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Novel bromide anion conducting refractory solid electrolytes based on lanthanum oxybromide

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A new type of high bromide anion conducting solid was artificially designed with the solids based on lanthanide oxybromide (LnOBr). LnOBr is selected as it is insoluble in water and also highly stable at temperatures around 800°C. The enhancement of Br^- anion conductivity was successfully realized by creating Br^- ion vacancies by doping divalent cation in the Ln site of the LnOBr host lattice. The Br^- anion conductivity was the highest among the conventional bromide anion conducting solids such as $Pb_{0.99}K_{0.01}Br_{1.99}$ (373°C) and $CsPbBr_3$ (500°C) which contain toxic lead in them. The Br^- anion conductivity of LnOBr based solid enters into the practically useful region ($\sigma > 10^{-3}$ S·cm^{-1}).

1. Introduction

The solids in which only single ion species migrate are called "Solid Electrolytes" or "Ion Conducting Solids" [1, 2]. Ion species conducting in solids are categorized into two groups, the cation and the anion. In order to realize the ion conduction in solids, requires small in ionic size and valence state. The monovalent and divalent cations and anions such as Li^+, Na^+, Mg^{2+}, F^-, Cl^-, and O^{2-}, have been well known to conduct in solids. The ionic radius of anion is considerably larger than that of cation. The larger anions as compared to O^{2-} and Cl^-, are S^{2-} in divalent state and Br^- in monovalent state. As far as S^{2-} is concerned, it would be very difficult to conduct in solids due to its large ionic size of 0.17 nm (6 coordinate) [3]. In contrast, there are some reports on bromide anion conductors of the type $Pb_{0.99}K_{0.01}Br_{1.99}$ [4] and $CsPbBr_3$ [5]. However, their ionic conductivity is still below the practically applicable region of 10^{-3} S·cm^{-1}. Again, the solids based on bromides are all soluble in hot water and contain toxic element like lead (Pb). Hence reasonable Br^- anion conducting solid electrolytes have not been developed yet. As reported in our earlier communication [6], we have succeeded in developing a new type of high bromide anion conducting solid based on lanthanum oxybromide by doping one of alkaline earth cations, strontium. Since oxybromides are insoluble in water and they are stable up to 700°C in the case for the lanthanoid oxybromide series [7], we have selected oxybromide as the host phase of Br^- anion conductors.

In this paper, we report the effect of various types of the alkaline earths doping including strontium into the LaOBr crystal matrix on the Br^- anion conducting properties.

2. Experimental

Ln_2O_3 (Ln = La and Nd) or Pr_6O_{11} was mixed with MCO_3 (M = Mg, Ca, Sr, and Ba) in a proper proportion and dissolved in the hydrobromide solution (47%). The corresponding bromide was obtained by heating the aqueous solution. The resulting bromide powder was heated at 800°C for 12 h in air to form oxybromide. The resulting $La_{1-x}M_xOBr_{1-x}$ powder was pelletized and heated at 800°C for 12 h in nitrogen. The pellet was pulverized and made into pellet again and then sintered at 800°C for 12 h in nitrogen. The X-ray powder diffraction analysis (Rigaku, Multi Flex) was performed by using Cu-K_α radiation. The XRD data were collected by a step scanning method in the 2θ range from 10° to 70° with a step scan width of 0.04°. Thermal analysis (TG) was conducted by using Rigaku set up (DTG-50 H).

The conductivity measurements were carried out using Hewlett Packard precision LCR meter (4192A), using the sample within two platinum electrodes. The polarization measurements were done by passing a dc current of 1 μA between two platinum mesh electrodes sandwiching the pellet at 600°C in oxygen atmosphere and monitoring the dc voltage as a function of time. The dc electrolysis was conducted at 600°C at 20 V for 1 day by setting two alkaline earth metal doped LaOBr pellets and one La_2O_3 pellet between two Pt electrodes.

3. Results and discussion

The crystal structure of LnOBr [8] is presented in Fig. 1a. LnOBr has the tetragonal PbFCl-type structure (space group *P4/nmm*) and it is reported that there

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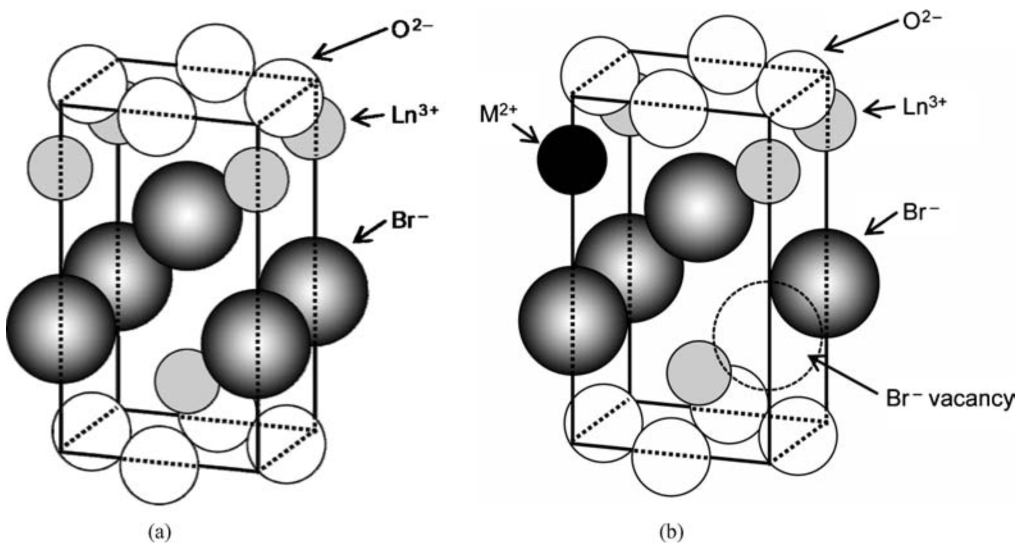

Figure 1 Crystal structure of pure LnOBr (a) and $Ln_{1-x}M_xOBr_{1-x}$ solid solution (b) (Ln: lanthanoid).

are some Br^- anion vacancies in the structure which are responsible for Br^- anion conducting characteristics. However, the Br^- anion conductivity is well below the practically applicable limit of conductivity (Fig. 5).

Fig. 2 shows the results of thermal gravimetric analysis (TGA) for lanthanoid oxybromides (Ln = La, Pr, Nd) up to 1000°C. It can be easily recognized that lanthanum oxybromide is thermally more stable among the three oxybromides. With the decrease in ionic radius from La^{3+} (0.130 nm (8 coordinate)) to Nd^{3+} (0.125 nm (8 coordinate)), the decomposition temperature to form individual oxide decreases, due to the lower stability of the crystal structure. Since the ionic radii of both Br^- (0.182 nm (6 coordinate)) and O^{2-} (0.126 nm (6 coordinate)) are large, and comparable to ionic radius is La^{3+} shows the highest stability. Among the three oxybromides, LaOBr is as stable up to 800°C which is some 300°C and 427°C more than that for conventional bromide based solid electrolytes [4, 5].

In the LaOBr crystal lattice, there are few anion vacancies to function as the anion migration path way. It is two orders of magnitude lower than those of conventional Br^- anion conductors of $CsPbBr_3$ and K doped $PbBr_2$. In order to enhance the ion conductivity of LaOBr, Mg^{2+} and other divalent alkaline earth cations were doped to replace the trivalent La^{3+}, to create the anion vacancies (Fig. 1b). From the X-ray powder diffraction analyses presented in Fig. 3, it is clear that the single phase LaOBr was obtained for M = Mg, Ca, and Sr, while the two phase mixture of BaO and La_2O_3 was observed for M = Ba. In the case that the Mg doped LaOBr solid solution is formed, the lattice should shrink due to the fact that the ionic radius of Mg^{2+} (0.103 nm (8 coordinate)) is considerably smaller than that of La^{3+} (0.130 nm (8 coordinate)). However, no peak deviation toward higher angles was observed as compared to that of pure LaOBr, indicating that the solid solution was not formed. In contrast, a clear deviation toward lower angle side was observed for M = Sr^{2+}, suggesting the formation of the Sr doped LaOBr solid solution. In the case for M = Ca^{2+}, no such a deviation was obtained since the ionic radius of Ca^{2+} is almost comparable with that of La^{3+}. However, from the ionic conductivity results described later, the solid solution was expected to be successfully obtained.

Since the difference in ionic radii of Mg^{2+}: 0.103 nm (8 coordinate), Ba^{2+}: 0.156 nm (8 coordinate) and La^{3+}: 0.130 nm (8 coordinate)) is considerably large

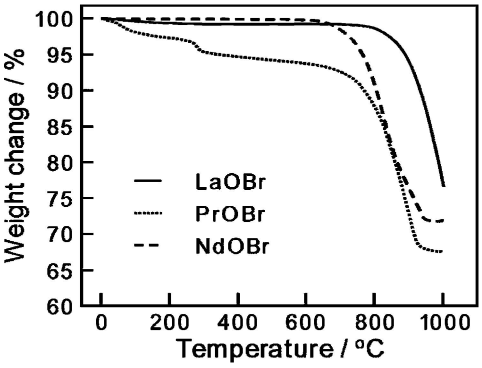

Figure 2 Thermal gravimetric results for LnOBr (Ln = La, Pr, Nd).

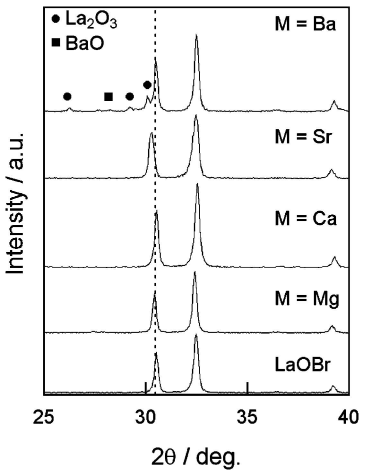

Figure 3 The X-ray powder diffraction results for LaOBr and $La_{0.9}M_{0.1}OBr_{0.9}$ solid solutions (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}).

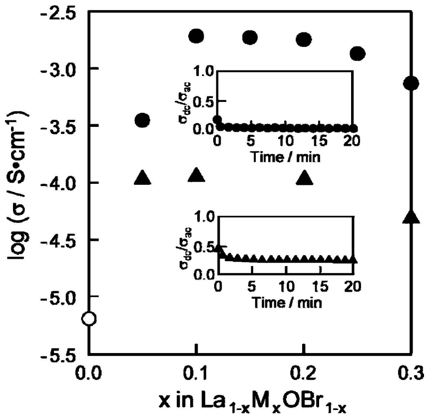

Figure 4 The compositional dependencies of the electrical conductivity for $La_{1-x}M_xOBr_{1-x}$ (M = Sr (●) and Ca (▲)). The results of polarization measurements in oxygen atmosphere are also inserted in the figure.

and it was not possible to form the corresponding solid solutions. The Ca^{2+} (0.126 nm (8 coordinate)) and Sr^{2+} (0.140 nm (8 coordinate)), however form a single phase LaOBr solid solution.

The variation of electrical conductivity with the alkaline earth cation content at 600°C for the $La_{1-x}M_xOBr_{1-x}$ series (M: Ca^{2+} and Sr^{2+}) is presented in Fig. 4. The polarization measurements in oxygen atmosphere (PO_2: 10^5 Pa) for both solid solutions are also plotted in the inserted figures, respectively. From the polarization measurements by measuring the dc to ac conductivity ratio (σ_{dc}/σ_{ac}) with time, an abrupt decrease in the ratio was observed in both cases, suggesting that the major conducting species is neither electron, hole nor oxide anion, but cation species [9]. Especially, in the case for $La_{1-x}Sr_xOBr_{1-x}$, the σ_{dc}/σ_{ac} ratio decreases down to less than 0.02, indicating that the conducting species in the solid is predominantly cation species (more than 98%). From Fig. 4, it is found that the conductivity increases with the alkaline earth cation content in the solid solution, and reaches a maximum value of 1.9×10^{-3} and 1.2×10^{-4} $S\cdot cm^{-1}$ for $La_{0.9}Sr_{0.1}OBr_{0.9}$ and $La_{0.9}Ca_{0.1}OBr_{0.9}$, respectively. In the region where there is higher than approximately 10 mol% doping, additional peaks correspond to La_2O_3 of the decomposition products and CaO are observed, respectively. This formation reduces the conductivity in both cases. By comparing two solid solution series, the Sr^{2+} doped LaOBr solid solution shows one order of magnitude higher conductivity as that of the Ca^{2+} doped LaOBr solid solution, and the value is more than two orders of magnitude higher than that of the pure LaOBr solid. This is mainly ascribed to the expansion of LaOBr lattice by partially substituting La^{3+} (0.130 nm (8 coordinate)) site for the larger Sr^{2+} cation (0.140 nm (8 coordinate)), while the ionic radius of Ca^{2+} (0.126 nm (8 coordinate)) is comparable to La^{3+}.

For the purpose of identifying the migrating cation species in the $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid solution, the modified Tubandt electrolysis was conducted (600°C, 20 V, 1 day). Fig. 5 shows the setup of the electrolysis. One La_2O_3 pellet (pellet A) on the anodic side and two pellets of the $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid solution (pellets B and C) on the cathodic side were set between two platinum bulk electrodes as illustrated in Fig. 5. The weight change of the three pellets after the electrolysis is tabulated in Table I. If the migrating anion species is bromide anion, weight gain should be observed in the pellet A according to Equation 1, and also weight loss should be observed in the pellet C following Equation 2. However no change could be recognized in the pellet B as shown by theoretical value listed in the Table.

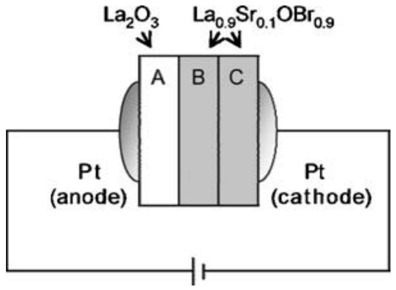

Figure 5 Set-up of the modified Tubandt electrolysis of $La_{0.9}Sr_{0.1}OBr_{0.9}$.

$$(1/2)\ La_2O_3 + Br^- \rightarrow LaOBr + (1/4)O_2 + e^- \quad (1)$$

$$(10/9)\ La_{0.9}Sr_{0.1}OBr_{0.9} + (1/4)O_2 + e^- \rightarrow (1/2)La_2O_3 + (1/9)SrO + Br^- \quad (2)$$

In the case that the migrating anion species is oxide anion, such a variation should not be observed in all pellets of A, B, and C. The weight change actually observed is weight gain in the pellet A, and weight loss in the pellets B and C. The sum of the weight loss both in pellets B and C is −0.37 mg and the value is almost consistent with the theoretical value of −0.35 mg from the Coulomb value of 0.104 C. The weight gain in the pellet A is relatively small in comparison with the expected value of +0.35 mg. It might be estimated that the migrating bromide anions mainly react with the pellet A of La_2O_3 as introduced in Equation 1. However, some of the bromide anions reaching the anode, might be released as Br_2 gas. From the modified Tubandt electrolysis, it is demonstrated that the Sr doped LaOBr solid is a pure Br^- anion conducting solid electrolyte.

Fig. 6 presents the temperature dependence of Br^- anion conductivity of $La_{0.9}Sr_{0.1}OBr_{0.9}$ with those reported for ($Pb_{0.99}K_{0.01}Br_{1.99}$ [4] and $CsPbBr_3$ [5]) and also with the data of pure LaOBr. Although lower temperatures than 250°C and 500°C for

TABLE I The weight change of the three pellets after the Tubandt electrolysis

Pellet	Theoretical weight change when Br^- ion migrates in the $La_{0.9}Sr_{0.1}OBr_{0.9}$ (mg)[a]	Measured weight change (mg)
A (La_2O_3)	+0.35	+0.26
B ($La_{0.9}Sr_{0.1}OBr_{0.9}$)	0	−0.05
C ($La_{0.9}Sr_{0.1}OBr_{0.9}$)	−0.35	−0.32

[a] Calculated from the total value of Coulomb during the electrolysis.

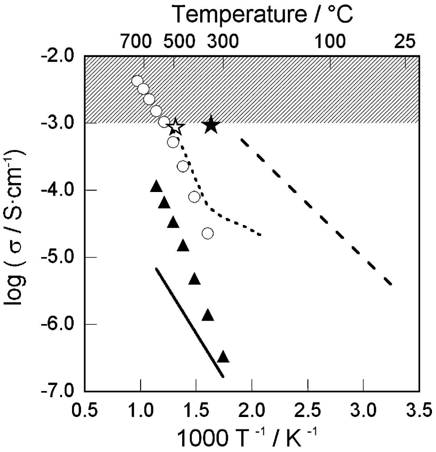

Figure 6 Temperature dependence of the Br^- ion conductivity for $La_{0.9}Sr_{0.1}OBr_{0.9}$ (○) and $La_{0.9}Ca_{0.1}OBr_{0.9}$ (▲) with the representative bromide anion conducting solid electrolytes reported ($Pb_{0.99}K_{0.01}Br_{1.99}$ [4] (broken line) and $CsPbBr_3$ [5] (dot line)) with the data of pure LaOBr (solid line). Open and closed stars represent the melting points of $Pb_{0.99}K_{0.01}Br_{1.99}$ and $CsPbBr_3$. The hatching area is the ion conductivity area showing a practically applicable region.

$Pb_{0.99}K_{0.01}Br_{1.99}$ and $CsPbBr_3$, respectively, the Br^- anion conductivity is higher than that of $La_{0.9}Sr_{0.1}OBr_{0.9}$, they can not be applicable at higher temperatures due to melting problem. In addition, they are soluble in hot water and contain toxic lead as the constituent.

A practically applicable region is regarded as the area of the ion conductivity higher than 10^{-3} S·cm^{-1} (-3.0 in log (σ/S·cm^{-1}) and as easily seen from Fig. 6, the Br^- anion conductivity of the present solid solution electrolyte enters this practical region and it can be stated that the present solid is the first solid electrolyte that reaches the applicable region.

4. Conclusions

For the purpose of developing novel bromide anion conducting solids suitable for practical use, the solid LaOBr was selected from the view point of water insolubility, thermal stability, and high temperature durability in addition to its satisfactory high Br^- anion conductivity. The enhancement of Br^- anion conductivity was realized by partially replacing the La^{3+} ion by divalent Ca^{2+} or Sr^{2+} cations to create Br^- anion vacancies. The highest Br^- anion conductivity of 1.9×10^{-3} S cm^{-1} at 600°C was realized in the case of $La_{0.9}Sr_{0.1}OBr_{0.9}$ whose conductivity enters into the practically applicable range of over -3.0 in log (σ/S·cm^{-1}).

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