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Short communication

Oxygen-ion conductivity of BaO- and MgO-doped LaGaO₃ electrolytesShin Kim^a, Myoung Chuel Chun^b, Ki Tae Lee^c, Hong Lim Lee^{c,*}^aEngineering Research Institute, Yonsei University, Seoul 120-749, South Korea^bResearch Institute of Industrial Sciences & Technology, Pohang 790-330, South Korea^cDepartment of Ceramic Engineering, Yonsei University, Seoul 120-749, South Korea

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Abstract

The oxygen-ion conductivity of LaGaO₃ electrolytes doped with BaO and MgO is studied. Curved behaviour of the oxygen ion conductivity observed in the Arrhenius plot. Therefore, the activation energy in the low-temperature region is higher than that in the high-temperature region. The dopant cation-oxygen vacancy association, especially the Mg_{Ga}' – V_o'' cluster, may contribute to increase the activation energy in the low-temperature region © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ceramic fuel cell; LaGaO₃; Electrolyte; Oxygen-ion conductivity; Association energy

1. Introduction

Oxygen-ion conductors are expected to be used for the electrolytes of ceramic fuel cells, oxygen sensors, and oxygen separation membranes [1]. Fluorite structures, including stabilized zirconia and doped ceria, have been reported to exhibit high oxygen-ion conductivity. Yttria stabilized zirconia (YSZ) is currently employed as the electrolyte material for the ceramic fuel cell because of relatively high oxygen-ion conductivity, good chemical stability, and low cost. Ceramic fuel cells with YSZ should be operated at about 1000°C for high power density. It is required, therefore, that other cell components should be composed of ceramic materials. It has been reported [2] that doped ceria electrolytes exhibit higher oxygen-ion conductivity than stabilized zirconia at high and intermediate oxygen partial pressures, but high electron conduction is observed at low oxygen partial pressures. Attempts have been made to manufacture YSZ thin films on a ceria electrolyte at the side of the reduced atmosphere in a fuel cell to block electron conduction.

The oxygen-ion conductivity of doped LnAlO₃ (Ln = lanthanide-ion) perovskite structures has been reported [3–7]. The oxygen-ion conductivity is too low, however, for these compounds to be applied as electrolyte materials for ceramic fuel cells. SrO- and MgO-doped LaGaO₃ was recently shown [8] to exhibit extremely high

oxygen-ion conductivity, i.e. above 0.1 cm S⁻¹ at 800°C, which is comparable with that of YSZ at 1000°C. In addition, single cells using La(Sr)Ga(Mg)O_{3-δ} electrolyte displayed excellent power density at an intermediate temperature of about 800°C [9,10]. This material is, therefore, expected to become a candidate electrolyte material for intermediate-temperature ceramic fuel cells which may be operated at about 800°C. Over the past few years, a considerable number of studies on doped LaGaO₃ perovskites have been conducted with respect to the crystal structure [11], the phase diagram [12,13], as well as the oxygen-ion conductivity [14–16]. Most of the studies have concentrated on SrO-doped compositions, but one study examined La_{0.90}Ba_{0.10}Ga_{0.80}Mg_{0.20}O_{3-δ} [15]. It was found that the thermal expansion coefficient of BaO-doped LaGaO₃ is slightly larger than that of a SrO-doped counterpart when the same amounts of the dopants are substituted [15]. No further studies of BaO- and MgO-doped LaGaO₃ were undertaken. In the work described here, therefore, the ionic conductivity of BaO- and MgO-doped LaGaO₃ perovskites is investigated.

2. Experimental procedure

La₂O₃, Ga₂O₃, BaCO₃ and MgO powders were used as the starting materials. All materials had a purity above 99.9%. Powders were properly weighed and mixed in an agate mortar for 2 h. The mixed powder was pressed into discs before being heated at 1100°C for 5 h in air. The heat-treated

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discs were crushed and milled into powder and pressed again. The process of heat treatment and crushing was repeated twice to ensure homogenization of the compositions of the final samples. The crushed powder was pressed into both bar-type and disc-type specimens and pressed isostatically under 138 MPa. The specimens were fired at 1500°C for 10 h in air and cooled down to room temperature at rate of 10°C min⁻¹. The oxygen-ion conductivity of the specimens was measured by the dc 4-probe method in a nitrogen atmosphere. The ac 2-probe method was also applied to observe the contribution of grain-boundaries to the total electrolyte resistance in the low-temperature region with disc-type specimens and an impedance analyzer (Solatron, Model 1260A).

3. Results and discussion

The X-ray diffraction patterns of the BaO- and MgO-doped LaGaO₃ compositions, which were sintered at 1500°C for 10 h, are presented in Fig. 1. For the La_{0.90}Ba_{0.10}Ga_{1-y}Mg_yO_{3-δ} system, a second phase is formed at a La_{0.90}Ba_{0.10}Ga_{0.85}Mg_{0.15}O_{3-δ} composition,

i.e. that containing the least MgO, whereas a single phase of LaGaO₃ perovskite is found for composition containing more than 15 at.% Mg²⁺. The second phase for a La_{0.90}Ba_{0.10}Ga_{0.85}Mg_{0.15}O_{3-δ} composition is analyzed as BaLaGa₃O₇ (JCPDS 24–107). It has been shown reported [13] that SrLaGa₃O₇ is formed as a second phase in the La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ} system. It has also been reported [17] that second phases are formed at compositions which contained less than 15 at.% Mg²⁺ in the La_{0.90}Ba_{0.10}Ga_{1-y}Mg_yO_{3-δ} system [17]. For the La_{0.90}Ba_{0.10}Ga_{1-y}Mg_yO_{3-δ} system, it was found that more than 20 at.% Mg²⁺ is required to obtain the single phase.

On the other hand, for the system La_{0.85}Ba_{0.15}Ga_{1-y}Mg_yO_{3-δ} in which more BaO was added, an unknown peak was observed for a La_{0.85}Ba_{0.15}Ga_{0.80}Mg_{0.20}O_{3-δ} composition but the LaGaO₃ single phase was observed for a La_{0.85}Ba_{0.15}Ga_{0.75}Mg_{0.25}O_{3-δ} composition. These results imply that the solubility limit of Ba²⁺ ions on La³⁺ sites in LaGaO₃ increases as the substitution amount of Mg²⁺ ions on Ga³⁺ sites increases. By substituting the large Mg²⁺ ions on the Ga³⁺ sites, the tolerance factor of the La(Ba)-Ga(Mg)O₃ structure decreases. The perovskite structure can accommodate large Ba²⁺ ions on La³⁺ sites, which results in

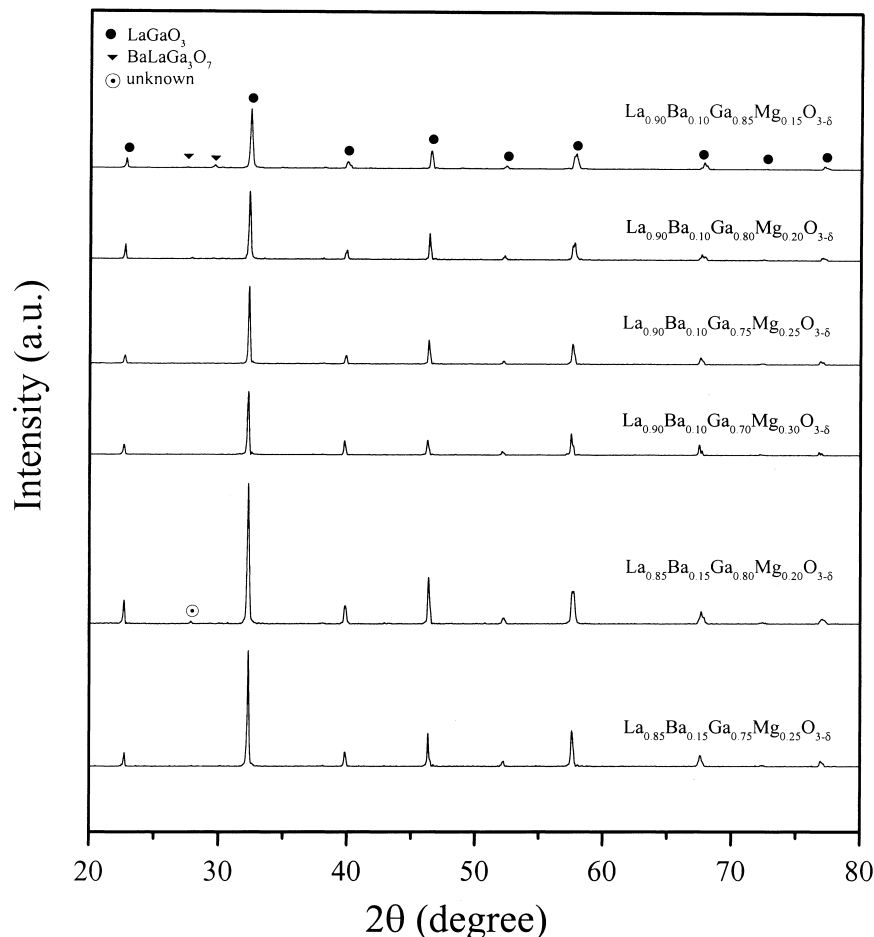


Fig. 1. X-ray diffraction patterns for La_{1-x}Ba_xGa_{1-y}Mg_yO_{3-δ} system sintered at 1500°C for 10 h.

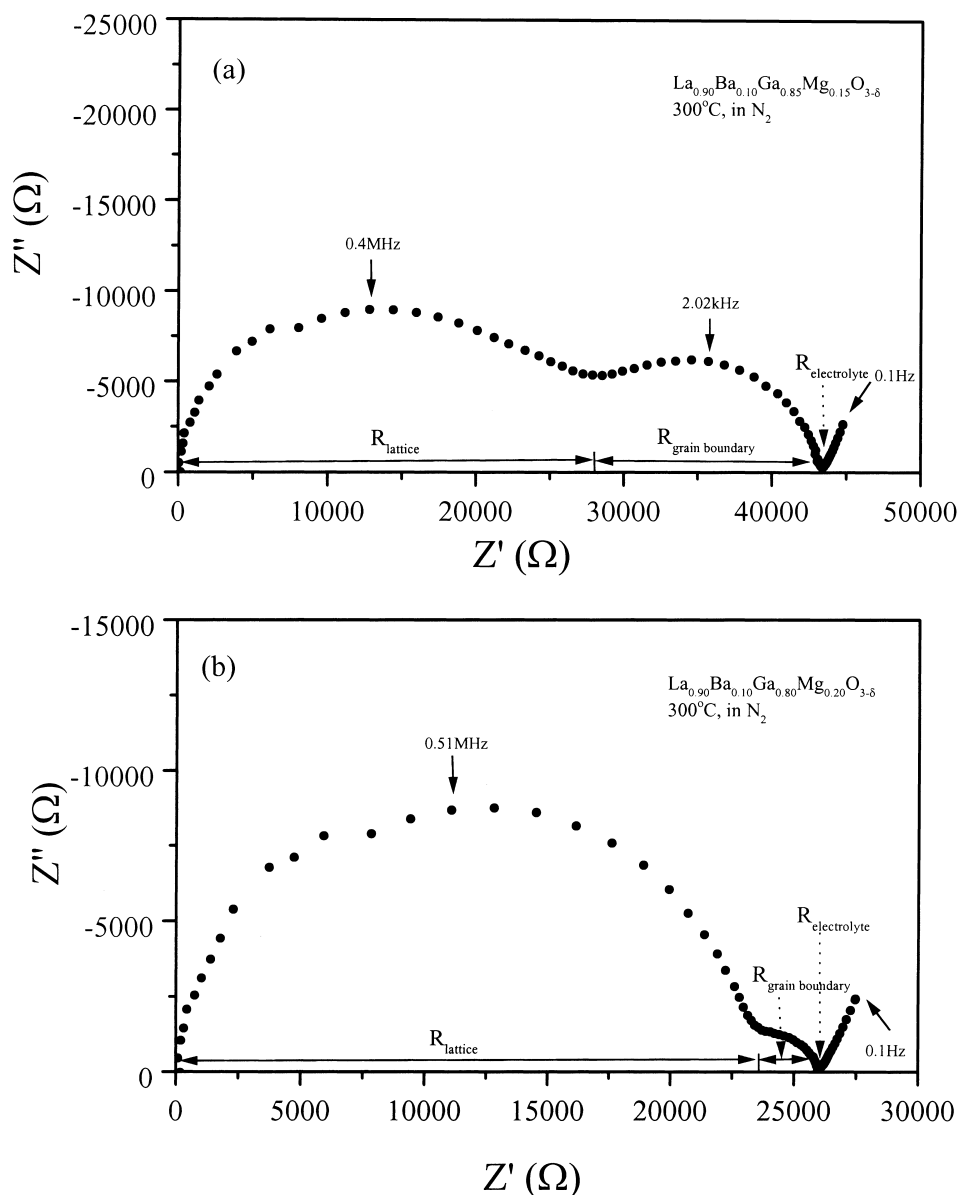


Fig. 2. Impedance data for (a) $\text{La}_{0.90}\text{Ba}_{0.10}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$ and (b) $\text{La}_{0.90}\text{Ba}_{0.10}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3-\delta}$ at 300°C in nitrogen atmosphere.

the recovery the tolerance factor of the structure. The data in this work is not sufficient, however, to confirm the suggestion and further studies may be required.

Impedance analyses for $\text{La}_{0.90}\text{Ba}_{0.10}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$ and $\text{La}_{0.90}\text{Ba}_{0.10}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3-\delta}$ compositions at 300°C in nitrogen are shown in Fig. 2. Two consecutive circular arcs and one small segment of the straight line are observed over the measured frequency range. The first circular arc in the high frequency region may correspond to the lattice resistance (R_{lattice}) and the lattice capacitance because of its extremely small capacitance value of about 10 pF, which was obtained from Eq. (1) at the minimum point in the imaginary part of the impedance data

$$C = \frac{1}{2\pi f R} \quad (1)$$

where C , f , and R are the capacitance, the frequency, and the resistance, respectively [18]. The second circular arc is considered to correspond to the grain-boundary resistance ($R_{\text{grain-boundary}}$) with a capacitance about 10 nF. The $\text{La}_{0.90}\text{Ba}_{0.10}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$ composition in which a second phase is formed has a very large grain-boundary resistance, as shown in Fig. 2 (a).

For the $\text{La}_{0.90}\text{Ba}_{0.10}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3-\delta}$ composition analyzed as the single phase (Fig. 2 (b)), the contribution of the grain-boundary resistance is considered to be too small to exert an effect on the electrolyte resistance ($R_{\text{electrolyte}}$), which is regarded as the sum of the lattice resistance and the grain-boundary resistance. Although a complete circular arc is not obtained in the low-frequency range, the impedance data of the small segment of the straight line are considered to contribute to the electrode resistance.

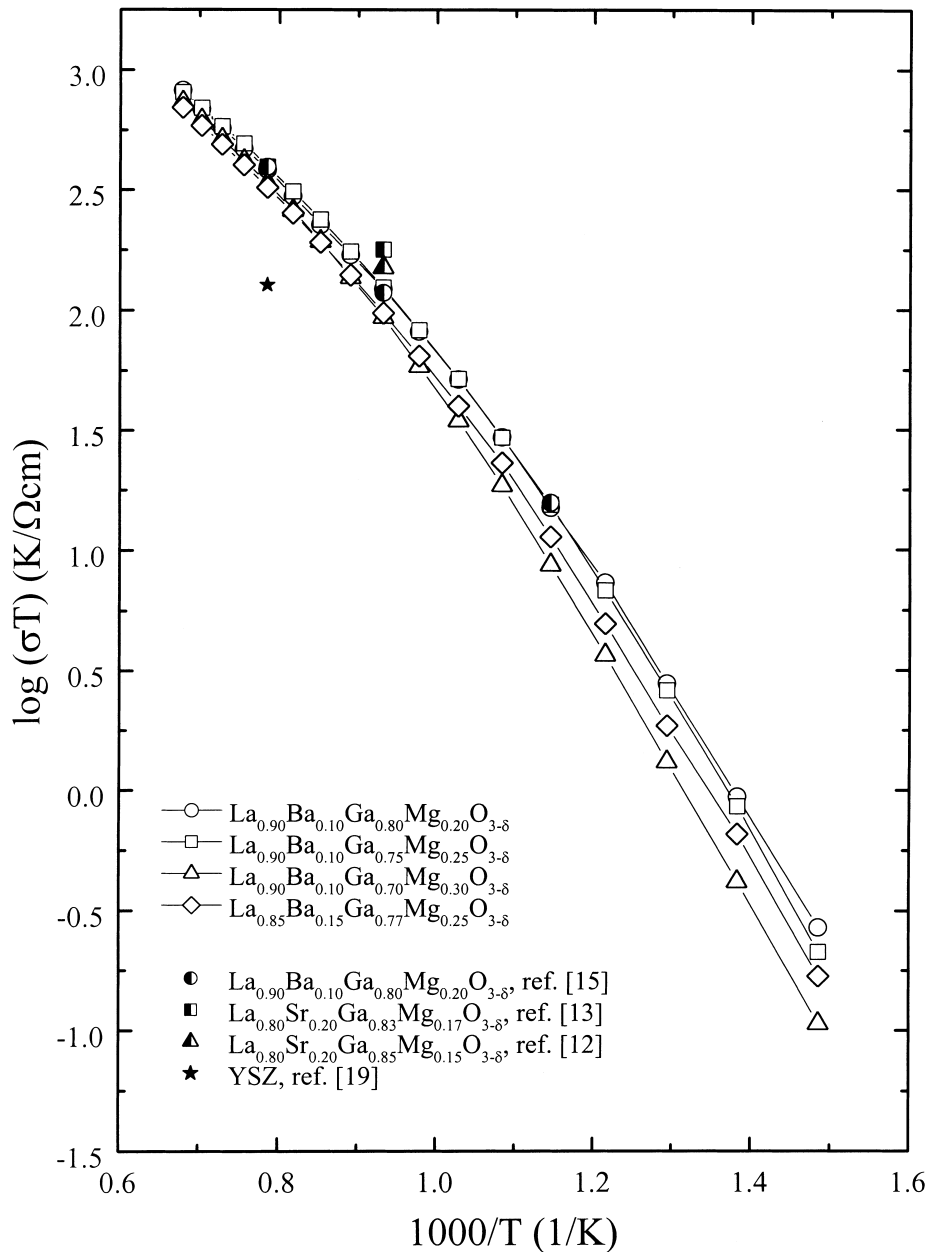


Fig. 3. Arrhenius plot of oxygen ionic conductivity for $\text{La}_{1-x}\text{Ba}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ system together with conductivity data for BaO- or SrO-doped LaGaO_3 system and YSZ.

The oxygen-ion conductivity values measured by the dc method for the $\text{La}_{0.90}\text{Ba}_{0.10}\text{Ga}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$ system ($x = 0.20, 0.25, \text{ and } 0.30$) and the $\text{La}_{0.85}\text{Ba}_{0.15}\text{Ga}_{0.75}\text{Mg}_{0.25}\text{O}_{3-\delta}$ composition are plotted in Fig. 3 according to the Arrhenius Eq. (2), i.e.

$$\sigma = \frac{A}{T} \exp\left(-\frac{\Delta E}{RT}\right) \quad (2)$$

where σ , A , T , ΔE , and R are the conductivity, the pre-exponential term, the absolute temperature, the activation energy, and the gas constant, respectively. The highest value of the ionic conductivity is obtained at the $\text{La}_{0.90}\text{Ba}_{0.10}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3-\delta}$ composition and the ionic

conductivity decreases with increasing amount of the dopant cation. The conductivity data for the $\text{La}_{0.90}\text{Ba}_{0.10}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3-\delta}$ composition used in this study are in good agreement with the published data for the same composition [15], as shown in Fig. 3. Although the oxygen-ion conductivity of the $\text{La}(\text{Ba})\text{Ga}(\text{Mg})\text{O}_{3-\delta}$ system is slightly lower than that of the $\text{La}(\text{Sr})\text{Ga}(\text{Mg})\text{O}_{3-\delta}$ system [12,13], it is still higher than that of YSZ [19], as can be seen in Fig. 3. This implies that the formed system can be regarded as a candidate electrolyte for intermediate-temperature ceramic fuel cells.

As shown in Fig. 3, curved behaviour of the conductivity in the Arrhenius plot of the oxygen-ion conductivity is

Table 1
Activation energy values in high-temperature and low temperature-regions for doped-LaGaO₃ system

La _{1-x} M _x Ga _{1-y} Mg _y O _{3-δ}			High-temperature activation energy (eV)	Low-temperature activation energy (eV)	
M	x	y			
Ba	0.10	0.20	0.62	1.03	This work
Ba	0.10	0.25	0.58	1.08	This work
Ba	0.10	0.30	0.63	1.12	This work
Ba	0.15	0.25	0.62	1.06	This work
Ba	0.10	0.20	0.71	0.95	Ref. [15]
Sr	0.10	0.20	0.74	1.08	Ref. [15]
Ca	0.10	0.20	0.75	1.20	Ref. [15]
Sr	0.10	0.20	0.66	1.13	Ref. [14]
Sr	0.20	0.17	0.82	1.08	Ref. [13]
Sr	0.20	0.15	–	1.06	Ref. [12]

observed for all compositions, which implies that the activation energy increases with decreasing temperature. There are reports [13–15] of the difference in the activation energy between the high-temperature and the low-temperature regions for the La(Sr)Ga(Mg)O_{3-δ} system. The temperature region between 600 and 850°C has been treated as the transition region of the conductivity by several workers [13–15]. Huang et al. [13] observed curved behaviour of the conductivity for the La(Sr)Ga(Mg)O_{3-δ} system and suggested that it might be caused by the trapping of oxygen vacancies by the dopant cations or the short range ordering of the oxygen vacancies below a critical temperature, T^* (~600°C). It was also advanced that all oxygen vacancies could be mobile above the critical temperature.

The variation of the activation energy for oxygen-ion conduction has been reported for oxygen-ion conductors such as stabilized zirconia. Bauerle and Hrizo [20] offered two hypotheses about the curved behaviour of the conductivity with temperature in the ZrO₂–Y₂O₃ system [20]. The first hypothesis assumed vacancy trapping by the yttrium ions, that is, the electrostatic association of opposite charged defects. The second hypothesis was based on the resistance of the grain-boundary layer. It was considered that the grain-boundaries affect primarily the total conductivity of stabilized zirconia at low and intermediate temperatures (<700°C), but have little influence on the conductivity at higher temperatures [1]. The grain-boundary resistance of the compositions which form the single phase perovskite in this work was too small, however, to have an effect on the total conductivity. Therefore, the suggestion that the grain-boundary layer is the cause of the curved behaviour of the conductivity can be discounted.

The activation energy values of oxygen migration in the La(Ba)Ga(Mg)O_{3-δ} system were measured as 0.61–0.63 eV, which are lower than those in the La(Sr)Ga(Mg)O_{3-δ} system, as can be seen in Table 1. The activation energy of La_{0.90}Ba_{0.10}Ga_{0.80}Mg_{0.20}O_{3-δ} in the high-temperature region measured in this study, viz. 0.62 eV, is lower than that reported by Stevenson et al. [15] for the same composition, viz. 0.71 eV. This is due to the fact that, in

this work, the activation energy was obtained from conductivity data for the high-temperature region. The activation energy values for the high-temperature region are similar to those calculated for LaCrO₃ (0.48 eV) and LaCoO₃ (0.61 eV) [21]. The calculated oxygen migration energy values of La_{0.90}Sr_{0.10}CoO_{3-δ} and La_{0.80}Sr_{0.20}CoO_{3-δ} has been reported [22] as 0.51 and 0.59 eV, respectively. A relatively low migration energy was obtained for B = Ga and Co in the LaBO₃ system, which is consistent with the high oxygen-ion conductivity in the high-temperature region for these compositions.

The activation energy in the low-temperature region for the La_{0.90}Ba_{0.10}Ga_{0.80}Mg_{0.20}O_{3-δ} composition in this study is found to be 1.03 eV, which is similar to the reported values for the same content of the substituted cations in the doped perovskite compositions, i.e. 1.08–1.13 eV for La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{3-δ} [12,13] and 0.95 eV for La_{0.90}Ba_{0.10}Ga_{0.80}Mg_{0.20}O_{3-δ} [15]. As shown in Fig. 3 and in Table 1, the La_{0.90}Ba_{0.10}Ga_{0.70}Mg_{0.30}O_{3-δ} composition has lower conductivity and higher activation energy than the La_{0.85}Ba_{0.15}Ga_{0.75}Mg_{0.20}O_{3-δ} composition in the low-temperature region, although both compounds contain the same concentration of oxygen vacancies. This result implies that the substitution of Mg²⁺ ions on the Ga³⁺ site is considered to cause the ionic conductivity to decrease in the low-temperature region. Therefore, the formation of the association Mg'_{Ga} – V_O may be one of the reasons for the curved behaviour of the ionic conductivity.

4. Conclusions

The solubility limit of BaO increases as the substitution amount of MgO is increased in the BaO- and MgO-doped LaGaO₃ system. A curved behaviour of the oxygen-ion conductivity is observed. It is considered that the conductivity data should be treated separately as the conductivity data for the high-temperature region and those for the low-temperature region, respectively. From the fact that the activation energy in the low-temperature region exhibits

higher values than in the high-temperature region, it is considered that the dopant cation-oxygen vacancy association, especially the $Mg_{Ga}^{\prime} - V^{\bullet}$ cluster, may contribute to the increase in the activation energy in the low-temperature region.

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References

- [1] N.Q. Minh, J. Am. Ceram. Soc. 76 (1993) 563.
- [2] H. Inaba, H. Tagawa, Solid State Ionics 83 (1996) 1.
- [3] T. Takahashi, H. Iwahara, Energy Conversion 11 (1971) 105.
- [4] H. Iwahara, T. Takahashi, Denki Kagaku 39 (1971) 400.
- [5] J.A. Kilner, P. Barrow, R.J. Brook, J. Power Sources 3 (1978) 67.
- [6] J.A. Kilner, R.J. Brook, Solid State Ionics 6 (1982) 237.
- [7] T. Ishihara, H. Matsuda, Y. Takita, J. Electrochem. Soc. 141 (1994) 3444.
- [8] T. Ishihara, H. Matsuda, Y. Takita, J. Am. Chem. Soc. 116 (1994) 3801.
- [9] M. Feng et al., J. Power Sources 63 (1996) 47.
- [10] T. Ishihara et al., Denki Kagaku 64 (1996) 642.
- [11] P.R. Slater et al., Solid State Ionics 107 (1998) 319.
- [12] P. Huang, A. Petric, J. Electrochem. Soc. 143 (1996) 1644.
- [13] K. Huang, R.S. Tichy, J.B. Goodenough, J. Am. Ceram. Soc. 81 (1998) 2565.
- [14] J. Drennan et al., J. Mater. Chem. 7 (1997) 79.
- [15] J.W. Stevenson et al., J. Electrochem. Soc. 144 (1997) 3613.
- [16] K. Huang, M. Feng, J.B. Goodenough, J. Am. Ceram. Soc. 79 (1996) 1100.
- [17] S.M. Choi et al., Solid State Ionics, 131 (2000) 221.
- [18] A. R. West, in: Solid State Chemistry and Its Application, Wiley, Chichester, 1984, p. 452.
- [19] T.H. Etsell, S.N. Flengas, Chem. Rev. 70 (1970) 339.
- [20] J.E. Baurele, J. Hrizo, J. Phys. Chem. Solids 30 (1969) 565.
- [21] M. Cherry, M.S. Islam, C.R.A. Catlow, J. Solid State Chem. 118 (1995) 125.
- [22] M.S. Islam, M. Cherry, C.R.A. Catlow, J. Solid State Chem. 124 (1996) 230.