High-temperature protonic conduction in LaBO₃ substituted with alkaline earth elements

Naoto KITAMURA,† Koji AMEZAWA,⁎ Nobuyuki TAKAHASHI,⁎⁎ Jun-ichi YAMADA,⁎⁎
Teiichi HANADA,⁎⁎ Naoya ISHIDA and Yasushi IDEMOTO

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science,
2641 Yamazaki, Noda, Chiba 278-8510, Japan
†Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
⁎Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606–8501, Japan
⁎⁎Graduate School of Human and Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606–8502, Japan

Electrical conduction properties of the aragonite-type LaBO₃-based materials, in which La was substituted partially by Ca, Sr and Ba, were investigated at 500–925°C with conductivity and transport-number measurements. From X-ray diffraction measurements, it was confirmed that a solubility limit of Sr to the La site is between 1 and 2 mol%. When the substitution content exceeded the solubility limit, the conductivities decreased with increasing the concentration. Such a deterioration in the conductivity was considered to be resulted from an impurity-phase formation. Regardless of substitution species, the LaBO₃ exhibited predominant protonic conduction by the partial substitution of the alkaline earth elements for La, and the Sr-substituted sample showed the highest conductivities. The proton transport numbers were estimated as 0.7–0.9 from electromotive forces of water-vapor and oxygen concentration cells.

Key-words : High-temperature protonic conduction, Borate, Defect

1. Introduction

High-temperature protonic conduction has been reported in many solid materials without intrinsic protons.⁵⁻¹³ Among the materials, some of acceptor-doped oxoacid salts, such as rare earth orthophosphates LnPO₄ (Ln=La, Pr, Nd, Sm and Y) doped with alkaline earth elements M (M=Ca, Sr and Ba),⁴⁻¹² were suggested as interesting materials because of the dominant protonic conduction and high chemical stability. In the case of the rare earth orthophosphates, it is considered that partial substitution of alkaline earth elements for rare earth elements lead to condensation of two neighboring orthophosphate-anion groups in order to satisfy the electroneutrality of the crystals.⁶ Under wet conditions, protons responsible for conduction are incorporated through an equilibrium between the condensed phosphate ion and ambient water vapor. This means that the condensed ion plays an important role for protonic conduction in the rare earth orthophosphates. Since such a condensation of oxoacid anion groups is also expected not only in the phosphate but also in other oxoacids, we investigated electrical conduction in an aragonite-type lanthanum orthoborate LaBO₃ (S. G. : Pnam) with 1 mol% substitution of Sr for La, and demonstrated that the Sr-substituted LaBO₃ exhibited protonic conduction at elevated temperatures.¹³ However, it has not been well understood how substitution species and its concentration affect electrical conduction properties of LaBO₃.

In this work, for the purpose of clarifying effects of a substitution element on electrical conduction in the orthoborates, Ca-, Sr- and Ba-substituted LaBO₃ were prepared and their electrical conductions were studied with conductivity measurements. In order to estimate charge carrier species and their transport numbers, EMF measurements of water-vapor and oxygen concentration cells were also performed.

2. Experimental

The aragonite-type LaBO₃ substituted with x mol% of Ca (x = 1), Sr (x = 1–10) and Ba (x = 1) were synthesized with a conventional solid-state reaction method. In this paper, the substitution level of the alkaline earth metal (M) represents [M]/(M+1+[La]). La₂O₃, B₂O₃, and CaCO₃, SrCO₃ or BaCO₃ were mixed in an appropriate proportion, and the mixture was calcined at 1000°C for 3 h in air. Then, the product was sintered at 1200°C for 5 h in air after a cold isostatic pressing at 400 MPa. A sintered compact for EMF measurements was prepared by the spark plasma sintering (SPS) at 1200°C for 5 min under a uniaxial pressure of 50 MPa. The obtained materials were characterized with X-ray diffraction (XRD) and density measurements.

Electrical conductivities of the sintered compacts were measured with four-probe d. c. method at 500–925°C under oxidizing conditions. For the measurements, the samples were cut to a bar shape with the size of 3 mm × 3 mm × 40 mm, and the electrodes were prepared by firing Pt paste at 930°C. Oxygen partial pressure, P(O₂), was varied from 0.01 to 100 kPa using pure O₂ or Ar/O₂ mixture gases. Water vapor partial pressure, P(H₂O), was changed from 0.4 to 5 kPa by bubbling the gas through pure H₂O or aqueous solutions saturated with LiCl or MgCl₂ at 30–40°C. Conductivities were also measured under D₂O-containing oxidizing conditions, where P(D₂O) was controlled by using pure D₂O instead.
In order to estimate charge-carrier species and their transport numbers, EMF measurements of water-vapor and oxygen concentration cells were performed at 600–900°C. In the measurements, a disk sample with a diameter of 14 mm and a thickness of 0.5 mm was used as an electrolyte. Pt electrodes with a diameter of 5 mm were attached to the both sides of the disk by firing Pt pastes at 930°C, and then the specimen was mounted to a homemade cell. For the water-vapor concentration cell, both sides of the specimen were exposed to 1 kPa of P(H2O), and P(H2O) was varied from 0.4 to 5 kPa at one side of the specimen while being kept at 1 kPa at the other side. This water vapor concentration cell was defined as below and proton transport number, \( n(H^+) \), was calculated on the basis of the following equation:

\[
\text{H}_2\text{O} \left( P^o(\text{H}_2\text{O}) = 4.2 \text{ kPa} \right), \text{Pt | Sample | Pt, H}_2\text{O} \left( P(\text{H}_2\text{O}) \right)
\]

\[
EMF = -n(H^+) \frac{RT}{2F} \ln \frac{P(\text{H}_2\text{O})}{P^o(\text{H}_2\text{O})}
\]  

(1)



In Eq. (2), the gas constant, temperature and the Faraday constant were 8.314 J/K·mol, 298 K, and 96,485 C/mol, respectively. In the case of the oxygen-concentration cell, both sides of the specimen were exposed to 4.2 kPa of P(H2O), and P(O2) was changed from 0.01 to 1 kPa at one side of the specimen while being kept at 1 kPa at the other side. From the EMF, one can determine the sum of transport numbers of proton, \( n(H^+) \), and oxide ion, \( n(O^{2-}) \):

\[
\text{O}_2\left( P^o(\text{O}_2) = 1 \text{ kPa} \right), \text{Pt | Sample | Pt, O}_2 \left( P(\text{O}_2) \right)
\]

\[
EMF = [n(H^+) + n(O^{2-})] \frac{RT}{4F} \ln \frac{P(\text{O}_2)}{P^o(\text{O}_2)}
\]  

(2)

In these measurements, the P(H2O) and P(O2) were achieved in the same manner as in the conductivity measurements mentioned above.

3. Results and discussion

3.1 Materials

Figure 1 shows X-ray diffraction patterns of \( x \) mol % Sr-substituted LaBO3 (\( x = 1, 2, 3, 5 \) and 10). In this figure, a pattern of LaBO3 without the substitution (\( x = 0 \)) is also presented. When \( x = 0 \) and 1, all the diffraction peaks could be attributed to the aragonite-type structure (PDF No.; 12-0762) and no other phases were detected. When the Sr concentration exceeded 1 mol %, however, diffraction peaks attributable to Sr3La2(BO3)4 (PDF No.; 30-1295) were observed in addition to the aragonite-type structure. The calculated lattice constants of these specimens are shown in Fig. 2. Up to 2 mol % of Sr concentration, the lattice constant of the a-axis increased with increasing Sr concentration. Considering that a larger ionic radius of Sr2+ than La3+\textsuperscript{3+}this result indicates that Sr can be substituted partially for La. The reason why only the a-axis was expanded by the substitution may be due to the layer-like structure of the aragonite-type LaBO3.\textsuperscript{13}

When the Sr concentration was more than 2 mol %, the lattice constants were essentially independent of the Sr amount. This indicates that a solubility limit of Sr to the La site is between 1 and 2 mol % and that higher Sr concentration than the solubility limit results in formation of Sr3La2(BO3)4 as an impurity phase. X-ray diffraction patterns of 1 mol % Ca- and Ba-substituted LaBO3 were also measured. It was confirmed that the materials had a single phase of the aragonite-type structure as well as the Sr-substituted sample with the same substitution level. This suggests that not only Sr but also Ca and Ba can be substituted for La at least up to 1 mol % of the concentration.

Densities of the sintered compacts of these substituted LaBO3 were 4.880–5.026 g cm\(^{-3}\), regardless of the species and the concentrations, corresponding to 92–95% of the theoretical density.

3.2 Effects of substitution amount

Figure 3 shows the conductivities of the Sr-substituted LaBO3 under the wet condition 500–600°C as a function of the Sr amount. At this temperature range, protonic conduction can be considered to be predominant as discussed in following sections. Unfortunately, we could not measure conductivity of the pure LaBO3 (\( x = 0 \)) with sufficient accuracy at 500–600°C due to the rather low value, but its conductivity at 800°C was 7.90 ×...
10⁻¹⁴ S cm⁻¹. Considering this fact, it can be concluded that the Sr substitution improves the conductivity of the LaBO₃ considerably. When the Sr concentration exceeded 1 mol%, however, the conductivities decreased with increasing the concentration. In the case of Sr-doped LaPO₄,¹¹ it was reported that formation of an impurity phase, such as Sr₃P₂O₇, deteriorated protonic conductivity. Because Sr₃La₂(BO₃)₄ was formed in the 2-10 mol% Sr-substituted LaBO₃ (Fig. 1), such an impurity phase should deteriorate protonic conductivity of the substituted LaBO₃ in the same way as the phosphate-based electrolytes.

3.3 Effects of substitution species

Figure 4 shows conductivities of the LaBO₃ with the 1 mol % Ca, Sr and Ba substitutions under H₂O, D₂O-moisturised and dry conditions at P(O₂) = 1 kPa. For the Sr-substituted LaBO₃, its conductivities were already reported in our previous work.¹³ Regardless of the alkaline earth element, conductivities under the moisturized conditions were much higher than those under the dry condition. It was also found that the conductivities were lower under the D₂O- than the H₂O-moisturized condition. At the lower temperatures, the conductivity ratios, σ(H₂O)/σ(D₂O), were around √2, which is a classical value for a pure protonic conductor by a simple hopping mechanism. As temperature increased, the conductivity ratios became slightly lower and became around 1.2 at 900°C. These results indicate that the LaBO₃ incorporates protons in order to compensate the effective negative charge of the divalent metal and site and conduct the protons predominantly although other charge carrier species than protons also contribute to the total conductivities at the higher temperatures. It was also found that the Sr-substituted LaBO₃ showed the highest conductivities among the substituted specimens and were 1.1 x 10⁻¹²-1.5 x 10⁻¹⁴ S cm⁻¹ at 500-925°C.

Figure 5 shows conductivities of the samples as a function of P(O₂) at P(H₂O) = 0.48 kPa. At the lower temperatures, the conductivities were almost independent of P(O₂). As temperature increased, however, the conductivities began to increase slightly with increasing P(O₂), indicating slight contribution of p-type conduction. Such a conclusion is consistent well with that derived from the H/D isotope effects on conductivity. Conductivities of the materials under various P(H₂O) at P(O₂) = 1 kPa are presented in Fig. 6. At all the studied temperatures, the conductivities were essentially proportional to P(H₂O)¹/². Considering the predominant protonic conduction in the samples, the P(H₂O) dependencies of the conductivity are considered to reflect those of the proton concentration. Therefore, the proton concentrations in the materials are supposed to be proportional to P(H₂O)¹/². This suggests that an acceptor substitution into the LaBO₃ induces formation of an oxygen deficit and then result in proton incorporation into crystals according to a defect equilibrium between the oxygen deficit and ambient water vapor. If we assume the oxygen deficit as a simple oxygen vacancy, this equilibrium can be described with the Körger-Vink notation as below:

\[
\frac{1}{2} V^{O\bullet} + \frac{1}{2} H_2O + \frac{1}{2} O^{2\bullet} \rightleftharpoons OH^{\bullet}
\]

In order to estimate charge-carrier species and their transport numbers, we measured EMF values of water-vapor and oxygen concentration cells. In this work, the transport-number measurements were carried out at 600-900°C only with the Sr-substituted specimen because all the substituted LaBO₃ exhibited protonic conduction as mentioned above. Figure 7 presents results of water-vapor concentration cells, and also gives the theoretical values for a pure protonic conductor, in which η(H⁺) is unity. At 600°C, the EMF values were almost equal to the theoretical ones, and the η(H⁺) could be estimated as 0.9. As temperature increased, the EMF values got smaller compared with the theoretical ones, and the η(H⁺) were estimated as 0.8, 0.7 and 0.7 at 700, 800 and 900°C, respectively. Figure 7 shows results of oxygen concentration cells with the theoretical values for a pure ionic conductor in which the sum of η(H⁺) and η(O²⁺) is unity. From the EMF values, it was confirmed that the total ionic transport numbers were close to those of the η(H⁺) derived from water-vapor concentration cells. This result indicates that the η(O²⁺) is negligibly small in the LaBO₃-based material. Therefore, the deviations of η(H⁺) from unity especially at the higher
temperatures are considered to be due to the contribution of electronic conduction. Such a result can explain well the H/D isotope effects and the $P(O_2)$ dependencies of the conductivity.

4. Conclusions

In this work, electrical conduction properties of LaBO$_3$ with partial substitutions of Ca, Sr and Ba were studied at 500–925°C, and effects of the alkaline-earth species and the concentrations on the electrical conduction properties were discussed. Regardless of substitution species, the LaBO$_3$ began to exhibit protonic conduction at the temperature range by substituting the alkaline earth elements for La partially. In the specimens with 1 mol% Ca, Sr and Ba substitutions, protonic conduction were considered to be predominant although contribution of p-type conduction became significant at the higher temperatures. When the substitution level exceeded the solubility limit, however, a deterioration of the proton conductivity was confirmed. This may be due to formation of an impurity phase. The proton transport number could be estimated as 0.7–0.9 for the 1 mol% Sr-substituted LaBO$_3$.

References

1) T. Norby, Solid State Ionics, 125, 1–11 (1999).
2) K.-D. Kreuer, Chem. Mater., 8, 610–641 (1996).
3) H. Iwahara, T. Shimura and H. Matsumoto, Electrochemistry, 68, 154–161 (2000).
4) T. Norby and N. Christiansen, Solid State Ionics, 77, 240–243 (1995).
5) K. Amezawa, S. Kjelstrup, T. Norby and Y. Ito, J. Electrochem. Soc., 145, 3313–3319 (1998).
6) K. Amezawa, H. Maekawa, Y. Tomii and N. Yamamoto, Solid State Ionics, 145, 233–240 (2001).
7) N. Kitamura, K. Amezawa, Y. Tomii and N. Yamamoto, Solid State Ionics, 162–163, 161–165 (2003).
8) S. Gallini, M. Hänsel, T. Norby, M. T. Colomer and J. R. Jurado, Solid State Ionics, 162–163, 167–173 (2003).
9) K. Amezawa, Y. Tomii and N. Yamamoto, Solid State Ionics, 162–163, 175–180 (2003).
10) K. Amezawa, Y. Tomii and N. Yamamoto, Solid State Ionics, 176, 135–141 (2005).
11) K. Amezawa, Y. Tomii and N. Yamamoto, Solid State Ionics, 176, 143–148 (2005).
12) N. Kitamura, K. Amezawa, Y. Tomii, T. Hanada, N. Yamamoto, T. Omata and S. Otsuka-Yao-Matsuo, J. Electrochem. Soc., 152, A658–A663 (2005).
13) K. Amezawa, N. Takahashi, N. Kitamura, Y. Tomii and N. Yamamoto, Solid State Ionics, 175, 575–579 (2004).
14) R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr., 32, 751–767 (1976).
15) A. Nakatsuji, O. Ohtaka, H. Arima, N. Nakayama and T. Mizota, Acta Crystallogr., Sect. E: Struct. Rep. Online, 62, i103–i105 (2006).