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Electrical conduction properties of Sr-doped $Bi_4(SiO_4)_3$ with the eulytite-type structure

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Abstract Electrical conduction in 1 mol% Sr-doped $Bi_4(SiO_4)_3$ with the eulytite-type structure at elevated temperatures was investigated with conductivity measurements. Conductivity of the material under wet condition was higher than that under dry condition, and were 1.2×10^{-6} – 9.7×10^{-5} S cm^{-1} at 500–850 °C. From H/D isotope effects and $p(O_2)$-dependencies of the conductivity, it was found that the Sr-doped $Bi_4(SiO_4)_3$ exhibited protonic conduction at all the temperatures investigated while contribution of p-type conduction became significant with increasing $p(O_2)$ and/or temperature. Protonic and p-type conductions in the material were discussed in terms of defect equilibria.

Introduction

A few decades ago, it was discovered that $SrCeO_3$ exhibited protonic conduction at elevated temperatures under wet conditions by partial substitution of lower-valent cations for the host cations, i.e., acceptor-doping [1]. Since then, it has been reported that many acceptor-doped oxides without intrinsic protons exhibited high temperature protonic conduction [2–4]. Among such high temperature protonic conductors, some of acceptor-doped oxoacid salts containing rare earth cations as host cations, such as M-doped $LnPO_4$ (M=Ca, Sr and Ba, and Ln=La, Pr, Nd, Sm and Y) [5–13], M-doped LaP_3O_9 [14, 15] and Sr-doped $La_7P_3O_{18}$ [16], were suggested as interesting materials because of their dominant protonic conduction and high chemical stabilities.

In our previous works, we investigated defect structures in these proton-conducting oxoacid salts, and proposed a proton dissolution model based on defect equilibria. In this model, partial substitution of alkaline earth cations for the rare earth cations leads to condensation of the oxoacid anions. In the case of Sr-doped $LaPO_4$ with the monazite structure, for instance, the substitution of Sr for La can be described as below with the Körger-Vink notation [7]:

$$\tfrac{1}{2}{}_2\mathrm{P_2O_7} \rightarrow \mathrm{Sr}'_{\mathrm{La}} + \tfrac{1}{2}(\mathrm{P_2O_7})^{\bullet\bullet}_{2\mathrm{PO_4}}, \qquad (1)$$

where $\mathrm{Sr}'_{\mathrm{La}}$ and $(\mathrm{P_2O_7})^{\bullet\bullet}_{2\mathrm{PO_4}}$ represent Sr^{2+} at La^{3+} sites and pyrophosphate ions at two neighboring orthophosphate ions' sites, respectively. The pyrophosphate ions can be regarded as oxygen deficits in the crystal. Under moisturized conditions, the material incorporates protons through equilibrium between the oxygen deficits and ambient water vapor:

$$\tfrac{1}{2}(\mathrm{P_2O_7})^{\bullet\bullet}_{2\mathrm{PO_4}} + \tfrac{1}{2}\mathrm{H_2O(g)} \rightleftarrows (\mathrm{HPO_4})^{\bullet}_{\mathrm{PO_4}}, \qquad (2)$$

where $(\mathrm{HPO_4})^{\bullet}_{\mathrm{PO_4}}$ represents hydrogen phosphate groups at orthophosphate ion sites. Protons in the hydrogen phosphate groups conduct with the hopping mechanism.

Assuming the above proton dissolution process, rare earth cations are not necessary for host cations of proton-conducting oxoacid salts, and other oxoacid salts are also

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expected to show protonic conduction at elevated temperatures by acceptor-doping. In this work, we had an interest in $Bi_4(SiO_4)_3$ with the eulytite-type structure, as oxoacid salts without rare earth cations. This material has SiO_4-tetrahedra in the crystal [17], and thus similar proton dissolution process to the monazite-type $LaPO_4$ is expected. 1 mol% Sr-doped $Bi_4(SiO_4)_3$ were synthesized, and its conductivity was measured at 500–850 °C under H_2O/O_2 oxidizing conditions. In order to confirm protonic conduction in the material, an H/D isotope effect on conductivity was examined. In the latter part of this paper, we discussed $p(O_2)$- and $p(H_2O)$-dependencies of the conductivity of the Sr-doped $Bi_4(SiO_4)_3$ in terms of defect equilibria.

Experimental

1 mol% Sr-doped $Bi_4(SiO_4)_3$ was synthesized with the solid state reaction using Bi_2O_3, SiO_2 and $SrCO_3$ as starting materials. Mixture of the starting materials in the desired proportion was calcined at 900 °C for 30 h with an intermediate grinding. The obtained powder was sintered at 950 °C for 5 h after a cold isostatic pressing with 400 MPa. The sintered compact was examined with X-ray diffraction and density measurements. In order to examine stability of the $Bi_4(SiO_4)_3$ under an H_2-cantaining condition, phase identification with X-ray diffraction method was carried out for a specimen after a heat-treatment at 700 °C for 5 h under 3 kPa of hydrogen partial pressure, $p(H_2)$, and 4.2 kPa of water vapor partial pressure, $p(H_2O)$. The $p(H_2)$ was achieved using an H_2/Ar mixture gas, and the $p(H_2O)$ was established by bubbling the mixture gas through pure H_2O at 30 °C.

Conductivity of the sintered compact of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ was measured at 500–850 °C under H_2O/O_2 oxidizing conditions. The partial pressure of oxygen, $p(O_2)$, was varied from 0.01 to 100 kPa using Ar/O_2 mixture gases or pure O_2. The $p(H_2O)$ was changed from 0.4 to 5 kPa by bubbling the gases through pure H_2O or saturated aqueous solutions of $MgCl_2$ or LiCl at 30–40 °C. In order to confirm protonic conduction, conductivity was also measured under D_2O-containing atmospheres where the partial pressure of D_2O, $p(D_2O)$, is fixed at 4.2 kPa and $p(O_2)$ was varied from 0.01 to 100 kPa. The $p(D_2O)$ was achieved using pure D_2O at 32.4 °C.

Results and discussion

Materials

Figures 1a and b show X-ray diffraction patterns of undoped and 1 mol% Sr-doped $Bi_4(SiO_4)_3$ synthesized in this work. It was confirmed that the Sr-doped specimen had a single phase of the eulytite-type structure as well as the undoped one and thus substitution of Sr^{2+} for Bi^{3+} could be performed successfully. Figure 1c exhibits an X-ray diffraction pattern of the $Bi_4(SiO_4)_3$ after the heat-treatment under the H_2/H_2O reducing condition. It was found that some diffraction peaks could be attributed to Bi. This indicates that the $Bi_4(SiO_4)_3$ is unstable under the H_2/H_2O reducing condition. Based on this result, conductivity measurements for the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ were carried out only under the H_2O/O_2 oxidizing conditions in this work.

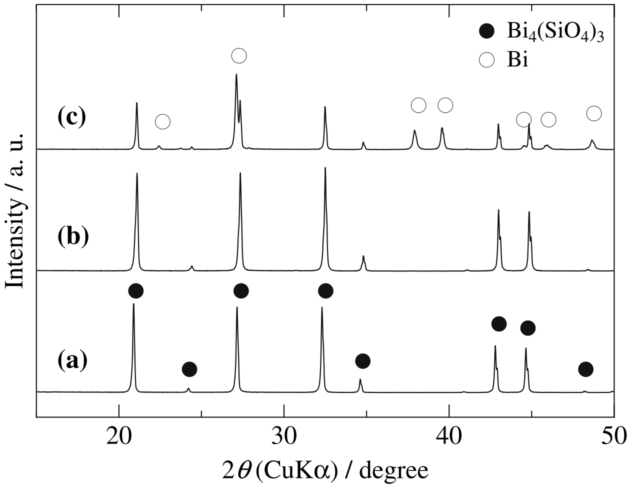

Fig. 1 X-ray diffraction patterns of (**a**) the undoped and (**b**) the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ after sintering in air, and (**c**) undoped $Bi_4(SiO_4)_3$ after the heat-treatment under the reducing condition ($p(H_2)$=3 kPa, $p(H_2O)$=4.2 kPa)

A density of the sintered compact of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ was 5.953 g cm^{-3}, corresponding to 88 % of the theoretical density.

Conductivities

Figure 2 exhibits conductivities of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ under wet and dry oxidizing conditions. The conductivity of the Sr-doped $Bi_4(SiO_4)_3$ under the wet condition was 1.2×10^{-6} - 9.7×10^{-5} S cm^{-1} at 500–850 °C, and was always higher than that under the dry condition. Such a humidity dependency of the conductivity suggests that the Sr-doped $Bi_4(SiO_4)_3$ incorporates protons from ambient water vapor and the protons can work as charge carriers in the material.

In order to investigate an effect of ambient $p(H_2O)$ on the conductivity of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ in detail, conductivity of the material was measured under various $p(H_2O)$ at $p(O_2)$=1 kPa. The result is given in Fig. 3. As $p(H_2O)$ increased, the conductivity increased at the temperatures investigated.

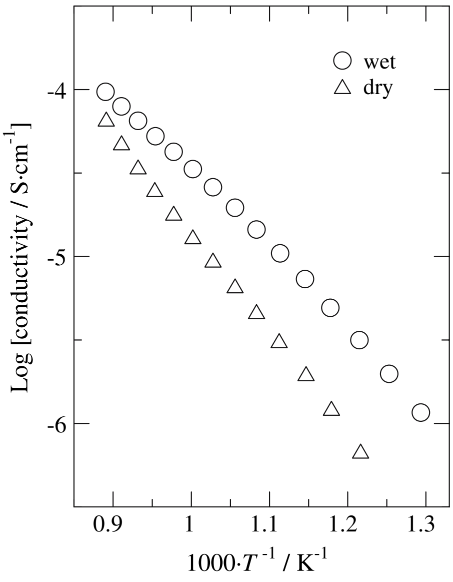

Fig. 2 Conductivities of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ under wet ($p(H_2O)$=4.2 kPa) and dry conditions at $p(O_2)$=1 kPa

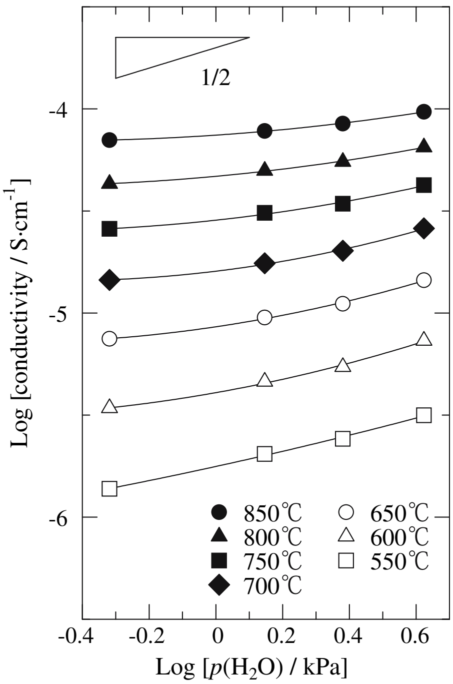

Fig. 3 Conductivities of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ under various $p(H_2O)$ at $p(O_2)$=1 kPa

Figure 4 shows conductivity of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ under various $p(O_2)$ at $p(H_2O)$=0.48 kPa. When $p(O_2)$ is lower, the conductivity was essentially independent of $p(O_2)$ at lower temperatures. As $p(O_2)$ and/or temperature increased, however, the conductivity began to increase with increasing $p(O_2)$. This result indicates that p-type electronic conduction contributes to the total conductivity with increasing temperature and/or $p(O_2)$.

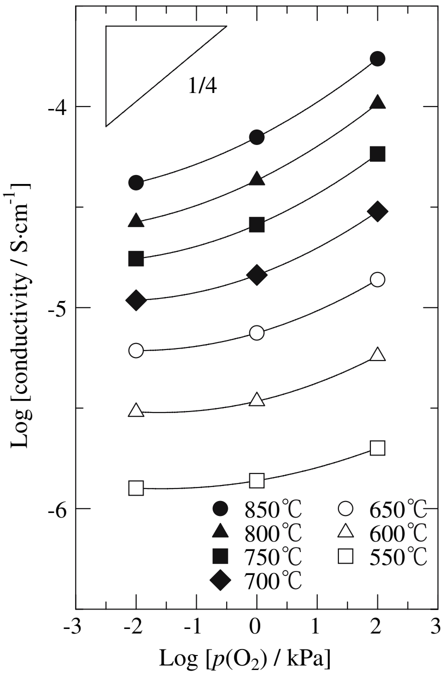

Fig. 4 Conductivities of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ under various $p(O_2)$ at $p(H_2O)$=0.48 kPa

H/D isotope effects on conductivity

For the purpose of confirming protonic conduction in the 1 mol% Sr-doped $Bi_4(SiO_4)_3$, an H/D isotope effect on conductivity was examined at 500–850 °C. Figure 5 shows

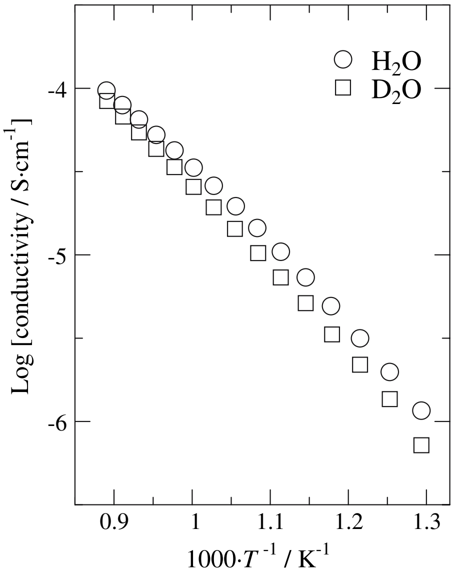

Fig. 5 Conductivities of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ at $p(H_2O)$ or $p(D_2O)$=4.2 kPa and $p(O_2)$=1 kPa

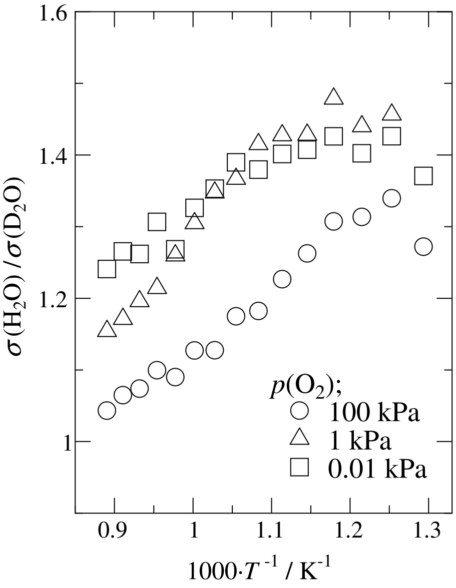

Fig. 6 Conductivity ratios, $\sigma(H_2O)/\sigma(D_2O)$, of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ under various $p(O_2)$; $p(H_2O)$ and $p(D_2O)$=4.2 kPa

conductivities of the material at $p(H_2O)$ or $p(D_2O)$=4.2 kPa and $p(O_2)$=1 kPa. As shown in this figure, the conductivity under the D_2O-containing condition was lower than that under the H_2O-containing condition. Such a clear H/D isotope effect on the conductivity confirms protonic conduction in the material under the wet conditions.

In order to discuss contribution of protonic conduction to the total conductivity in detail, an H/D isotope effect on conductivity was investigated under various $p(O_2)$. Figure 6 presents the conductivity ratio, $\sigma(H_2O)/\sigma(D_2O)$, as a function of temperature. At $p(O_2)$=0.01 and 1 kPa, the conductivity ratios at lower temperatures were approximately $\sqrt{2}$, which is the classical value for a pure protonic conductor with the hopping mechanism. This indicates that the material conduct predominantly protons at lower temperatures under these $p(O_2)$ region. At $p(O_2)$=100 kPa, however, the conductivity ratios at lower temperatures were around 1.3 and were lower than the classical values of $\sqrt{2}$. This indicates that contribution of protonic conduction to the total conductivity was less significant at $p(O_2)$=100 kPa than $p(O_2)$=0.01 and 1 kPa. From such a decrease in $\sigma(H_2O)/\sigma(D_2O)$, it is concluded that the material shows p-type conduction in addition to protonic conduction at $p(O_2)$=100 kPa. As temperature increased, the conductivity ratios decreased regardless of $p(O_2)$. This indicates that protonic conduction become insignificant at higher temperatures even under lower $p(O_2)$ due to contribution of p-type conduction.

From these results, it is concluded that the material exhibits protonic conduction under all the applied conditions although contribution of protonic conduction to the total conductivity is less significant due to contribution of p-type conduction at higher temperatures and/or $p(O_2)$.

Defect situations

From the results of the conductivity measurements described in ‘Conductivities’ and ‘H/D isotope effects on conductivity’, it was found that the Sr-doped $Bi_4(SiO_4)_3$ exhibited protonic and p-type conditions, and that the contribution of each conduction to the total conductivity depended on ambient atmospheric conditions. In this section, we discuss the electrical conduction properties in terms of defect equilibria.

As described in ‘Conductivities’, protons responsible for conduction in the Sr-doped $Bi_4(SiO_4)_3$ are considered to be introduced into the material from ambient water vapor. In the material, it is considered that partial substitution of Sr^{2+} for Bi^{3+} leads to formation of oxygen deficits in order to compensate the charge difference between dopant ions Sr^{2+} and host cations Bi^{3+}. Considering structural similarity of the material to $LaPO_4$, one possible form of the oxygen deficits in the Sr-doped $Bi_4(SiO_4)_3$ is condensed silicate ions, such as $Si_2O_7^{6-}$ which results from condensation of two neighboring SiO_4^{4-}. Since we do not know what type of oxygen deficits exists in the material at this moment, we simply express the oxygen deficits as $V_O^{\bullet\bullet}$, which means oxygen vacancy, in this paper. Then, the proton dissolution process of the material can be described as below:

$$\frac{1}{2}V_O^{\bullet\bullet} + \frac{1}{2}O_O^{\times} + \frac{1}{2}H_2O(g) \rightleftarrows OH_O^{\bullet}, \tag{3}$$

where $O_O^{\times}$ and $OH_O^{\bullet}$ represent oxide ions at oxide ions’ sites and interstitial protons coordinating oxide ions, respectively. The interstitial protons might be regarded as a part of hydrogen silicate ions like protons of hydrogen phosphate ions in proton conducting phosphates.

In addition to protonic conduction, the Sr-doped $Bi_4(SiO_4)_3$ showed p-type conduction. It is supposed that the following defect equilibrium induces p-type conduction in the Sr-doped $Bi_4(SiO_4)_3$:

$$\frac{1}{2}V_O^{\bullet\bullet} + \frac{1}{4}O_2(g) \rightleftarrows \frac{1}{2}O_O^{\times} + h^{\bullet}, \tag{4}$$

where $h^{\bullet}$ represents electron holes.

If we assume only the defects in Eqs. 3 and 4 for the Sr-doped $Bi_4(SiO_4)_3$, concentrations of the defects should satisfy the following electroneutrality condition:

$$2\left[V_O^{\bullet\bullet}\right] + \left[OH_O^{\bullet}\right] + p = \left[Sr_{Bi}'\right] \tag{5}$$

where square brackets mean concentrations of defects. The denotation of p represents concentration of electron holes. In the case of materials exhibiting ionic conduction like the Sr-doped $Bi_4(SiO_4)_3$, concentration of electron holes can be regarded as negligible, because mobility of electron holes is generally much larger than that of ions. Thus, the electroneutrality condition can be simplified as below:

$$2\left[V_O^{\bullet\bullet}\right] + \left[OH_O^{\bullet}\right] = \left[Sr_{Bi}'\right] \tag{6}$$

From Eqs. 3, 4 and 6, when oxygen vacancies are major positive defects, concentrations of the defects can be expressed as Eqs. 7–9:

$$\left[V_O^{\bullet\bullet}\right] = \frac{\left[Sr_{Bi}'\right]}{2} \tag{7}$$

$$\left[OH_O^{\bullet}\right] = K_3\left(\frac{\left[Sr_{Bi}'\right]}{2}\right)^{\frac{1}{2}} p(H_2O)^{\frac{1}{2}} \tag{8}$$

$$\mathrm{p} = K_4\left(\frac{\left[Sr_{Bi}'\right]}{2}\right)^{\frac{1}{2}} p(O_2)^{\frac{1}{4}}, \tag{9}$$

where K_3 and K_4 represent equilibrium constants of Eqs. 3 and 4, respectively.

When interstitial protons are major positive defects, one can describe concentrations of the defects as Eqs. 10–12:

$$\left[OH_O^{\bullet}\right] = \left[Sr_{Bi}'\right] \tag{10}$$

$$\left[V_O^{\bullet\bullet}\right] = K_3^{-2}\left[Sr_{Bi}'\right]^2 p(H_2O)^{-1} \tag{11}$$

$$\mathrm{p} = K_3^{-1}K_4\left[Sr_{Bi}'\right] p(H_2O)^{-\frac{1}{2}} p(O_2)^{\frac{1}{4}} \tag{12}$$

As shown in Fig. 3, the conductivity of the 1 mol% Sr-doped $Bi_4(SiO_4)_3$ was approximately proportional to $p(H_2O)^{1/2}$ at lower temperatures under 1 kPa of $p(O_2)$. Such $p(H_2O)$-dependencies of the conductivity are supposed to correspond to Eq. 8. This indicates that protonic conduction is predominant at lower temperatures although oxygen deficits are major positive defects. This conclusion is also supported by the fact that the $p(O_2)$-dependencies of the conductivity were insignificant at lower temperatures as shown in Fig. 4. As temperature increased, the conductivity began to depend considerably on $p(O_2)$, and were almost proportional to $p(O_2)^{1/4}$ at the highest temperature. Contrarily, $p(H_2O)$-dependency of the conductivity began less significant with increasing temperature. These changes in partial pressure dependencies of the conductivity are supposed to be explained by the change in the situation from Eq. 8 to 9 with increasing temperature. That is, as temperature increased, major charge carriers are changed from protons to electron holes, while major positive defects are oxygen deficits regardless of temperature. Such a conclusion on major charge carriers is considered to be consistent with the conclusion deduced from the H/D isotope effects on the conductivity described in the 'H/D isotope effects on conductivity'.

Conclusions

In this work, electrical conduction in 1 mol% Sr-doped $Bi_4(SiO_4)_3$ with the eulytite-type structure was investigated at 500–850 °C under oxidizing conditions. At lower temperatures, it was found that the material conducted protons dominantly under lower $p(O_2)$. As temperature and/or $p(O_2)$ increased, however, the material began to show p-type conduction in addition to protonic conduction. Such electrical conduction properties were also indicated by the discussion based on defect equilibria.

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