DEPENDENCE OF ACTIVATION ENERGY ON TEMPERATURE AND STRUCTURE IN LANTHANUM GALLATES

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ABSTRACT

The parent phase of the lanthanum gallate series of electrolytes, LaGaO3, is orthorhombic at room temperature and rhombohedral between 250 and 1000°C (1-3). Our high resolution neutron powder studies on the doped phases, La0.9Sr0.1Ga0.8Mg0.2O3 and its Ba-analogue, show significant structural differences from the parent phase that have direct bearing on the ionic conduction process that can easily be understood in terms of the degree of tilting of the GaO6 octahedra. The monoclinic form at room temperature has a higher degree of distortion associated with the octahedra and undergoes phase transitions at elevated temperatures that relate to the change in activation energy for the ionic conduction obtained from AC impedance spectroscopy data. In particular the gradual alignment of the octahedra above 300°C (Ba) or 500°C (Sr) as the cell heads toward cubic symmetry produces a slow, temperature-dependent decrease in $E_a$ for ionic conduction as the tilting of the GaO6 octahedra is reduced, thereby facilitating the migration of the oxide ion. AC impedance studies of the doped lanthanum gallates reveal a similar activation energy dependence for the barium and strontium analogues with an activation energy of 1 eV below the transition to rhombohedral with a gradual decrease towards 0.6 eV at the highest temperature.

INTRODUCTION

Although the idealised perovskite structure contains no oxygen vacancies, and conductivity is therefore typically electronic in character, a perovskite oxide is capable of accommodating a large number of oxygen vacancies. Substitution by aliovalent cations allows oxygen deficiencies to be incorporated into the structure, resulting in significant oxide ion conductivity (1). Ishihara et al. (2,3) reported similar ionic conductivity to YSZ at 1000°C in the doped perovskite LaGaO3 system but at the much lower temperature of 850°C, making it a likely candidate as the electrolyte for the next generation of solid oxide fuel cells (SOFCs).

The high oxide ion conductivity and thermal stability of these systems at intermediate SOFC operating temperatures are the principal material properties driving research. Ideally, the operating temperature needs to be reduced to around 750°C to allow the use of stainless steel, as both interconnect and main body support, and also to reduce the stringent materials requirements placed on researchers for use at higher operating...
temperatures, principally the close matching of thermal expansion coefficients of all the cell components. A further benefit of reducing the temperature of operation will be to prolong the life expectancy of the fuel cell by improving the chemical stability of the components with respect to each other (4). It has been found that over time LaGaO$_3$-based materials often react with adjacent electrode or electrolyte materials at higher temperatures, forming unwanted secondary phases at electrode/electrolyte interfaces (5–8). The secondary phases are a result of Ga depletion at the external surfaces of the materials (9). In reducing atmospheres vaporisation of Ga$_2$O$_3$ from both pure and doped lanthanum gallates is rate dependent on the dopant levels within the material and the temperature of operation. A lower operating temperature for the fuel cell would therefore also favor the use of a lanthanum gallate electrolyte.

In LaGaO$_3$ the large La$^{3+}$ ions occupy the A sites in a cuboctahedral co-ordination with respect to oxygen, and the smaller Ga$^{3+}$ ions the B sites in an octahedral environment. Doping of the A site with Sr$^{2+}$ and the B site with Mg$^{2+}$ leads to oxygen deficiencies in the structure given in Kröger-Vink notation by

\[
\text{A site: } \text{SrO} + \text{La}_{1-x}^{3+} + \frac{1}{2}\text{O}_2^{-} = \text{Sr}^{+} + \frac{1}{2}\text{VO}^{2-} + \frac{1}{2}\text{La}_2\text{O}_3 \quad [1]
\]

\[
\text{B site: } \text{MgO} + \text{Ga}_{1-x}^{3+} + \frac{1}{2}\text{O}_2^{-} = \text{Mg}^{+} + \frac{1}{2}\text{VO}^{2-} + \frac{1}{2}\text{Ga}_2\text{O}_3 \quad [2]
\]

leading to a general formula, La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-(x+y)}$.

The system La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$ (LSGM) initially reported by Ishihara et al. (2) has been extensively studied with its structure being determined from powder neutron diffraction data (10), showing the structure to be rhombohedral above 700°C for this system and above 250°C for the parent system, LaGaO$_3$.

The proposed mechanism for ionic transport in this system is that of vacancy hopping. For this to occur, the oxygen ion must pass through a bottleneck defined by a triangle involving 2A and 1B site ions. The results of the powder neutron diffraction experiments carried out by Slater et al. (10) show that the effect of doping LaGaO$_3$ is to widen this aperture with respect to the parent system by reducing the tilt angle of the GaO$_6$ octahedra, and therefore presenting the opening more face-on to the migrating ion. Thus the activation energy for the hopping mechanism is reduced. It can also be seen from Figure 1 that the size of the cations also plays a crucial role in determining the extent of the opening of the aperture; doping with a smaller cation on the La site would reduce the size of the opening, and hence the activation energy would be expected to increase.

The role of Sr$^{2+}$ as dopant, ionic radius 1.44 Å in 12-fold coordination compared to 1.32 Å for La$^{3+}$, can therefore be emphasised on structural grounds alone as playing a major part in increasing the ionic conductivity. The maximum amount of strontium that could be doped into LaGaO$_3$ was found to be 10 mol% on the La site without a second dopant on the Ga site (2). The conductivity has been found to increase with increasing Sr content due to the larger number of oxide ion vacancies, as it did to a lesser extent with Ca and Ba doping.
Equal doping of the Ga site of La_{0.9}Sr_{0.1}GaO_{3.5} was then investigated with Mg, Al and In (2), all of which increased the conductivity with the increased vacancy contribution of Mg^{2+} doping giving the highest conductivity in La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{2.9}. Investigation by Ishihara et al. then switched to the level of Mg^{2+} dopant in the La_{0.9}Sr_{0.2}Ga_{1-y}MgyO_{3.5} system; the optimum for this system giving an ionic conductivity of 0.08 Scm^{-1} at 1073K for y = 0.2 (2).

However, the rate of Ga depletion increases with increasing Sr content while Mg doping appears to have no effect (11), so the lower Sr-doped system, La_{1.9}Sr_{1.1}Ga_{0.9}Mg_{0.1}O_{3.5}, was chosen in this study for investigation using AC impedance spectroscopy. Later work by Huang and Petrie (12) focused on the solid solution range of La(Sr)Ga(Mg)O_{3}, finding that the amount of soluble Sr increased with Mg doping to a maximum value of 25 mol\% on the La site. While the conductivity increased with both Sr and Mg ion doping the activation energy for the ionic conduction process decreased with increasing Sr content but increased with increasing Mg.

Table 1. Reported Conductivities of Various Lanthanum Gallates.

| Compound                        | $\sigma$ (Scm^{-1}) at 1000 K from graphical data |
|--------------------------------|--------------------------------------------------|
| La_{0.9}Sr_{0.1}GaO_{3.5}      | 6.4\times10^{-3} (2)                             |
| La_{0.9}Ba_{0.1}GaO_{3.8}     | 2.8\times10^{-3} (2)                             |
| La_{0.9}Ca_{0.1}GaO_{3.8}     | 2.3\times10^{-3} (2)                             |
| La_{1.9}Sr_{1.1}Ga_{0.9}Mg_{0.1}O_{3.5} | 5.6\times10^{-2} (2), 5.7\times10^{-2} (5)     |
| La_{1.9}Sr_{1.1}Ga_{0.9}Al_{0.1}O_{3.5} | 1.1\times10^{-2} (2)                             |
| La_{1.9}Sr_{1.1}Ga_{0.9}In_{0.1}O_{3.5} | 2.0\times10^{-2} (2)                             |
| La_{1.9}Sr_{1.1}Ga_{0.8}Mg_{0.2}O_{3.5} | 6.8\times10^{-2} (2), 6.9\times10^{-2} (5)     |
| La_{1.9}Sr_{1.2}Ga_{0.9}Mg_{0.1}O_{3.8} | 8.3\times10^{-2} (5)                             |
| La_{1.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3.5} | 8.0\times10^{-2} (5)                             |

The effect of doping the La site with other lanthanides has also been investigated (3), with conductivity found to decrease with decreasing ionic radius, and preliminary work on other divalent B site dopants (13), mainly with Mg as the primary dopant, has been carried out to further enhance oxide ion conductivity.

Undoped LaGaO_{3} has a distorted perovskite structure with tilting of the GaO_{6} octahedra (Figure 1) resulting in an orthorhombic cell at room temperature and a transformation to a rhombohedral cell at about 150°C (5-7). It was initially thought that the room temperature structure of the doped phase of La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85} was also orthorhombic (8). In previous work we investigated the structure of this phase by powder neutron diffraction and showed that this was not the case, with the room temperature structure actually being monoclinic (pseudo-orthorhombic) (9). The symmetry change from orthorhombic to monoclinic on doping has a direct effect on the tilting of the GaO_{6} octahedra. For octahedral LaGaO_{3} the GaO_{6} octahedra tilts about the [001]_{p}, and [110]_{p} primitive perovskite directions are in phase when successive octahedra along the same axis are considered, whereas for La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85} the [001]_{p} tilt is now antiphase (9).

Studies of the structure at elevated temperatures, 250, 500, 750, and 1000°C, showed significant structural changes occurring with temperature, indicating that the material is a
much more complex system than initially thought, exhibiting a wealth of structural chemistry (10). As the temperature was raised there appeared to be two-phase transitions: monoclinic (pseudo-orthorhombic) \(\rightarrow\) monoclinic (pseudo-rhombohedral) \(\rightarrow\) rhombohedral. Because of the limited number of temperatures examined, it was impossible to determine exactly where the transitions occurred. Therefore, we performed a more detailed study on a separate sample, examining it at 11 temperatures between 25\(^\circ\) and 825\(^\circ\)C and obtaining a more-detailed description of the structural changes that take place as the temperature increases. In addition, we examined the structure of the Ba-doped analogue \(\text{La}_{0.9}\text{Ba}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\) to compare with \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\). The results of these studies are reported here and discussed in relation to the observed conductivities for the two samples.

**EXPERIMENTAL**

\(\text{La}_{0.9}\text{Ba}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\) and \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\) were prepared from high-purity \(\text{La}_2\text{O}_3\), \(\text{SrCO}_3\), \(\text{BaCO}_3\), \(\text{Ga}_2\text{O}_3\), and \(\text{MgO}\). Stoichiometric amounts were ground and then precalcined at 1000\(^\circ\)C for 6 to 12 hr. The resulting powder was reground and then heated to 1500\(^\circ\)C for 6 to 24 hr with intermediate regrinding. Time-of-flight powder neutron diffraction data were collected on diffractometer HRPD, ISIS, Rutherford Appleton Laboratory. For the \(\text{La}_{0.9}\text{Ba}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\) sample, data were collected at temperatures of 25, 150, 300, 450, 600, 750, and 900\(^\circ\)C. For \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\), data were collected at temperatures of 25, 150, 225, 300, 375, 450, 525, 600, 675, 750, and 825\(^\circ\)C. Structural refinement was performed by the Rietveld method using the program TF12LS, which is based on the Cambridge Crystallographic Subroutine Library (CCSL) (11,12). Scattering lengths of 0.827, 0.702, 0.525, 0.729, 0.5375, and 0.5805 (all \(10^{-12}\text{cm}\)) were assigned to La, Sr, Ba, Ga, Mg, and O, respectively. Conductivity measurements were made primarily by AC impedance spectroscopy, complemented by four-probe DC conductivity measurements. Samples were formed into 1.2-cm-diameter pellets of varying thickness by sintering at 1400\(^\circ\)C for 8 hr. The pellets were coated on either face with platinum ink and fired at 900\(^\circ\)C to form electrodes prior to testing.

**Structural Refinement**

The structural data previously obtained (10) were used as initial starting parameters, with the space group I2/a for the monoclinic symmetry, Pbnm for the orthorhombic symmetry, and R3c for the rhombohedral symmetry (hexagonal setting employed). In the refinements, the La/Sr, La/Ba and Ga/Mg site occupancies were fixed at the weighed-out compositions. The relative oxygen site occupancies were refined with the constraint that the total oxygen content was equal to 2.85, as expected from the cation composition.

**RESULTS**

**Structural Studies**

\(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\). As observed in previous studies of \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\) (9,10), the refinements indicated a monoclinic (pseudo-orthorhombic) cell at low
temperatures, with transitions to a monoclinic (pseudo-rhombohedral) cell and subsequently to a rhombohedral cell as the temperature was raised. The larger number of data sets collected in this study, however, meant that a more accurate indication of the temperatures, at which the phase changes were occurring, could be determined. From these data it was concluded that the monoclinic (pseudo-orthorhombic)-monoclinic (pseudorhombohedral) phase transition occurs between 375 and 450°C, while the subsequent transition to rhombohedral symmetry occurs in the range 600 to 675°C.

$La_{0.9}Ba_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$. In the case of $La_{0.9}Ba_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$, the refinements indicated that the structure at room temperature was monoclinic (pseudo-rhombohedral) rather than monoclinic (pseudo-orthorhombic as for $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$. The refinement of the 150 and 300°C data sets also indicated the monoclinic (pseudo-rhombohedral) cell for these temperatures. Above 300°C no improvement in the R factors were observed in comparison to the rhombohedral cell. Thus the data suggested that the transition to rhombohedral symmetry occurred in the range 300 to 450°C. As the temperature was raised further, it was apparent the peak splitting and extra peaks associated with the rhombohedral symmetry decreased, thus indicating that the sample was approaching cubic symmetry. However by 900°C, the structural change to cubic symmetry was still not complete.

Conductivity Studies

Conductivity data for $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ and $La_{0.9}Ba_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ are shown in Figure 1, from which it can be seen that the Sr-doped sample has a slightly higher conductivity above 500°C. Both sets of data appear to show curvature of the Arrhenius plots at high temperature, with the deviations from linearity being observed at around the same temperatures as the monoclinic (pseudorhombohedral)-rhombohedral phase transition, approximately 625 and 450°C, respectively, for $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ and $La_{0.9}Ba_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$. It was not clear from the data as plotted whether it could be explained simply by two straight lines corresponding to a changeover from a high activation energy at low temperature to a lower one, shown in Figure 2 for $La_{0.9}Ba_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$, or whether the activation energy was continuously changing.

![Graph](image)

Figure 1. Arrhenius conductivity plots for $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ and $La_{0.9}Ba_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$.

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Figure 2. Arrhenius conductivity plot for La$_{0.9}$Ba$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$, shows low temperature linear region.

with temperature. Therefore, we performed careful AC impedance spectroscopy to extract the bulk conductivity and eliminate any grain boundary contributions, which for the gallates at low temperature were quite significant.

Analysis of the data involved calculating activation energies at each temperature by fitting the whole Arrhenius plot of the bulk component to a third-order polynomial and taking the derivative of the function to obtain the tangent at each measured temperature. This gave us the plots in Figure 3 showing activation energies versus temperature for La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$ and La$_{0.9}$Ba$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$. From these latter data it is clear that the activation energy in the low-temperature monoclinic phases is approximately constant, while the activation energy for the rhombohedral regime decreases with increasing temperature from about 1 eV to about 0.6 eV. Therefore, it appears as if in these doped phases, the rhombohedral symmetry is more conducive to oxide ion conduction than the low-temperature monoclinic symmetry.

Figure 3. Plot of effective activation energy as a function of temperature La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$ and La$_{0.9}$Ba$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$; arrows show deviation from temperature independent regions.
DISCUSSION

For both the Sr- and Ba-substituted lanthanum gallates, the effective active energy shows a transition from a temperature-independent value of 1 eV at low temperature to a temperature dependent value as temperature increases. This change occurs at a temperature of 340°C for the Ba-substituted material and 510°C for the Sr-substituted sample. Although activation energy is well documented to be a function of defect interactions in many systems, this is not thought to be the most important factor in this system due to the very large changes in structure with temperature. Figures 4 and 5 show the variations in octahedral tilt angles (θ) with temperature for the Ba- and Sr-doped systems.

Figure 4. Plot of octahedral tilt angles against temperature for La₀.₉Ba₀.₁Ga₀.₈Mg₀.₂O₂.₈₅; marked region shows onset of transition to rhombohedral region.

Figure 5. Plot of octahedral tilt angles against temperature for La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₂.₈₅; marked region shows onset of transition to rhombohedral region.

Comparing Figure 3 with Figures 4 and 5 shows that the deviation from the temperature independent activation energy region occurs just below the temperature of the structural transition to rhombohedral symmetry. This can be further seen in changes in O-O bond distances (Figures 6, 7). From these plots it can be seen that clearest correlation between structure and conductivity is in the octahedral tilt angle. In the region where activation energy is constant, tilt angles are fairly invariant, whereas in the region where the activation energy is decreasing with temperature, the tilt angle is also decreasing.
Figure 6. Plot of oxygen-oxygen distances (Å) against temperature for La_{0.9}Ba_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}, dotted line shows monoclinic to rhombohedral transition.

Figure 7. Plot of oxygen-oxygen distances (Å) against temperature for La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}, dotted line shows monoclinic to rhombohedral transition.

This observation can readily be explained by considering the long term migration of oxygen ions. A high tilt angle and antiphase ordering of octahedra will result in alternating short and long jump distances along that direction, giving rise to a high-activation energy. A decrease in tilt angle will cause a decrease in activation energy, as is observed for both these doped lanthanum gallate systems.

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