$ (a significant tendency for Mg to cluster).

This model also allows an estimation of the maximum conductivity achievable in the non-substituted mayenite sample, based on Eq. A.8 and A.9 of appendix A. We assume that the fraction of conducting sites occupied by carriers remains 2/12, a jump frequency of $\sim 10^{13}$ s⁻¹, and an average jump distance of 0.3 nm [115, 126]. If we furthermore assume that all the O²⁻ reacts with H₂ in the hydrogenation process, and that every H⁻ releases an electron after UV irradiation, giving 4 conducting cages per unit cell, the total density of conducting sites will be 12 per unit cell. Using these values and setting the hopping energy to zero, Eq. A.8 gives a maximum conductivity of ~100 S/cm, which agrees well with the results obtained by Matsuishi et al. on Ca-treated, fully reduced (no O²⁻ species) mayenite [45], however subsequent studies (see Chapter 7) show that highly-reduced systems can reach 1000 S/cm.

Furthermore, the carrier content (*Nc*) can be estimated by combining the fraction of occupied sites (from thermopower) with the total density of conducting sites (from σ_0 coefficient). By combining the carrier content values with the conductivity, the mobility for the different substitution levels can be obtained as shown in Table 5.2. These results are consistent with mobility values typical for small polaron conduction (< 1 cm²/Vs) [110].

Mobility 125°C (cm ² /Vs)	$4.12 \cdot 10^{-3}$	$5.18 \cdot 10^{-3}$	$5.41 \cdot 10^{-3}$	$5.07\cdot 10^{-3}$	$6.22 \cdot 10^{-3}$	$7.04 \cdot 10^{-3}$
Conductivity	0.711	0.534	0.515	0.384	0.318	0.234
Mobility 25°C (cm ² /Vs)	$1.57 \cdot 10^{-3}$	$2.35 \cdot 10^{-3}$	$2.19 \cdot 10^{-3}$	$2.18 \cdot 10^{-3}$	$2.56 \cdot 10^{-3}$	$3.19 \cdot 10^{-3}$
Conductivity	$\frac{20 - 0}{0.270}$	0.242	0.209	0.165	0.131	0.106
Carrier Content (cm ⁻³)	$1.08 \cdot 10^{21}$	$6.43 \cdot 10^{20}$	$5.94 \cdot 10^{20}$	$4.72 \cdot 10^{20}$	$3.19 \cdot 10^{20}$	$2.08 \cdot 10^{20}$
Substitution Level (v)		0.1	0.3	0.5	0.8	1.0

Table 5.2. Transport data for $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ at room temperature and 125 °C.



Figure 5.11. Optical properties of $Ca_{(12-x)}Mg_xAl_{14}O_{33}$.

5.8. Optical properties

Finally, diffuse reflectance spectra shown in Fig. 5.11 characterize the optical properties of the $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ system. Transmission increases with the doping level; however, the energy of the optical gap remains constant at 2.6 eV and is in good agreement with previous results [25]. Increased transmission is consistent with the drop in the number of carriers from the electrical measurements (see Table 5.2) and is concomitant with the decrease in green color intensity as shown in Fig. 5.12.

5.9. Summary

Electrical property measurements of $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (x = 0.1, 0.3, 0.5, 0.8, 1) offer evidence for small polaron conduction. The electrical conductivity is activated, whereas the thermoelectric coefficient remains temperature-independent. The activation energy



Figure 5.12. Color difference of UV-irradiated H-doped $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ samples. obatained for all compositions is the same and equal to 0.12 eV. Carrier contents on the order of $10^{20}-10^{21}$ cm⁻³ were calculated from the conductivity pre-exponential factor and the Seebeck coefficient (~-206 μ V/K). The mobilities obtained for the Mg-substituted samples at 125 oC range from 4·10⁻³ to 7·10⁻³ cm²/Vs are consistent with the small polaron transport mechanism.

CHAPTER 6

The $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ phase

6.1. Phase and Rietvield analysis

Silicon-substituted mayenite samples were prepared by hydrothermal synthesis using the technique described in section 3.1.2. As mentioned in that section, the component oxides are placed in a pressure vessel with water, where the following reaction takes place (Eq. 6.1).

(6.1)
$$3 \operatorname{Ca}(\operatorname{OH})_2 + 2\gamma - \operatorname{Al}_2\operatorname{O}_3 + (3-y)\operatorname{SiO}_2 \xrightarrow{\operatorname{H}_2\operatorname{O}} \operatorname{Ca}_3\operatorname{Al}_2(\operatorname{SiO}_4)_{(3-y)}(\operatorname{OH})_{4y}$$

The dried hydrogarnet phase was analyzed by X-ray diffraction and compared to the excistent JCPDS card, with the resulting match shown in Fig. 6.1.

After calcination at 800 °C, the desired phase of $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ (x = 1, 2, 3, 4) is obtained along with a considerable amount of CaO that decreases with the substitution level.

$$(6.2) \quad (7 - \frac{x}{2}) \operatorname{Ca_3Al_2} (\operatorname{SiO_4})_{(3-y)} (OH)_{4y} \rightarrow \operatorname{Ca_{12}Al_{14-x}Si_xO_{33+\frac{x}{2}}} \\ + (9 - \frac{3x}{2}) \operatorname{CaO} + (14y - xy) \operatorname{H_2O} \\ + (21 - 7y - \frac{x}{2}(1+y)) \operatorname{SiO_2}$$



Figure 6.1. Powder X-ray diffraction pattern of $Ca_3Al_2(SiO_4)_{(3-y)}(OH)_{4y}$ (y =) compared to Hydrogarnet JCPDS card [5].

Phase analysis of the powder products of this reaction was done by X-ray diffraction. An example of the resulting patterns is shown in Fig. 6.2 for the case of x = 2; a good match with the corresponding JCPD card for mayenite (00-009-0413) and lime (00-037-1497) is observed. As mentioned in section 3.1.2, the CaO phase cannot be eliminated from the mixture due to the metastability of the Ca₁₂Al_(14-x)Si_xO_(33+ $\frac{x}{2}$) phase.

Figure 6.3 shows a 3D representation of the $\operatorname{Ca}_{12}\operatorname{Al}_{(14-x)}\operatorname{Si}_x\operatorname{O}_{(33+\frac{x}{2})}$ XRD patterns for the different substitution levels, where the relative intensities of the lime peaks versus the mayenite peaks follow the expected trend given by Eq. 3.3. The same figure shows an intensity map of the Si-substituted diffraction peaks compared to the pure mayenite specimen obtained by solid state reaction. It can be observed in the intensity map that the decay of the lime peak intensity with substitution level and a gradual shift of the mayenite diffraction peaks to higher angles (2θ) are consistent with the fact that the effective ionic



Figure 6.2. Powder X-ray diffraction pattern of $\operatorname{Ca}_{12}\operatorname{Al}_{(14-x)}\operatorname{Si}_x\operatorname{O}_{(33+\frac{x}{2})}$ (x = 2) compared to may enter and Lime JCPDS cards [4, 6]. Labels indicate Miller indices for diffracting planes.

Ion	Electron	Coordination	Effective
	configuration	number	ionic radii
Al^{3+}	2p 6	IV	0.39
		V	0.48
		VI	0.53
Si^{4+}	2p 6	IV	0.26
		VI	0.4

Table 6.1. Effective ionic radii from Shannon et al.[2].

radius of Si^{4+} is smaller than that of Al^{3+} when both atoms occupy a tetrahedral site. Table ?? lists the effective ionic radii for both of these atoms from Shannon et al. [2].

The lattice shift observed in the intensity map of Fig. 6.2 was quantified by Rietvield refinement. The results are shown in Fig. 6.4 and are in good agreement with the values reported by Fujita et al. [57].



Figure 6.3. Powder X-ray diffraction pattern of $\operatorname{Ca}_{12}\operatorname{Al}_{(14-x)}\operatorname{Si}_x \operatorname{O}_{(33+\frac{x}{2})}$ (x = 1, 2, 3, 4) and intensity map showing lattice contraction and consistent shift of the diffraction peaks to higher 2θ with increasing substitution level.



Figure 6.4. Latice parameters of $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ (x = 1, 2, 3, 4) and $Ca_{12}Al_{14}O_{33}$ determined by X-ray Rietveld refinement.

Hydrogen doping was performed by ion implantation, as described on section 3.2.2, and subsequent UV irradiation was performed following the steps mentioned in section 3.2.3. Figure 6.5 shows the phase analysis of the samples after activation; no structural difference with the as-prepared specimens is evident.

6.2. Conversion from hydrogarnet to $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$

Thermogravimetric studies were conducted on powder samples of as-prepared $Ca_3Al_2(SiO_4)_{(3-y)}(OH)_{4y}$ in order to confirm the substitution level by measuring the water loss when calcined. Samples were heated in air to the calcination temperature (800 °C) while monitoring the weight loss. Figure 6.6 shows the weight loss by each sample and Table 6.2 compares the experimental loss to that calculated on the basis of Eq. 3.3.



Figure 6.5. Powder X-ray diffraction pattern of $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ and UV:H: $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$.



Figure 6.6. Thermogravimetric analysis of $Ca_3Al_2(SiO_4)_{(3-y)}(OH)_{4y}$ powders heated to 800 °C in air.

Substitution level (x)	Calculated weight loss	Experimental weight loss
1	26.32%	28%
2	24.13%	24.13%
3	22.1%	21.51%
4	19.93%	19.8%

Table 6.2. Expected weight loss from Eq. 3.3 vs. experimental weight loss from TGA measurements.

The experimental values are in very good agreement with the calculated values confirming the substitution levels and their correspondence to the previously calculated lattice parameters.

6.3. Oxygen species

The only existent reports on the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ phase have to do with its catalytic activity, based upon the ability of the system to fixate anions at high temperatures [127, 58, 57]. In order to look at the oxygen species present in this phase and responsible for the oxidation properties, Raman spectroscopy was undertaken on powdered $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ (x = 1, 2, 3, 4) and results were compared to the pure mayenite spectra. Figure 6.7 shows the measured Raman spectra for all the samples. Similar to the observations made on the Mg-substituted samples, a band corresponding to the characteristic vibration of the cubic crystalline lattice occurs at 540 cm⁻¹. The bands at 780 cm⁻¹ and 860 cm⁻¹, also present in the Mg-substituted specimen, are assigned to the stretching vibrations of the AlO₄ tetrahedra forming the framework and the O_2^{-2} species, respectively. Furthermore, it can be observed that a peak at 970 cm⁻¹ arises with increasing substitution level. This band is generally related to the SiO₄ tetrahedra


Figure 6.7. Raman spectrum of hydrothermally synthesized $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ (x = 1, 2, 3, 4) vs. pure may nite obtained by solid state.

stretching vibration and is consistent with previous findings [57]. Finally, a band closer to the end of the spectra, $\sim 1080 \text{ cm}^{-1}$, appears in the Si-substituted samples; consistent with previous reports and Raman tables, this vibration corresponds to O_2^- species. It is evident from Fig. 6.7 that the intensities go down as the substitution level increases; this is probably related to the decreased crystallinity of the samples with increasing Si content as could also be observed in the X-ray patterns. Overall, these results relate well with the observation of a higher oxidation activity with a higher substitution level.

6.4. Electrical measurements

With the substitution of Al^{3+} for Si^{4+} , the unit cell has to accommodate more free oxygens ions O^{-2} to balance the framework. Thus, more hydrogen will be incorporated into the sample and more electrons should be released after UV light irradiation. Equations for the hydrogen treatment and UV light activation are now dependent on the substitution level

Free oxygen per unit cell:

(6.3)
$$2\left[\operatorname{Ca}_{12}\operatorname{Al}_{14-x}\operatorname{Si}_{x}\operatorname{O}_{33+\frac{x}{2}}\right] \rightleftharpoons 2\left[\operatorname{Ca}_{12}\operatorname{Al}_{14-x}\operatorname{Si}_{x}\operatorname{O}_{32}\right]^{(x+2)-} + (x+2)\operatorname{O}^{2-1}$$

Hydrogen treatment:

(6.4)
$$(x+2) O^{-2} + (x+2) H_2 \rightarrow (x+2) OH^- + (x+2) H^-$$

UV-irradiation:

(6.5)
$$(x+2) H^- + Energy \rightarrow (x+2) H^0 + (x+2) e^- + phonon$$

Figure 6.8 shows the temperature dependence of the conductivity for proton-implanted / UV-irradiated Si-substituted mayenite between room temperature and ~ 100°C. The results follow the assumption presented above, where an increase in the substitution level is accompanied by a conductivity increase. At room temperature the conductivity goes from 0.15 S/cm for the non-substituted specimen to 0.61 S/cm for the maximum substitution, $Ca_{12}Al_{10}Si_4O_{35}$. The low values of the conductivity suggests a small incorporation of hydrogen into these samples, which is most probably due to the low temperatures used for the hydrogen implantation (300 °C). Higher temperatures were tried, but as mentioned in section 3.2.2, the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ phase decomposed, this is also the reason why measurements on these samples were not undertaken above 100 °C. Within experimental error the slopes on Fig. 6.8 are essentially identical, giving a hopping energy (E_H) of 0.13 eV.

Small polaron conduction was established in the previous two chapters for $Ca_{12}Al_{14}O_{33}$ and $Ca_{(12-x)}Mg_xAl_{14}O_{33}$, and this seems to also be the case for the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ system. Thermopower measurements in Fig. 6.9 show a slight dependence on substitution level, consistent with the model proposed in Eq. 6.5, but no apparent variation with temperature. Thus, a thermally activated mobility exists and the small polaron conduction model is valid for this phase as well.

Table 6.3 summarizes the thermoelectric results obtained for the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ phase at room temperature. Data for the sample $Ca_{12}Al_{13}Si_1O_{33.5}$ was difficult to obtain probably due to the high amount of the insulating CaO phase in it. It is important to mention that the lime content in the Si-substituted samples, even though small, may be playing a role in increasing the Seebeck coefficients.



Figure 6.8. Temperature dependence of the conductivity for UV-irradiated proton implanted $\operatorname{Ca}_{12}\operatorname{Al}_{(14-x)}\operatorname{Si}_x\operatorname{O}_{(33+\frac{x}{2})}$ (x = 2, 3, 4) vs. UV-irradiated proton implanted pure may enter obtained by solid state.

Table 6.3. Thermoelectrical properties of UV-irradiated proton implanted $Ca_{12}Al_{14}O_{33}$ and $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ (x = 2, 3, 4).

Substitution	Conductivity (RT)	Thermopower	Fraction of occ. sites
level	(S/cm)	$(\mu V/K)$	С
0	0.15	-220 ± 12	0.134
2	0.25	-232 ± 16	0.119
3	0.37	-238 ± 13	0.112
4	0.61	-241 ± 12	0.108

Following the previous small polaron analysis, Eq. A.10 was used to calculate the fraction of occupied sites (c) using the values of thermopower listed in Table 6.3. The decrease of c with substitution level is significant (see Table 6.3). In order to relate these data to the conductivity, the product c(1 - c) was calculated and plotted versus



Figure 6.9. Thermopower for UV-irradiated proton implanted $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ (x = 2, 3, 4) vs. UV-irradiated proton implanted pure may enite obtained by solid state.

the pre-exponential value (σ_0) taken from the intercepts of Fig. 6.8. Figure 6.10 shows that the factor c(1-c) follows the opposite trend as the pre-exponential value (σ_0) with substitution level. It is clear from Fig. 6.10 that the difference between the trends increases with substitution level. When analyzing the variables in the pre-exponential term given by Eq. A.9:

(6.6)
$$\sigma_0 = \frac{g.c.N.(1-c).e^2.a^2.\nu}{k}$$

of these parameters, we expect the geometric factor (g), the vibrational frequency (ν) and the jump distance (a) will change only slightly with substitution level. It is clear that the number of available sites N must increase in proportion to the Si substitution level, which is consistent with the equations introduced at the beginning of this chapter



Figure 6.10. Pre-exponential values and c(1-c) versus substitution level $\operatorname{Ca}_{12}\operatorname{Al}_{(14-x)}\operatorname{Si}_{x}\operatorname{O}_{(33+\frac{x}{2})}$ (x = 2, 3, 4).

(Eq. 6.4 and 6.5). This suggests that the substitution level not only increases the number of carriers per unit cell, but also the number of hopping centers. Experimental results suggest that the total number of available sites for hopping increases faster with the Si content in $\text{Ca}_{12}\text{Al}_{(14-x)}\text{Si}_x\text{O}_{(33+\frac{x}{2})}$ than the number of carriers, which is consistent with theoretical predictions [128].

6.5. Optical properties

Diffuse reflectance data for the proton-implanted/UV-irradiated $Ca_{12}Al_{10}Si_4O_{35}$ phase are shown in Fig. 6.11, compared with the $Ca_{12}Al_{14}O_{33}$ system that underwent the same treatment. Both systems are highly transparent before activation, showing a 95% transmission in the visible spectrum, and band gaps of 4.43 eV and 4.76 eV, for the $Ca_{12}Al_{14}O_{33}$ and $Ca_{12}Al_{10}Si_4O_{35}$, respectively. After activation, transmission decreases



Figure 6.11. Diffuse reflectance of UV-irradiated proton implanted $\rm Ca_{12}Al_{10}Si_4O_{35}$ compared to $\rm Ca_{12}Al_{14}O_{33}$.

to 65% for pure mayenite and to 53% for the Si-substituted specimens, results that are consistent with the higher carrier content of the later sample.

6.6. Theoretical calculations

Highly accurate density-functional electronic band structure investigations have already revealed the origin of the light-induced conductivity in H-doped $Ca_{12}Al_{14}O_{33}$, and provided detailed understanding of the conduction mechanism at the microscopic level [115]. As mentioned in section 4.9, the conductivity results from the electrons excited by UV irradiation from the H⁻ ions into the conduction band. The charge transport occurs by electron hopping through the encaged hydrogen ions and OH⁻ complexes. Knowledge of the exact paths for the carrier migration suggested that a way to improve the electronic transport and increase the conductivity would be to increase the concentration of hopping centers. For this, Si substituted mayenite was a promising candidate, as shown in Eqs. 6.3, 6.4 and 6.5 of this chapter. The important feature of the electronic band structure of



Figure 6.12. Electronic band structure for $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ with x =0 (a), x =2 (b) and x = 4 (c).

nano-porous Ca₁₂Al₁₄O₃₃ is the presence of a so-called cage conduction band [50] (or cavity conduction band [49]) located close to the framework conduction band formed from the Cad states. In mayenite, the cage conduction band consists of five bands (Fig. 6.12(a)) that corresponds to the five empty cages out of the total six cages in the unit cell. One cage is occupied by O²⁻ ion resulting in a splitting of one band from the cage conduction band and its shift to a lower energy; a triply degenerate band that corresponds to p_x , p_y and p_z orbitals is fully occupied and located below the Fermi level (Fig. 6.12(a)). Upon substitution with Si, the cage conduction band, which consists of four and three bands for x =1 and 2, respectively, Fig. 6.12(b) and 6.12(c), splits from the framework conduction band by about 1 eV, as obtained in LDA calculations.

Significanly, it was found that the band gap between the states of the encaged oxygen ions and the cage conduction band decreases from 1.6 eV for x = 0 to 1.3 eV and 0.9 eV for x = 1 and 2, respectively. Incorporation of hydrogen, which occurs according to the chemical reaction of Eq. 6.4, results in the appearance of new bands: filled σ , non-bonding π , and unoccupied σ' bands (these correspond to the OH⁻ complex) and a fully occupied band below the Fermi level formed from the 1s states of the encaged H⁻ [26]. For x = 2 or 4, the number of bands increases accordingly to two or three occupied bands for the two or three encaged H⁻ ions, and two or three empty σ' bands for two or three OH⁻ complexes, respectively.

Figure 6.13 shows the electronic band structure of H-doped and UV-activated $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ systems. Similar to unsubstituted mayenite [26], the UV irradiation of the Si-doped structures results in the appearance of a new hybrid band that crosses the Fermi level making the system conducting. For x =0, 2 and 4, the new band consists of two, four and six bands, respectively (Fig. 6.13). This corresponds to the total number of the encaged defects, i.e., the hydrogen ions and the OH⁻ complexes, in the unit cell.

Analysis of the atomic contributions to the band suggests that only the encaged defects and their nearest Ca atoms participate in the charge transport. The most energetically favorable spatial arrangement of the atoms which contribute to the density of states near the Fermi level corresponds to the shortest hopping path. For unsubstituted mayenite (x =0), there is only one hopping path in the unit cell, as mentioned in section 4.9 [26]. Strong Coulomb repulsion between the electrons that move along this narrow path leads to the appearance of a soft gap in the density of states at the Fermi level. Upon Si substitution, the number of the hopping centers (the encaged hydrogen ions and OH⁻ complexes) as well as the number of carriers (the electrons excited off the H⁻ ions) increases. As a result, the UV-released electrons have more freedom (Fig. 6.14) and the density of states at the



Figure 6.13. Electronic band structure (left column) and density of states, in states/eV·cell, (right column) for H-doped and UV-irradiated $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ with x =0 (top row), x=2 (middle row) and x=4 (bottom row).



Figure 6.14. Contour map of the charge density distribution within a slice passing through the center of a cage with hydrogen ion and its nearest Ca atoms for $\operatorname{Ca}_{12}\operatorname{Al}_{(14-x)}\operatorname{Si}_x\operatorname{O}_{(33+\frac{x}{2})}$ with x = 0 (left) and x = 4 (right).

Fermi level increases (Fig. 6.13), leading to the observed increase in the conductivity compared to unsubstituted may nite (x = 0).

6.7. Summary

Hydrothermal synthesis of the metastable phase $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ was achieved as well as H-doping by ion implantation. Insulator-to-conductor conversion was observed as in the case of $Ca_{12}Al_{14}O_{33}$ and $Ca_{(12-x)}Mg_xAl_{14}O_{33}$. The electrical conductivity of the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ system doubled on tripled the conductivity of non-substituted Mayentite, with values of 0.25 S/cm when introducing two Si in the unit cell and 0.61 S/cm when introducing four. The Seebeck coefficient show no temperature dependence, but seems to be affected by the substitution level, with a slight increase from -220 μ V/K (x = 0) to -240 μ V/K (x = 4) can be observed. Similar to the previous two systems, the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ phase appears to obey the small polaron conduction model, with a slightly higher hopping energy of 0.13 eV. From thermopower measurements, one can observe a decrease in the fraction of occupied sites, which does not explain the increase in conductivity. However, every increase in the electrons population in the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ system is accompanied by an even higher increase in the number of hopping centers, which explains why the conductivity increase even though the fraction of occupied sites slightly decreases.

Calculations of probable hopping paths and the number of available sites for hopping becomes a complicated problem in this system, making the estimation of the mobility and carrier content impossible. Optical properties are consistent with the electrical results, showing a decrease in transmission with the increase in Si content, concomitant with the increase in carrier content. All these results show a remarkable correlation with the theoretical predictions but the experimental manipulation of this metastable phase make any practical application based on it electrical conductivity extremely cumbersome. On the other hand the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ phase serves as a perfect proof of concept of the thermally activating hopping mechanism characteristic of all these mayenite based systems and based on the oxygen radicals it possess it may have a future in catalysis.

CHAPTER 7

The $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻ system

7.1. Phase analysis

7.1.1. $Ca_{12}Al_{14}O_{33}$ single crystals

Single crystals of $Ca_{12}Al_{14}O_{33}$ were prepared following the steps of section 3.1.3. The resulting crystals rods were cut into disks and analyzed by XRD to confirm phase purity. Figure 7.1 shows the pattern obtained for these crystals, where only the peaks corresponding to the (211) and (422) planes appear. Moreover, Laue diffraction showed that the samples are highly oriented although several domains exist in each, i.e., they are not perfect single crystal.

To confirm that these peaks correspond to the mayenite crystal structure, XRD measurements were performed on crushed powders. The diffraction pattern is shown in Fig. 7.2, where a very clean mayenite pattern can be observed.

Finally, small pieces of the crystal ($< 1 \text{mm}^2$) where taken to the Analytical Service Laboratory (Northwestern University) to gather unit cell data and confirm the preferred orientations of the as-grown crystals. The (211) and (422) reflections are indeed the preferred directions for the crystal growth, and Table 7.1 shows the acquired unit cell data.



Figure 7.1. X-ray diffraction pattern of $Ca_{12}Al_{14}O_{33}$ single crystals prepared by the floating zone method.



Figure 7.2. Powder X-ray diffraction on crushed single crystals of $\rm Ca_{12}Al_{14}O_{33}$.

a	b	с	α	eta	γ
11.9758	11.9883	11.9759	89.968	89.968	89.991
0.0035	0.0022	0.0035	0.016	0.019	0.018

Table 7.1. Lattice parameters and standard deviations of $Ca_{12}Al_{14}O_{33}$ grown by the floating zone method.

7.1.2. Ca-treated $Ca_{12}Al_{14}O_{33}$

As mentioned in section 3.2.4, single crystal samples were reduced in the presence of Ca shot at $\sim 800^{\circ}$ C inside vacuum-sealed quartz tubes. The objective of the treatment was to remove the clathrated oxygen ions from the crystallographic cages following the reaction: (7.1)

$$\left[\operatorname{Ca}_{24}\operatorname{Al}_{28}\operatorname{O}_{64}\right]^{4+} + 2\operatorname{O}^{2-} + \operatorname{Ca} \rightarrow \operatorname{CaO} + \left[\operatorname{Ca}_{24}\operatorname{Al}_{28}\operatorname{O}_{64}\right]^{4+} + (2-x)\operatorname{O}^{2-} + (2x)\operatorname{e}^{-1}$$

Once the reaction was completed, phase analysis was undertaken on the surface of the single crystal disk in order to characterize the deposited layer. Figure 7.3 shows the XRD pattern for this external surface which coincides with the PDF card of CaO as expected according to Eq. 8.3.

After mechanically polishing the surface of the Ca-treated single crystals X-ray diffraction was used to confirm that the phase beneath the CaO was still mayenite. Figure 7.4 shows the resulting diffraction pattern, where the $Ca_{12}Al_{14}O_{33}$ phase remains intact, but many more reflections appear, suggesting that a rearrangement of atoms take place under the reducing conditions, transforming the samples into dense polycrystalline specimens. Table 7.3 shows the unit cell data gathered by the Analytical Service Laboratory confirming that no major changes occur to the crystal lattice during the reduction treatment.



Figure 7.3. X-ray diffraction pattern of deposited layer after Ca-treatment of $Ca_{12}Al_{14}O_{33}$ single crystals.



Figure 7.4. X-ray diffraction pattern of Ca-treatment $Ca_{12}Al_{14}O_{33}$ single crystals after mechanical polishing.

a	b	с	α	eta	γ
11.9947	11.9804	11.9869	90.1051	90.0917	90.0035
0.0040	0.0048	0.0016	0.0353	0.0270	0.0296

Table 7.2. Lattice parameters and standard deviations of $Ca_{12}Al_{14}O_{33}$ grown by the floating zone method.

7.1.3. Ti-treated $Ca_{12}Al_{14}O_{33}$

Titanium was also used as a reducing agent, principally because results based on Catreated samples were hard to reproduce [3]. In addition, titanium treatment can be done at ~ 1100°C, enhancing the diffusion of the free oxygen ions and the kinetics of Eq. 8.3. Furthermore, the fact that Ti reacts with oxygen, forming non-stoichiometric stable compounds over a wide a range of compositions ($1 < x < 2 \operatorname{TiO}_{(2-x)}$) favors the continuous out-diffusion of the free oxygen, even if a large quantity of titanium deposits on the surface of the crystal [129, 130, 131]. Figure 7.5 shows the deposited layers of titanium oxide for different samples.

Contrary to the Ca-treatment, where it seems that the CaO layer acts as a diffusion barrier and treatment times are high (~12 days), striking results can be seen after a couple of days with Ti-treatment. After mechanically polishing the titanium oxide layer phase, analysis was perform on the Ti-reduced $Ca_{12}Al_{14}O_{33}$. Similar to the Ca treatment, the diffraction pattern corresponds to the mayenite crystal, and again, many more reflections appear in the resulting pattern. Figure 7.6 shows the diffraction patterns for three samples treated under the same conditions for different periods of time (4 days, 8 days, 12 days). From Fig. 7.6(a) it seems that the re-orientation of the crystal domains changes randomly with treatment time, and no significant changes in lattice parameter are observed. To



Figure 7.5. X-ray diffraction pattern of deposited layer after Ti-treatment of $Ca_{12}Al_{14}O_{33}$ single crystals.

confirm that no major structural changes are involved in this process, pieces of the three samples were crushed and analyzed by XRD. Results for the three powder samples are shown in Fig. 7.6(b), where it can be corroborated that apart from some change in the relative intensities, no major lattice change happens during the reduction.

7.2. Microstructure

Some of the reduced samples (Ca and Ti) present an uncommon microstructure throughout the crystal, with thick "grain boundaries" relative to the size of the grain core. This effect seems to depend on the quality of the original crystal and the pretreatment performed prior to the reduction. By quality of the crystal, we refer to bubbles and cracks generated during crystal growth, as mentioned in the experimental section. It seems from the micrographs that the "grain boundaries" tend to connect all these defects as if they were out-gassing channels. To evaluate this idea, pre-treatment of the singlecrystals was performed under different atmospheres; the crystal disks were annealed at 1330 °C in vacuum and air. Figure 7.7 shows the resulting microstructures, where it is evident that grain boundaries form around the crystal's bubbles, and the increase in the size and extent of the grain boundaries increases with the amount of gasses trapped in the sample. This phenomenon is not completely clear at the present time, but the concept of out-gassing channels within the samples is a working hypothesis.

7.2.1. Composition of the grains and grain boundaries

In order to have a better understanding of the origin of the microstructure, Energy Dispersive Spectroscopy (EDS) was performed in the two regions, grain core and grain boundary. The resulting spectra are identical for both regions, as can be seen in Fig. 7.8. To take this compositional analysis one step further, SIMS was performed in the two different regions,



Figure 7.6. X-ray diffraction pattern of three Ti-treated Ca₁₂Al₁₄O₃₃ after mechanical polishing (a) crystals treated for 4, 8 and 12 days (b) crushed crystals treated for 4, 8 and 12 days.



Figure 7.7. Micrographs of $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ systems (a) when the single crystal was pre-treated in vacuum and (b) when it was pre-treated in air.



Figure 7.8. Energy Dispersive Spectroscopy (EDS) for the grain and grain boundary regions.

showing that neither a composition change nor any kind of impurity segregation is involved in this phenomenon. Figure 7.9 shows the composition map of the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ surface (the map does not change after sputtering some of the surface away). It can be observed that the only elements present are Ca and Al, and their maps coincide very well



Figure 7.9. Secondary Ion Mass Spectroscopy (SIMS) of the grain and grain boundary regions.

with the total ion map. Finally the composition profiles for Ca and Al were taken from the cross section of the composition map to ensure that no segregation happens in the vicinity of the grain boundary. As it can be seen in Fig. 7.10, the profiles for Ca and Al are identical.



Figure 7.10. Secondary Ion Mass Spectroscopy (SIMS) profile of Ca and Al content.



Figure 7.11. Conducting Atomic Force microscopy (cAFM) of the grain and grain boundary regions.

7.2.2. Conductivity of the grains and grain boundaries

So far we have seen that the grain and grain boundary are compositionally identical, and the idea that the grain core is mostly $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ while the boundaries are $Ca_{12}Al_{14}O_{33}$ was checked by conducting Atomic Force Microscopy (cAFM). The samples were polished to the nanometer scale, cleaned following the appropriate protocols, and grounded to the cAFM using silver paste. A bias was applied to the diamond tip in order to generate a flow of current, while the interface between the grains and grain boundary was scanned. Figure 7.11 shows the resulting map, where a clear difference in conductivity can be observed between the grain and the grain boundary.

Topography map

We conclude from these experiments that the grain boundaries are composed of the insulating $Ca_{12}Al_{14}O_{33}$ phase and the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ phase forms the majority of the bulk. This results are very significant for conductivity measurements, as a sample with extensive and connecting boundaries will result in an underestimate of the conductivity of the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ bulk. The samples reported hereafter were all pre-annelaed in vacuum to minimized the amount of trapped gasses inside the crystals and were always checked under the optical microscope for the existence of grain boundaries.

7.3. Electrical properties and metal-insulator transition

Figure 7.12 shows the Arrhenius plot of the electrical conductivities (σ) for the Titreated and Ca-treated single crystals. The Arrhenius plot has a negative slope (positive activation energy) when the electron concentration is low (Ca-treated samples), indicating that a thermally-activated mechanism, e.g., hopping, controls the migration of carriers. The temperature dependence vanishes for the 12-day Ca-treated sample, indicating the onset of highly degeneration or semi-metallic behavior. Finally, the slope becomes positive for the Ti-treated samples, consistent with an insulator-to-metal transition.

To analyze this further, conductivity data were collected at low temperatures. Figure 7.13 shows typical metallic conduction, where above ~140 K, the resistivity (ρ) is proportional to the temperature and the phonon scattering dominates. At lower temperatures, resistivity is proportional to T², indicative of electron-electron interaction. Metal-insulator transitions (MIT) are typically divided into two groups, according to the mechanism assumed: either structural or electronic. In the first category, some change in the crystal lattice leads to a splitting of the electronic conduction band and hence to



Figure 7.12. Temperature dependence of conductivity for $Ca_{12}Al_{14}O_{33}$ single crystals Ti-treated for 4 days, 8 days, 12 days $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-3}$ systems treated.



Figure 7.13. Low temperature dependence of conductivity for $Ca_{12}Al_{14}O_{33}$ single crystal Ti-treated for 4 days.

a MIT. In the second category, the transition is purely electronic in origin and can be described by models in which the lattice is fixed. Mott's original model for a transition triggered by electronic correlations was based on an array of atomic potentials, with one electron per atom and a Coulomb interaction between them. For a high electron density, the ion cores will be screened and the system will be metallic. For a small electron density, the screening will break down and the system will undergo a transition to an insulator. The Mott criterion for the electronic transition is given by

(7.2)
$$(n_c)^{1/3} \alpha_H \approx 0.25$$

where n_c is the critical electron density and α_H is the Bohr radius given by [132, 133].

(7.3)
$$\alpha_H = \frac{\hbar^2 \varepsilon}{m^* e^2}$$

here ε is the dielectric constant, \hbar is Planck's constant and m^* and e are the effective mass and the charge of the electron. As an approximation, we can use the radii of the crystallographic cages (~ 0.2 nm) as the electron orbital radii, which gives a critical electron density of $1.9 \cdot 10^{21}$ cm⁻³ that is equivalent to removing ~ 80% of the clathared oxygens ions. Thus, it is feasible that the MIT in e⁻-doped mayenite occurs following a Mott-Hubbard mechanism.

It should be mentioned that determination of the carrier content by Hall measurement is difficult if the carrier content is high (R_H , the Hall coefficient is inversely proportional to carrier content) and / or if carrier mobility is low (the Hall voltage is proportional to the inplane current density). Both factors mitigate against accurate Hall effect measurements in bulk degenerately-doped mayenite. One solution would be to grow thin films, to enhance



Figure 7.14. Temperature dependence of the thermopower for $Ca_{12}Al_{14}O_{33}$ single crystal Ti-treated.

both the magnetic field gradient and the in-plane current density. Another alternative would be to measure and fit optical reflectance data (*not diffuse reflectance data*), the subject of an ongoing collaboration with Ecole Superieure de Physique et de Chemie Industrielles (France).

Thermopower values in the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system are consistent with the higher carrier content of these samples and their dependence on Temperature is shown in Fig. 7.14. A charge carrier reversal for the Ti-treated samples is observed, which is not inconsistent with the MIT transition, and is a consequence of more carriers being injected into the Ti-treated specimen than in the Ca-treated ones. Table 7.3 summarizes the thermoelectric properties at room temperature of the reduced $Ca_{12}Al_{14}O_{33}$ single crystals, where it can be seen that the Seebeck coefficient goes from negative for the Ca-treated samples to positive for the Ti-treated ones.

Sample	Conductivity	Thermopower	E_a
	S/cm	$\mu { m V/K}$	eV
Ca - 4d	0.02	-280	*
Ca - 5d	3.7	-240	+0.05
Ca - 10d	282.68	-7.86	+0.02
Ti - 12d	567	-12.9	-0.015
Ti - 8d	1053	+4.6	-0.02
Ti - 4d	1416	+6.97	-0.05

Table 7.3. Electrical properties of the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system at room temperature obtained by Ca-treatment and Ti-treatment. (*) No temperature dependence data exists for this sample.

7.4. Small polaron interpretation

An alternative interpretation for this data could be made using the small polaron conduction model, by the means of the Jonker-type of analysis described in section A.3. As we mentioned in appendix A the usual means for demonstrating small polaron behavior is by showing an activated mobility. This is generally straightforward when the conductivity is thermally activated and the thermopower is not, or when the conductivity has a significantly larger activation energy compared to that of the thermopower. In certain cases, however, the hopping or activation energy (E_a) is on the order of kT (0.025 eV at room temperature). This means that the changes in thermopower and conductivity are almost indistinguishable. An unambiguous approach was introduced by Jonker as described in the appendix of this document. The analysis consists of a plot of the Seebeck coefficient versus the logarithm of the normalized conductivity; at large carrier concentrations small polaron behavior is significantly different from that of a conventional semiconductor.



Figure 7.15. N-type small polaron Jonker plot for Ca-treated $Ca_{12}Al_{14}O_{33}$ (circles) compare to Matsuishi's first report data (rhombi)[3].

In order to plot the data from Table 7.3 in a Jonker form, we need to normalize the conductivity values to the value of the maximum conductivity. Nell et al showed that this occurs when c = 0.5 and $Q = \pm 59 \ \mu\text{V/K}$ [134].

Data for the Ca-treated samples is plotted in a Jonker fashion in Fig. 7.15. For comparison, Matsuishi's data on the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system are also included. As can be seen, both systems nicely follow the n-type small polaron curve.

Figure 7.16 shows the Ti-treated data together with one Ca-treated datum used as a reference. Again, striking agreement is found between the experimental results and the Jonker plot for n-type small polarons. In this approach the change in sign of the thermopower is not associated with a change of mechanism, but rather with a monotonic increase in the fraction of occupied sites through the reversal condition demonstrated by



Figure 7.16. N-type small polaron Jonker plot for Ti-treated $Ca_{12}Al_{14}O_{33}$ (squares) vs. Ca-treated $Ca_{12}Al_{14}O_{33}$ (circle).

Nell et al., i.e., $c > \frac{2}{3}$ [134]. This reversal of sign has been observed before in systems such as $Fe_{(1-x)}O$, $CeO_{(2-x)}$ and V_2O_5 glasses [134, 135]

The temperature dependence of the conductivity can be explained if in Eq. A.8 we consider a value of $E_H \sim 0$. This would make the exponential term equal to unity and $\rho = 1/\sigma \propto T$.

(7.4)
$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E_H}{k.T}\right) \to \sigma \propto T^{-1}$$

The question now becomes which model describes the conduction mechanism of the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system – metallic behavior or small polaron behavior with negligible

hopping energy ? One means to resolve this controversy is to establish the relevant limits of the mobility, μ .

For the case of a small polaron conductor, an upper limit of the mobility can be estimated. From the Nerst-Einstein equation we have

(7.5)
$$\sigma = n q \mu$$

By solving for μ and replacing σ for the small polaron equation, we obtain the mobility of a small polaron conductor

(7.6)
$$\mu = \frac{g.(1-c).e.a^2.\nu}{k.T} \exp\left(\frac{-E_H}{k.T}\right)$$

In the case of the Ti-treated sample, $E_H \sim 0$, c can be estimated from thermopower to be 0.62 for the Ti-12d sample and 0.68 for the Ti-4d sample, and the optical phonon frequency, ν , was calculated in section 4.9 and is equal to $\sim 3 \cdot 10^{13} \text{ s}^{-1}$. As we do not have information of the hopping path, we will have to estimate the jump distance, a, to be approximately equal to the diameter of the cage (0.4 nm), given that there are no species (H⁻, OH⁻, etc.) inside the cages. Finally, the geometric factor, g = z/6, where z depends on the number of available sites surrounding a site, can be estimated for this system to be ~ 2 . The resulting upper limit of the mobility is $\sim 1.4 \text{ cm}^2/\text{Vs}$ if the [Ca₂₄Al₂₈O₆₂]⁺⁴+4e⁻ system were to follow a small polaron model.

In a band model, the lower limit of μ depends on the width of the band compared to kT. Thus, for broad energy bands like in our case (see section 7.5) where the band width

is much bigger than kT/2 we have

(7.7)
$$\mu \ge 30 \frac{m_0}{m^*} \frac{300}{T} \qquad (\frac{cm^2}{Vs})$$

where m^* is the effective mass of the electrons and m_0 is the mass of the electron. If we take the width of our band from Fig. 7.17(b) to be ~ 2 eV and by using

(7.8)
$$m^* = \frac{\hbar^2}{2.J.L^2}$$

where L is the lattice parameter (11.98 Å), J is the resonance of the electron-transfer integral and can be estimated to be W/4 where W is the band width, the resulting lower limit for the electron mobility if the system obeys a band conduction model is ~ 1.9 cm²/Vs

So we can conclusively establish the origin of the conductivity by knowing the mobility of the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system. If the mobility is much smaller than 1.4 cm²/Vs, the system is described by a small polaron mechanism and if it is larger than ~ 1.9 cm²/Vs the mechanism is instead govern by band conduction. As mentioned before, collection of this data is not possible through hall effect measurements on bulk specimens, however, it could be obtained from thin films and / or optical data, which is an ongoing work.

7.5. Theory calculations

The calculated electronic densities of states (DOS) for $Ca_{12}Al_{14}O_{33}$:H⁰ and $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻ are found to be similar, cf. Figs. 7.17(a) and 7.17(b). In both cases, oxygen 2p states form the top of the valence band, Ca 3d states form the bottom of the conduction band, and a hybrid band in the band gap crosses the Fermi level, making

both systems conducting. Using optical selection rules, the joint DOS that determine the positions of the characteristic absorption bands was calculated (Figs.7.17(c) and 7.17(d)). As one can see, the overall structure of the absorption spectra is similar for the two systems and is in good agreement with previous experiments. In particular it is found that: (i) in $Ca_{12}Al_{14}O_{33}$:H⁰, the 0.4 eV absorption peak is narrow, well defined, and separated from the 2.8 eV peak, which corresponds to transitions from the occupied states of the hybrid band to the conduction band; (ii) by contrast, in $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻ the pronounced DOS at E_F gives the nonzero absorption in the large wavelength limit; and (iii) in addition, due to the increased width of the hybrid band, the absorption band centered at 0.4 eV substantially overlaps with the one at 2.8 eV, resulting in the observed black coloration of the samples.

Despite the apparent similarity of the characteristic optical absorption peaks, we found that the conductivity mechanism in these two mayenite-based compounds is qualitatively different. This is clearly seen from a comparison of the charge-density distributions calculated in a 25-meV-energy window below E_F (cf. Fig. 7.18). In the case of $Ca_{12}Al_{14}O_{33}$:H⁰, the connected charge-density maxima along the hopping path demonstrates the hopping nature of the conductivity. In contrast to this trapping of the electrons on particular atoms, in $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻ the conduction electrons are found to be highly delocalized. Their extended wave function suggests a bulk mechanism (metallic) for the conductivity in agreement with one of our experimental hypotheses. Indeed, in $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻, all Ca and the encaged empty spheres give comparable contributions to the DOS in the vicinity of E_F (on average, 3.1% and 2.6%, respectively), while



Figure 7.17. Total density of states of (a) $Ca_{12}Al_{14}O_{33}$:H⁰ and the enlarged DOS near E_F in the inset which shows the predicted Coulomb gap, and (b) $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻; the Fermi level is at 0 eV. The joint DOS (solid lines) for (c) $Ca_{12}Al_{14}O_{33}$:H⁰ and (d) $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻; dashed lines are guide to the eyes; energy values and arrows show the positions of the observed absorption peaks.

in $Ca_{12}Al_{14}O_{33}$:H⁰, only four of the 12 Ca atoms, i.e., the neighbors of the encaged H⁰ and OH⁻, contribute significantly to the DOS near E_F .

Consistent with previous calculations, we found that in $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$, the conduction electrons are not localized inside the cages (see Fig. 7.18). The Ca-Ca distances are the same for an empty cage in pure mayenite (away from O²⁻ ions) and for $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-} = 5.7\mathring{A}$, therefore there are no electrons inside the cages in the



Figure 7.18. Contour map of the charge density distribution within a slice passing through the center of (a) a cage with H0 in $Ca_{12}Al_{14}O_{33}$ H⁰ and (b) an empty cage (vacancy) in $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻.

 $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^-$. When a cage is filled the distances between Ca-Ca decreases, as for the cage with O^{2-} , the distance = 4.3 Å and for the cage with H⁻, the distance = 5.1 Å (consistent with Hayashi et al and Matsuishi et al [25, 3]. This indicates that $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^-$ cannot be considered to be an electride, which is essentially classified as a compound in which the electron density is confined within structural cavities and tends to avoid the regions occupied by cations. Our results are in contrast with a theoretical study of $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^-$ that was based on the embedded defect cluster approach, which excluded possibilities other than electron localization inside the cages, i.e., formation of the F^+ center; strikingly, the resulting schematic picture of the energy levels (cf. Fig. 3 of Ref. [50]) disagreed with the observed optical absorption energies.

Thus, first-principles band-structure calculations provide a clear physical explanation of the 100-fold enhancement of the conductivity for the Ca-treated $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-4}$ and the 1000-fold enhancement for the Ti-treated. In the H-doped case, the released electrons migrate along a well-defined channel: the hopping path showed in section 4.9.
Moving one-by-one, they interact (repel) strongly with each other, resulting in the formation of the parabolic Coulomb gap in the DOS at E_F (see Fig. 7.17 inset). The value of the gap can be estimated as $e^2/\varepsilon r_{ch}$, where e is the elementary charge, ε is the dielectric constant, and the characteristic distance between two electrons in the unit cell, r_{ch} , is equal to the cube root of the unit cell volume divided by 2. Using the lattice parameter of cubic mayenite, 1.198 nm , and $\varepsilon = 2.56$, yields 0.3 eV for the value of the Coulomb gap, which agrees well with the calculated splitting of the hybrid band, 0.38 eV, and with the observed absorption peak at 0.4 eV.

This interpretation of the transport properties in $Ca_{12}Al_{14}O_{33}$:H⁰ suggests a way to improve the conductivity: an increased number of transport channels should alleviate the electron repulsion. Consistent with this view, a 100-fold increase of the conductivity is observed for $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ where, loosely speaking, the number of conducting channels can be considered very large so that the injected electrons have more freedom and the Coulomb blockade does not occur.

The p- / n-type behavior in the same material can happen only when some sort of band splitting exists. In the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system, we can explain this phenomenon as when the band which represents the empty cages ("cage conduction band" [49]) is split from the rest of the conduction band (framework CB). If a few electrons are injected, the CCB starts to fill up, giving a n-type behavior. This is consistent with calculations and experimental results on the Ca-treated samples. Now, if more electrons are pumped into the system, enough to almost fill up the CCB, then we can consider this band as a valence band and not a conduction band, and p-type conductivity is achieved. Then the question we did not address before, of why p-type character appears after 4 days of Ti-treatment and then disappears after 12 days of treatment also finds a good explanation. When even more electrons are injected in the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system (12-day Ti-treated samples), the CCB gets overdoped and begins to fill up the framework CB, thus n-type character appears again.

Finally, we stress that the enhanced conductivity in $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ comes at the cost of greatly increased optical absorption. The latter occurs due to the increase of (i) the DOS of the hybrid band in the band gap and (ii) the width of this hybrid band, resulting in intense transitions from the occupied states of the hybrid band to the conduction band in the visible range, which excludes the possibility of using this oxide as a transparent conducting material.

7.6. Summary

Removal of the free oxygen ions from the crystallographic cages was achieved by reducing a $Ca_{12}Al_{14}O_{33}$ single crystal in the presence of Ca or Ti metal. The degree of reduction and the "microstructure" seems to be controlled by the amount of trapped gasses inside the single crystal. Conductivities for the Ca-treatment ranged from 0.02 S/cm to 200 S/cm and for the Ti-treatment from 120 S/cm to 1400 S/cm, that many more oxygen ions are removed through Ti-treatment and many more carriers are injected into the sample. This enhancement of the conductivity is accompanied by very small values of activation energies (~ 0.05 eV) and a reversal in its sign with increasing carrier concentration. A metal-insulator transition is believed to happen for the Ti samples and is responsible for the high conductivities, consistent with our theoretical predictions. Reversal of the thermopower sign was observed for the two most conducting samples and it is understood as the filling of the "cage conduction band" that is split from the framework conduction band.

CHAPTER 8

Conclusions and Recommendations for Future Work

The purpose of the present work was to investigate the unusual insulator-to-conductor conversion that takes place in the cage-structure material, $Ca_{12}Al_{14}O_{33}$, and its applicability as an n-type transparent conducting oxide. The $Ca_{12}Al_{14}O_{33}$ system was initially reported by Hayashi et al. [25], who found it be rendered conductive by hydrogen-doping and UV-light irradiation. They suggested that appropriately treated mayenite could be an indium-free TCO candidate. Since their first report, little work had been done in the understanding of the conduction mechanism of this system. Only simplified calculations/models had been proposed, some of them in striking disagreement with each other and/or experimental results. With that in mind, the transport and defects governing this system were thoroughly investigated. The system can be rendered conductive by two different techniques:

1) Hydrogen treatment and UV-light irradiation, following the reactions

(8.1)
$$O^{-2} + H_2 \rightarrow OH^- + H^-$$

(8.2)
$$H^- + Energy \rightarrow H^0 + e^- + phonon$$

2)Reduction by a base metal (Ca or Ti) following the reaction

(8.3)

$$\left[\operatorname{Ca}_{24}\operatorname{Al}_{28}\operatorname{O}_{64}\right]^{4+} + 2\operatorname{O}^{2-} + \operatorname{Ca} \to \operatorname{CaO} + \left[\operatorname{Ca}_{24}\operatorname{Al}_{28}\operatorname{O}_{64}\right]^{4+} + (2-x)\operatorname{O}^{2-} + (2x)\operatorname{e}^{-1}\right]^{4+}$$

In order to investigate this ceramic system, single crystals and powder samples were prepared. In situ conductivity and thermopower measurements were undertaken to study the effects of temperature on this material. Other techniques, such as thermogravimetric analysis, powder X-ray diffraction, Raman spectroscopy, secondary ion mass spectroscopy and impedance spectroscopy were used to complement this work.

The cage-structure mayenite system, $Ca_{12}Al_{14}O_{33}$, adopts a polaron hopping mechanism for electronic conduction when doped with hydrogen and activated by UV-light. However, there is an insulator-to-metal transition once enough free oxygen ions are removed from the crystallographic cages.

8.1. H-doped UV-irradiated mayenite based materials

As previously mentioned this work shows conclusive evidence that the transport mechanism of hydrogen treated/UV-irradiated mayenite based materials is governed by an activated mobility. Samples of Ca₁₂Al₁₄O₃₃, Ca_(12-x)Mg_xAl₁₄O₃₃ (x = 0.1, 0.3, 0.5, 0.8, 1) and Ca₁₂Al_(14-x)Si_xO_(33+ $\frac{x}{2})$ (x = 2, 3, 4) were tested between room temperature and ~ 130°, all showing an activated mobility, leading to an activated conductivity:</sub>

(8.4)
$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E_H}{k.T}\right)$$

(8.5)
$$\sigma_0 = \frac{g.c.N.(1-c).e^2.a^2.\nu}{k}$$

where the hopping energy E_H , ranges from 0.11 eV - 0.13 eV for all the specimens studied.

Further consideration of the above equation can be made, from which an upper limit can be placed on conductivity of $Ca_{12}Al_{14}O_{33}$ and $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ (systems for which we know the hopping path). The geometric factor, g, is approximately 1/2 for these materials, N is the density of available sites for polaron occupation, which is on the order of 6.97·10²¹, the term c(1-c) is the maximized fraction of occupied sites when c = 0.5; e is the charge of the electron; ν is the optical phonon frequency, which is on the order $3 \cdot 10^{13} \text{ s}^{-1}$, k is Bolztmann's constant and a is the average jump distance from theoretical calculations, ~ 2.8 Å. By assuming a negligible hopping energy, the exponential term is unity and the maximum conductivity that the H-doped/UV-irradiated system can have at room temperature is 82.5 S/cm. For the case of the $Ca_{12}Al_{(14-x)}Si_xO_{(33+\frac{x}{2})}$ system, it is clear that N increases with the substitution level, but its estimation is far more complicated as almost every cage will contain an encaged "defect" (H^0, OH^-) for electron hopping. Thus, it is not possible to calculate the upper limit of the conductivity, although it was shown that the alleviation of the strong electronic interaction along the narrow conduction path enhances the conductivity. As can be seen from the above equations, a non-zero value for E_H will have a strong deleterious impact on the maximum conductivity value.

All these experimental results were shown to be in good agreement with the theoretical calculations, which predict a thermally activated conductivity along an optimal hopping path for conduction.

8.2. The $[Ca_{24}Al_{28}O_{62}]^{+4}$ +4e⁻ system, MI transition vs. small polaron

By removing the free oxygen ions from the crystallographic cages, electrons are injected into the structure. The conductivity reaches 1400 S/cm after Ti-treatment of single crystal samples, and a reversal in sign of the Seebeck coefficient is observed.

 $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ samples prepared by Ti-reduction acquire higher conductivity in shorter treatment periods. This is attributed to the ability of Ti to dissolve greater amounts of oxygen, forming a wide range of non stoichiometric stable titanium oxides.

The resistivity below room temperature is proportional to T, which could be explained by either an insulator-to-metal transition or by a small polaron system with a negligibly small hopping energy. It has been established that an unambiguous way of solving this dilemma is by gathering information on the mobility of this system.

The enhancement in conductivity in the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system comes at the cost of greatly increased absorption, making the Ti- or Ca- treated oxides unsuitable for practical use as a TCO, however such materials maybe useful as electron emitters [136]

8.3. Hydrogen and oxygen species

This study showed that hydrogen is intimately involved in the conduction process of the H-doped/UV-irradiated materials, where it takes part in the conduction path, and loss of it when the decomposition temperature is exceeded leads to a permanent reduction in the conductivity. The reactivity of the free oxygen ion and the positive character of the framework give rise to the absorption of a wide variety of species such as O_2^{-2} , O_2^{-} and water. In order to optimize the electronic conductivity, the preparation of samples should minimize the existence of such species. On the other hand, may enite crystalites maybe find applications in catalysis. It would be of interest to study the diffusion and interaction of the radicals absorbed in the may enite-based materials, and analyze their applicability as a catalyst.

8.4. On the theoretical calculations

Our description of the transport properties in $Ca_{12}Al_{14}O_{33}$:H⁰ differs from the original interpretation, which was based on the formation of F^+ -centers (i.e., electron trapping on the oxygen vacancy) inside positively charged cages. In the framework of the F^+ model, the released electron could hop between empty cages (there are eight of them per unit cell), which strongly contradicts our calculations that demonstrate clearly that the conducting channels do not involve empty cages and are formed only in the UV-irradiated regions. Our major disagreement with the embedded cluster technique used by Sushko et al. [51] is that their model does not take into account all the "defects" present in the H-doped/UV-irradiated $Ca_{12}Al_{14}O_{33}$ systems: H⁰, e⁻, H⁻ and OH⁻. Also they do not include the neighboring cages in their calculations (even if they are empty) to provide the right distribution of charge on the cage walls. Their approach should only be applicable in the dilute limit of carrier concentration, thus extrapolation of the results from the H-doped UV-irradiated $Ca_{12}Al_{14}O_{33}$ system to the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ is not valid.

According to the calculations associated with the present work, the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-4}$ system should not be considered to be an electride (in agreement with Li et al. [49]), which is essentially classified as a compound in which the electron density is confined within structural cavities and tends to avoid the regions occupied by cations. The Ca-Ca distances are the same for an empty cage in pure mayenite (away from O^{2-} ions) and for $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-} = 5.7$ Å. Therefore there are no electrons inside the cages in the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ material. This result is again in contrast with Sushko et al. [51] and their theoretical study of $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ that was based on the embedded defect cluster approach, which excluded possibilities other than electron localization inside the cages as mentioned above. Strikingly, even their resulting schematic picture of the energy levels (cf. Fig. 3 of Ref. [50]) disagrees with the observed optical absorption energies.

8.5. A new kind of TCO

Despite the failure to achieve low optical transparency and useful electrical conductivity in the mayenite-based oxides, the nature of their electronic band structure suggests that these materials belong to a conceptually new class of TCO.

As one can see, hydrogen annealing and the subsequent UV-irradiation of $Ca_{12}Al_{14}O_{33}$ result in the formation of a new hybrid defect band in the band gap of insulating mayenite. This band crosses the Fermi level, making the system conducting. Furthermore, transitions from the occupied part of the band to the unoccupied one are below the visible range, owing to the narrowness of the hybrid band (< 1.2 eV), while the interband transitions to the bottom of the conduction band are rather weak since they are provided by the low density of states (DOS) in the hybrid band near E_F . Consequently, any increase of the DOS at E_F that favors a higher conductivity would result in an increase of light absorption, reducing the optical transmission. Indeed, this was observed for $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$,



Figure 8.1. The schematic band structure of ideal TCO: $\Delta W < 1.8 \text{ eV}$, $\Delta v > 3.1 \text{ eV}$ and $\Delta c > 3.1 \text{ eV}$ provide 100% transparency in the visible range.

where the DOS at E_F is found to be 24 times larger than in the H-doped/UV-irradiated mayenite. Thus, in striking contrast to conventional TCOs, where the optical absorption cannot be eliminated for fundamental reasons (as discussed above), the band structure analysis of mayenite-based oxides suggests an approach to combine 100% optical transparency and high electrical conductivity. The schematic band structure of such an ideal TCO is shown in Fig. 8.1. The introduction of a deep impurity band in the bandgap of an insulating material would help to keep intense interband transitions (from the valence band to the impurity band and from the impurity band to the conduction band) above the visible range. This requires the band gap of a host material to be more than 6.2 eV. Furthermore, the impurity band should be narrow enough (less than 1.8 eV) to keep intraband transitions (as well as the plasma frequency) below the visible range.

In order to achieve high conductivity, the concentration of impurities should be large enough so that their electronic wave functions overlap and form an impurity band. The formation of the band would lead to a high carrier mobility owing to the extended nature of these states and correspondingly small scattering. For this purpose, a material with a close-packed structure should not be used, because a large concentration of impurities would result in i) an increase of ionized impurity scattering which limits electron transport, and ii) a large relaxation of the host material, affecting its electronic structure and, most likely, decreasing the desired optical transparency. Therefore, an introduction of a deep impurity band into a wide-band gap insulator with a close-packed structure would make the material neither conducting nor transparent. In sharp contrast, cage-structure materials offer a way to incorporate a large concentration of impurities without any significant changes in the band structure of the host material, e.g., H^- and OH^- in the spacious cages of mayenite.

In mayenite, however, the encaged impurities are well separated from each other and, therefore, do not form by themselves an impurity band that is necessary for creating extended well-conducting electronic states. Although the applied UV-irradiation overcame this problem, giving rise to a 10 order of magnitude increase of the conductivity, it led to a degradation of the optical properties. Since the new hybrid band was formed not only from states of the encaged impurities but also from states of atoms belonging to the cage wall (3d states of Ca atoms, which form the bottom of the conduction band [26]), this band was effectively shifted towards the conduction band minimum.

Alternatively, the coupling between impurities can be achieved by choosing a material where an array of connected structural cavities (channels) will allow the interaction of the nearby impurities, unlike the mayenite-type materials where the encaged impurities are isolated. Finally, while the conductivity in the proposed new type of TCO materials may not reach the maximum value of conventional TCOs, i.e., $\sim 10^4$ S/cm, their optical transparency can be expected to be as high as 100% in the visible wavelength range.

8.6. Recommendations for future work

In the course of conducting this research, several interesting ideas worthy of further consideration emerged.

Firstly, thin film growth of $Ca_{12}Al_{14}O_{33}$ -based materials should be considered. This would enable better optical studies and Hall effect measurements, among other advantages. Along this lines, future work should involve acquiring transport data of the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ system from perfectly polished single crystals or thin films (Hall effect or from reflectivity measurements). By obtaining consistent values of mobility the conduction mechanism for the $[Ca_{24}Al_{28}O_{62}]^{+4}+4e^{-}$ could be confirmed. If future studies show a mobility, $\mu>1.4$ cm²/Vs, then we could clearly refer to the conduction mechanism as metal-like behavior.

It will be of interest to prove the validity of the conduction path and reveal whether H^0 or H^+ are hopping centers. In future work, our magnetoresistance studies can be taken one step further by analyzing the dependence of the conductivity at very high magnetic fields and very low temperatures. The idea is based on trying to align the spins of the hopping electrons and the 1s¹ electron on the H^0 center. These two electrons should interact, and if both have the same spin, the hopping electron will not hop through this center and the conductivity will "turn off". The experiment should be pursued using an applied magnetic field $B > kT/\mu_B$ where μ_B is the Bohr magnetron, so temperature will not reverse the spins, which would mean going to liquid He temperature and ~ 9 T. At this temperature the experiment needs to be done on H-doped/UV-irradiated thin films or on high quality single crystals to be able to detect any changes.

In a different note, it would be of interest to study the diffusion and interaction of the radicals absorbed in the mayenite-based materials, and analyze their applicability as a catalyst. The fact that $Ca_{12}Al_{14}O_{33}$ can host oxidizing species such as O_2^- , O_2^{-2} , O^- inside its cavities is promising for catalytic applications.

Also, regarding the oxygenous species inside the $Ca_{12}Al_{14}O_{33}$ cages, it will be interesting to study how to enhance the ionic conductivity of this material. The fact that as-prepared mayenite shows a conductivity only an order of magnitude less than YSZ opens the question of how more O^{-2} ions could be incorporated in the structure, at the same time minimizing their conversion to oxygen radicals. We showed that Si⁴⁺ on the Al³⁺ sites forces the structure to incorporate more oxygen, however this system was highly unstable and its ionic conductivity was impossible to measure. It will be interesting to search for a more stable substitution of a (3+) cation for Ca^{2+} or a (4+) cation for Al^{3+} , especially a material that could be treated at high temperatures in order to optimize the O^{-2} content.

Finally, by using the new TCO concepts learned from the mayenite system, a whole new variety of host materials could be investigated. It has been shown that zeolitic structures like ITQ-4, with a channel structure, doped with (Na, K, Rb, Cs) present promising electrical properties [137, 138, 139]. Theoretical studies show that the different dopants will make the materials change from insulator to semimetal and to metal with increasing Na or Rb doping [140, 141, 142].

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APPENDIX A

Small Polaron Conduction

A.1. Overview

There are many different electronic transport mechanism in materials. In ionic crystals, the electron-phonon interaction is particularly strong. If we consider an electron propagating through a crystal we can envision how its negative charge will tend to attract positive ions towards it and repel negative ions away from it. Thus this moving carrier induces lattice vibrations as it propagates, in particular the vibrations in which positive and negative ions move in opposite directions (optical modes). Then the electron and its associated lattice vibration is thought as a pseudo particle called *polaron*. In ordinary circumstances this pseudoparticle is a large polaron, where the associated lattice deformation extends several interionic distances from the original electron. Transport properties for this large-polarons are characterize by a tight-binding approach of the band conduction model.

When an electron is localized in the vicinity of a particular ion in a crystal, a local lattice deformation is induced. Similar to the large polaron the positive ions are attracted to the electron and the negatives are repelled. This induced deformation can acts like an attraction potential, which can bind the electron so its no longer free to move around the lattice. If the distortion of the lattice extends over distances smaller than the lattice constant we are in the presence of a small polaron. Transport in this kind of systems happens by thermally activated hopping in which, contrary to all other conduction mechanism, lattice vibrations do not reduce the electron mobility but rather enable it [143]. Large effective masses and narrow band characterized this type of mechanism. The result of this are low but activated mobilities, usually lower than 1 cm²/Vs combined typically with large carrier concentrations that give rise to conductivities in the order 10^{0} - $10^{2.5}$ S/cm. This intermediate conductivities are often accompanied by a very small and some times negligible activation energies.

A more mathematical approach was introduced by Mott [133] by defining a dimensionless coupling constant, α , given by

(A.1)
$$\alpha = e \left(\frac{2\pi}{2r_p h \omega \kappa_p}\right)^{\frac{1}{2}}$$

where e is the electron charge; ω is the optical phonon frequency and $1/\kappa_p = 1/\kappa - 1/\kappa_0$ where κ and κ_0 are the optical and static dielectric constants, respectively.

The polaron radius, r_p is defined by

(A.2)
$$r_p = \frac{\epsilon_p h^2}{4 \pi^2 m^* e^2}$$

where m^* is the effective mass of the electron. If r_p is larger than the lattice parameter, $\alpha > 1$, and the polaron formed is a large polaron. On the other hand, if r_p approaches the lattice parameter the polaron is called small and α is approaches big values, e.g. 10.

A.2. Small polaron conduction mechanism

Mott attributed two different hopping mechanisms to small polaron theory [144, 133].

1. At low temperatures, $T < \frac{1}{2} \Theta_D (\Theta_D, Debye temperature)$ the electron moves from site to site without the aid of thermal energy. The hopping frequency is given by:

(A.3)
$$v_H = \omega \, \exp\left(\frac{-E}{\frac{1}{2}\omega \,\hbar}\right)$$

and this mechanism describes small polaron band conduction, also known as variable range hopping.

2. At high temperatures, $T > \frac{1}{2} \Theta_D$, it moves by thermally activated "hopping" and the frequency with which it "hops" from one site to another is given by:

(A.4)
$$v_H = \omega \exp\left(\frac{-E_H}{kT}\right)$$

where E_H is the intermediate energy required for "hopping" given by:

(A.5)
$$E_H = \frac{1}{4} \frac{e^2}{\kappa_p} \left(\frac{1}{r_p} - \frac{1}{R} \right)$$

where R is the distance from one site to another and the mechanism is known as small polaron hopping.

A.2.1. Conductivity of small polaron conductors

The small polaron hopping is a diffusion process characterized by an activated mobility as describe in the previous section. Therefore the mobility can be related to the polaron diffusivity as described by the Nernst-Einstein relation, $\mu = \frac{eD}{kT}$, where

(A.6)
$$D = g (1-c) a^2 \nu \exp\left(\frac{-E_H}{kT}\right)$$

and mobility is given by:

(A.7)
$$\mu = \frac{g (1-c)ea^2\nu}{kT} \exp\left(\frac{-E_H}{kT}\right)$$

where g is a geometric factor related to the probability that the carrier will hop to an adjacent site, c is the fraction of occupied sites by carriers, ν is the optical mode phonon frequency, E_H is as mentioned above the hopping energy and a is the hopping distance from site to site. The conductivity is then given by the product, $\sigma=ne\mu$ such that:

(A.8)
$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E_H}{k.T}\right)$$

(A.9)
$$\sigma_0 = \frac{g.c.N.(1-c).e^2.a^2.\nu}{k}$$

where N is the total number of available sites and n=N e. As it can be seen from the above equations the hopping energy can be determine from the slope of $\ln(\sigma T)$ vs. 1/T

In contrast to many other mechanism, lattice vibrations do not reduce electron mobility but rather enable it, resulting in very low but activated mobilities ($<1cm^2/Vs$) and large carrier concentrations ($\sim10^{22}$ cm⁻³) yielding conductivities in the range of 1 - $10^{2.5}$ S/cm.

A.2.2. Thermopower of small polaron conductors

The thermopower or Seebeck coefficient, Q, is a useful estimation of the carrier content. For a small polaron mechanism Q can be written as:

(A.10)
$$Q = \pm \frac{k}{e} \left(\ln \frac{2(1-c)}{c} \right)$$

where all entities have been defined before and the \pm sign indicates that the polaron can be due to a hole or an electron. However, it was demonstrated by Nell et al. [134] that the sign of the thermopower does not establish the character of the conductor (p-type or n-type) given that at high values of c the Seebeck coefficient can reverse it sign.

A.3. Jonker analysis of small polaron conductors

As mentioned before the usual way for demonstrating small polaron conduction is via an activated mobility (see Eq. A.7). This is evident when the conductivity is temperature activated but the thermopower is not, when the conductivity has a significantly larger activation energy than the Seebeck coefficient and when conductivity is analyzed under constant Q in systems where both properties vary with the composition. However, is difficult to demonstrate the T⁻¹ dependency of the conductivity unless the carrier content remains constant and the electrical conductivity is measured over a wide range of temperatures. In many cases, small polaron is difficult to confirm specially when the hoping energy, if at all observed, is on the orther of kT what makes the difference between the activation energy of the conductivity and thermopower indistinguishable. In this work we use the approach introduced by Nell et al. in 1989 using the jonker-type analysis for small polarons, which can unambiguously establish whether or not we are in the presence



Figure A.1. Thermopower vs. logarithm of normalized conductivity for n-type and p-type small polaron conductors compare to typical band semiconductor behavior.

of a small polaron conductor. The analysis consist on plotting the Seebeck coefficient values vs. logarithm of the conductivity. Figure A.1 shows an schematic of the difference between a small polaron system and a typical band conduction mechanism.

where all the lines have been normalized to the value of maximum conductivity, which occurs at c=0.5 and $Q = \pm 59 \ \mu\text{V/K}$. For both conduction mechanism the slope in the intrinsic regime, at low carrier concentration, is the same and equal to \pm k/e. It is clear from this figure that a small polaron will manifest in the vicinity of the maximum conductivity, where the small polarons presents a nose, this requires a high carrier concentration and a low absolute value of the Seebeck coefficient. Otherwise, any linear fit with a slope of \pm k/e could be obtained regardless of the mechanism.
APPENDIX B

Oxide Ion Conductivity

B.1. Grain boundary

The a.c. impedance results of Chapter 4 and Chapter 5 for the oxide ion conductivity of $Ca_{12}Al_{14}O_{33}$ and $Ca_{(12-x)}Mg_xAl_{14}O_{33}$ showed that a grain boundary resistance was also present. The Arrhenius plot of the bulk and grain boundary conductivity are compared in Fig. B.1, where both components are thermally activated and show a linear behavior with very different activation energies. The bulk conduction has a an activation energy of 0.73 eV and the grain boundary conductivity has an activation energy of 1.7 eV. Both components cross at approximately 1200 °C for the particular sample shown in Fig. B.1 and consequently, for temperatures below 1200 °C the grain boundary resistance dominates. It has been suggested by Irvine et al. that sintering conditions considerably affect the grain boundary resistance, and that prolonged sintering at temperatures near the melting point (1400 °C) will reduce the grain boundary effect [33].

In air, $Ca_{12}Al_{14}O_{33}$ is an oxide ion conductor with transport number of unity [145, 33]. On gentle reduction, Irvine et al. reported that the bulk is unaffected, but the grain boundary resistance increases dramatically, suggesting an increase in the grain boundary thickness [33]. Upon reduction at high temperatures it was shown by Hayashi et al. that $Ca_{12}Al_{14}O_{33}$ acts as a mixed ionic/electronic conductor, where the H⁻ introduced in the crystallographic cages can act as an electron source [35].



Figure B.1. Ionic conductivity of the grain boundary and bulk components of $\rm Ca_{12}Al_{14}O_{33}$.