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Ionic conducting properties in LaOCl–LaOBr solid solutions

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Abstract

High halide ion conduction in a solid was realized for the $La_{1-x}M_xO(Cl_{1-y}Br_y)_{1-x}$ solid solution (M: alkaline earth metal). The ion conductivity in $LaOCl_{1-y}Br_y$ increased by partially replacing the La^{3+} site with Sr^{2+} and the highest halide ion conductivity of 1.2×10^{-2} S cm^{-1} at 600 °C was obtained for $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.85}$, which was 2.2 and 6.2 times higher than those for $La_{0.8}Ca_{0.2}OCl_{0.8}$ and $La_{0.9}Sr_{0.1}OBr_{0.9}$, respectively. The conducting ion species in the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.85}$ solid solution were directly identified to be Cl^- and Br^- ions by the dc electrolysis method.

Keywords: Solid electrolyte; Chloride ion; Bromide ion; Lanthanum oxyhalide

1. Introduction

Solid electrolytes are unique functional materials in which only single ion species can migrate in solids, and many cation species whose oxidation numbers are from +1 to +4 are already reported to conduct in solids. On the other hand, O^{2-}, F^-, Cl^-, and Br^- are known to be conducting anion species, and F^- and O^{2-} ion conducting solid electrolytes have been already commercialized such as ion electrodes and chemical sensors. Although the solids based on chlorides such as $PbCl_2$ [1], $BaCl_2$ [2], $SrCl_2$ [3] and $CsPbCl_3$ [4] and bromides of $PbBr_2$ [5,6] and $CsPbBr_3$ [7] have been reported as Cl^- and Br^- conductors with high Cl^- and Br^- ion conductivities, these solid electrolytes exhibit a low thermal stabilities. This low thermal stability becomes critical disadvantages in practical application use.

In our previous study, we have succeeded in developing a high Cl^- conducting $La_{0.8}Ca_{0.2}OCl_{0.8}$ solid electrolyte with high chemical and thermal stabilities [8,9] by selecting LaOCl as a mother phase. By doping the lower valent Ca^{2+} ion in the trivalent La^{3+} site, Cl^- ion vacancies were successfully produced in the crystal lattice and, as a result, the highest Cl^- ion conductivity was obtained. We have also developed a $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid electrolyte showing the highest Br^- ion conductivity by using LaOBr as a mother phase [10]. Since both LaOCl and LaOBr possess the same PbFCl type structure (JCPDS 26-0311), the LaOCl–LaOBr solid solutions are expected as another mother phase of new halide ion conductor. In addition, it is possible to control the lattice size of the LaOCl–LaOBr solid solution by changing the Cl^- (0.167 nm [11]) and Br^- (0.182 nm [11]) ratio. Therefore, the optimum amount of halide anion vacancies and the suitable lattice size for halide ion conduction in lanthanum oxyhalide can be investigated by using the LaOCl–LaOBr solid solutions.

In this study, we synthesized the $La_{1-x}M_xO(Cl_{1-y}Br_y)_{1-x}$ (M: alkaline earth metals) solid solutions and the ion conducting properties were studied in detail.

2. Experimental

$LaOCl_{1-y}Br_y$ was synthesized by mixing La_2O_3, NH_4Cl and NH_4Br in a stoichiometric ratio by means of planetary

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ball milling apparatus (Pulverisette 7, FRITSCH GmbH), and heating at 800 °C for 12 h after a heating step of 400 °C for 2 h in air. $La_{1-x}M_xO(Cl_{1-y}Br_y)_{1-x}$ was prepared by mixing the stoichiometric $LaOCl_{1-y}Br_y$ solid solution and $M(NO_3)_2$ with the planetary ball mill and heating at 800 °C for 12 h in N_2. After identifying the obtained sample by X-ray powder diffraction (XRD) analysis (Multiflex, Rigaku), the powders were pelletized and sintered at 800 °C for 12 h in N_2. The electrical conductivity was measured by ac and dc methods using the sample pellet with the two Au electrodes in air and the conducting ion species in the $La_{1-x}M_xO(Cl_{1-y}Br_y)_{1-x}$ solid solution was identified by the dc electrolysis method.

3. Results and discussion

Fig. 1 shows the X-ray powder diffraction patterns of the $LaOCl_{1-y}Br_y$ series. The peaks of $LaOCl_{1-y}Br_y$ ($0 \leq y \leq 1$) were the same as those of pure LaOCl with the PbFCl structure and a peak shift to lower angle was observed with the increase of the Br^- (0.182 nm [11]) substitution amount for Cl^- (0.167 nm [11]) site. Furthermore, the lattice volume linearly increased with the Br^- substitution. This result clearly indicates that $LaOCl_{1-y}Br_y$ forms a solid solution in a whole composition range. However, these solid solutions showed similar low conductivities because no halide ion vacancies were produced in the lattice.

In order to introduce the halide ion vacancies in the $LaOCl_{1-y}Br_y$ solid lattice, we prepared the $La_{1-x}M_xO(Cl_{1-y}Br_y)_{1-x}$ solid solutions (M: alkaline earth metals). Fig. 2 displays the representative XRD patterns of $La_{0.9}M_{0.1}O(Cl_{0.5}Br_{0.5})_{0.9}$ ($x = 0.1$, $y = 0.5$). In the case of M = Ba, the sample did not form the single phase solid solution but results in the mixture of mother $LaOCl_{0.5}Br_{0.5}$, La_2O_3, and BaO. This is because Ba^{2+} ion (0.156 nm [11]) is too large to substitute the La^{3+} site (0.130 nm [11]) and the decomposition of the mother $LaOCl_{0.5}Br_{0.5}$ solid solution was promoted. While the $LaOCl_{0.5}Br_{0.5}$ doped with other M^{2+} ions possessed the single phase from the XRD patterns, the peak shift was not observed for the Mg^{2+} doped $LaOCl_{0.5}Br_{0.5}$ solid. If the Mg^{2+} ions replace the La^{3+} sites, the shrinkage of the $LaOCl_{0.5}Br_{0.5}$ lattice should occur. Therefore, it was found that the Mg^{2+} ions did not substitute the La^{3+} sites in $LaOCl_{0.5}Br_{0.5}$. The samples doped with Ca^{2+} (0.126 nm [11]) and Sr^{2+} (0.140 nm [11]) showed a clear peak shift to higher and lower angle, respectively, in their XRD patterns. Although the 20 mol% Ca^{2+} doped $LaOCl_{0.5}Br_{0.5}$ held the single phase in the XRD pattern, the lattice of the $LaOCl_{0.5}Br_{0.5}$ solid solution did not expand in comparison with the 10 mol% Ca^{2+} doped sample. Therefore, it was concluded that the substitution limit of Ca^{2+} for the La^{3+} site was around $x = 0.1$. The reason for the low solubility of Ca^{2+} into La^{3+} site for the $LaOCl_{0.5}Br_{0.5}$ solid compared with the case for LaOCl (solubility limit was reported to be $x = 0.2$) is that the Ca^{2+} size is relatively small for the $LaOCl_{0.5}Br_{0.5}$ lattice, which is expanded by partially replacing the Cl^- sites with larger Br^- ions. In the case of the Sr^{2+} doped $LaOCl_{0.5}Br_{0.5}$ solid solution, the single phase sample was obtained for the sample with $x \leq 0.15$ accompanying with the lattice expansion. For the sample doped with Sr^{2+} more than $x > 0.15$, La_2O_3 formed as a secondary phase. These results indicate that the substitution limit of Sr^{2+} for La^{3+} site was $x = 0.15$.

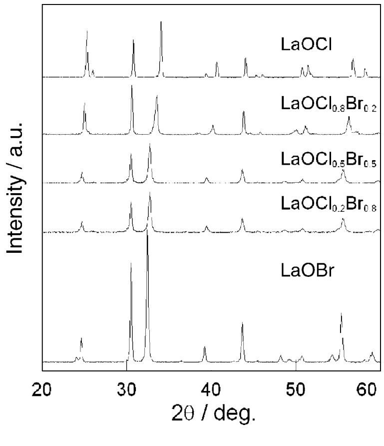

Fig. 1. XRD patterns of the $LaOCl_{1-y}Br_y$ solid solutions.

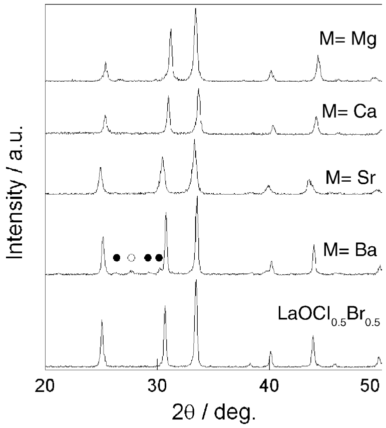

Fig. 2. XRD pattern of $La_{0.9}M_{0.1}O(Cl_{0.5}Br_{0.5})_{0.9}$ (M = Mg, Ca, Sr, and Br; $x = 0.1$; $y = 0.5$). (○) and (●) represent the peaks of BaO and La_2O_3, respectively.

In our previous works, we have reported that the highest halide ion (Cl^- and Br^-) conductivity was obtained for the M^{2+} solubility limit composition of $La_{0.8}Ca_{0.2}OCl_{0.8}$ [8,9] and $La_{0.9}Sr_{0.1}OBr_{0.9}$ [10], respectively. Therefore, the conductivities were measured for the $La_{0.9}Ca_{0.1}O(Cl_{1-y}Br_y)_{0.9}$ and $La_{0.85}Sr_{0.15}(Cl_{1-y}Br_y)_{0.85}$ ($y = 0.2$, 0.5, 0.8) solid solutions which are the solubility limit composition for M = Ca and Sr system, respectively. In the case of the $La_{0.9}Ca_{0.1}O(Cl_{1-y}Br_y)_{0.9}$ solid solutions, all the samples showed lower conductivities than those of the $La_{0.8}Ca_{0.2}OCl_{0.8}$ and $La_{0.9}Sr_{0.1}OBr_{0.9}$ solids which have been reported as the highest Cl^- and Br^- ion conducting solid electrolytes, respectively. On the other hand, the $La_{0.85}Sr_{0.15}(Cl_{1-y}Br_y)_{0.85}$ ($y = 0.2$, 0.5, 0.8) solid

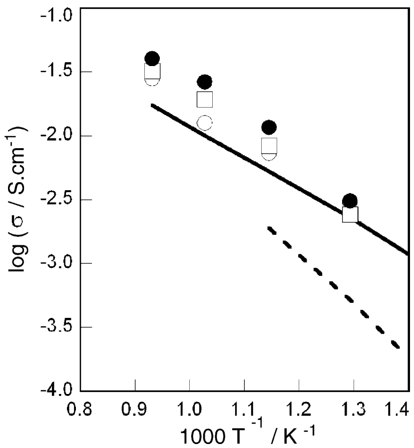

Fig. 3. Temperature dependencies of the electrical conductivity for the $La_{0.85}Sr_{0.15}O(Cl_{1-y}Br_y)_{0.85}$ solid solution ((●) $y = 0.2$, (□) $y = 0.5$, (○) $y = 0.8$) with the corresponding data for $La_{0.8}Ca_{0.2}OCl_{0.8}$ (solid line) [8,9] and $La_{0.9}Sr_{0.1}OBr_{0.9}$ (broken line) [11].

solutions possessed higher conductivities than those for the $La_{0.8}Ca_{0.2}OCl_{0.8}$ and $La_{0.9}Sr_{0.1}OBr_{0.9}$ solids as shown in Fig. 3, and the highest conductivity of 1.2×10^{-2} S cm^{-1} was obtained for the $La_{0.85}Sr_{0.15}(Cl_{0.8}Br_{0.2})_{0.85}$ ($y = 0.2$) at 600 °C and the value was 2.2 and 6.2 times as high as those of $La_{0.8}Ca_{0.2}OCl_{0.8}$ and $La_{0.9}Sr_{0.1}OBr_{0.9}$, respectively.

In order to investigate the conducting species in the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ solid solution, the time dependence of the dc to ac conductivity ratio (σ_{dc}/σ_{ac}) for the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ solid solution was measured at 800 °C in air. In the case where the sample shows an electronic conduction, the σ_{dc}/σ_{ac} ratio maintains a constant value of unity in any atmosphere because electrons are supplied from the metal used for the electrodes and, as a result, the σ_{dc} is equal to σ_{ac}. Also, the σ_{dc}/σ_{ac} ratio should be unity when the conducting ion species was supplied from the surrounding atmosphere as described in ref. [9]. Therefore, if O^{2-} anion conduction appears in the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ solid solution, the σ_{dc}/σ_{ac} ratio does not decrease close to zero in air. However, the σ_{dc}/σ_{ac} ratio for the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ solid solution drastically decreased with time and reached to 0.003 after 30 min, which strongly supports the idea that the conducting species in the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ solid solution is limited to be only ion which could not be supplied from air, that is, La^{3+}, Sr^{2+}, Cl^-, and Br^-.

For the purpose of directly identifying the conducting ion species, the dc electrolysis was carried out for the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ solid solution at 600 °C by applying a dc voltage of 3 V for 168 h. The set-up of the dc electrolysis and the results of EPMA line analysis after the electrolysis are shown in Fig. 4. If the conducting ion is cation, the conducting cations migrate to cathodic direction in the sample according to the potential gradient, and segregate near the cathodic surface. In the case of the Cl^- or Br^- anions as conducting ion species, although such halide anions conduct to anodic side, these ions may diffuse into the ambient atmosphere as gaseous Cl_2 and Br_2 after arriving at anodic surface. Therefore, we attached the La_2O_3 pellet at the anodic side of the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ pellet as a halide capturing solid. After the dc electrolysis, it was clearly recognized that Cl and Br existed in the La_2O_3 pellet. This result strongly supports the idea that both Cl^- and Br^- ions conduct toward the anodic direction in the solid and react with La_2O_3. Since the cation species such as La^{3+} and Sr^{2+} did not segregate near the cathodic surface of the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ pellet at all, which means no cation conduction appeared in the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ solid solution, it was clearly identified that the conducting ion species in the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ solid solution are Cl^- and Br^- ions.

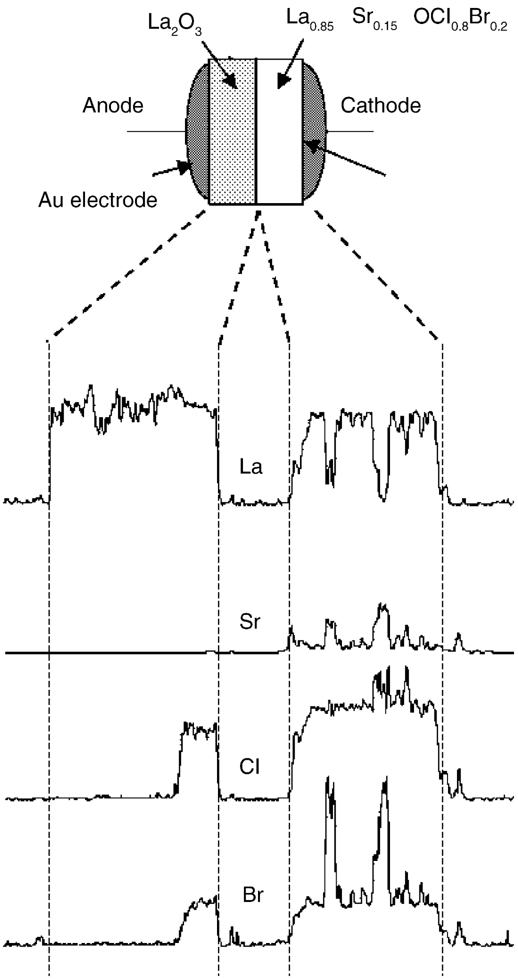

Fig. 4. The set-up of the dc electrolysis and the result of EPMA line analysis after the electrolysis of the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.85}$ solid solution.

From the above results, it is found that the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ solid solution is a dual halide ion conducting solid electrolyte with the highest halide ion conductivity except for the F^- ion species (for example, β-PbF_2 shows the F^- ion conductivity of ca. 1 S cm^{-1} at 600 °C. [12]). The reason why such a high halide ion conductivity was realized for the $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$

solid solution, is attributed to the simultaneous realization of both the appropriate amount of halide ion vacancies in the solid lattice and the suitable crystal lattice size for Cl^- and Br^- ion conduction at this composition.

4. Conclusions

High halide ion conduction in a Sr^{2+} doped LaOCl–LaOBr solid solution was developed. Both the suitable lattice size and the appropriate amount of anion vacancies for halide ion conduction was successfully realized not only by substituting the La^{3+} site of the $LaOCl_{1-y}Br_y$ solid solution with larger Sr^{2+} ion but also by intentionally adjusting the lattice size by changing the composition. The $La_{0.85}Sr_{0.15}O(Cl_{0.8}Br_{0.2})_{0.8}$ solid solution exhibited the highest halide ion conductivity among the halide ion conductors ever reported except for the F^- ion conducting solids. The present solid solution electrolyte showing a high thermal stability as well as the considerable high ion conductivity was greatly expected to be applied as a functional material in several practical applications.

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