Crystal phase control and ionic conductivity of magnesium ion-doped lanthanum oxyfluoride

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Novel F⁻ ion conducting solid electrolytes of La₁₋ₓMgₓO₁₋ₓF were developed by doping Mg²⁺ cation into the La³⁺ site of lanthanum oxyfluoride (LaOF) solid. By doping the smaller size and lower valent Mg²⁺ cation into the La³⁺ site, both the suppression of the phase transition from α- to β-form and the improvement of ionic conductivity were simultaneously realized. Among the samples holding the single phase of α-LaOF type structure, the La₀.₈Mg₀.₂O₁₋ₓF solid showed the highest F⁻ ion conductivity, which was ca. 46 times higher than that of non-doped LaOF solid.

1. Introduction

Recently, an interest to the next-generation rechargeable batteries whose energy density is over the lithium ion batteries (LIB) is gradually increasing, and many researchers are trying to develop the all solid-state fluoride ion batteries (FIB) as the candidate, due to its higher theoretical energy density compared to LIB.¹⁻⁴ For this end, the development of highly fluoride ion (F⁻)-conducting solid electrolyte is a key issue, and various kinds of fluoride ion conductors have been studied such as PbSnF₄⁻³⁵) BaF₂⁻⁶) and LaF₃⁻⁷) Among them, while PbSnF₄ has been expected to be a promising candidate due to its extraordinarily high F⁻ ion conductivity (1.5 × 10⁻³ S·cm⁻¹) even at room temperature,⁵) PbSnF₄ cannot be applied because of its tetragonal (space group: P4/mmm) and LaF₃⁻⁷) cannot be applied due to its critical disadvantage of low chemical stability, especially in reducing condition. Therefore, development of a novel F⁻ ion conducting solid with both high ionic conductivity and chemical stability is greatly requested.

Lanthanum oxyfluoride (LaOF) is known to have chemical stability in both oxidizing and reducing atmospheres, and F⁻ ion conduction in LaOF has been also reported.⁸) These properties are important factors for the practical F⁻ ion conductor applied for the batteries. However, its ionic conductivity is so low that LaOF itself is difficult to be applied for the FIB. Moreover, there is a report on the phase transition of LaOF of which LaOF can possess a tetragonal α-phase (space group: P4/mmm) and a trigoinal β-phase (space group: R-3m),⁸⁻¹¹) and their conductivities are different depending on the crystal phase.¹¹) Although it has been reported that such structural transition may occur at around 500°C, the origin of phase transition is still unknown. Therefore, it is highly required for developing the practical F⁻ ion conducting solid with control of crystal phase via an understanding of the origin of the phase transition.

In this study, we tried to improve the F⁻ ion conducting property in LaOF solid by suppressing the phase transition. Here, we partially replace the La³⁺ ion (ionic size: 0.130 nm [coordination number (CN): 8]¹²) site in LaOF with smaller size of Mg²⁺ [0.103 nm (CN = 8)]²²) to reduce the crystal lattice size. The Mg²⁺ substitution can suppress the displacement of ions in the lattice, which causes the phase transition. Moreover, formation of anion defects which should accelerate the F⁻ ion conduction in solid is also expected. Therefore, in this paper, we describe the F⁻ ion conducting property in the La₁₋ₓMgₓO₁₋ₓF solids.

2. Experimental procedures

Magnesium ion doped LaOF, La₁₋ₓMgₓO₁₋ₓF, solids were synthesized by a solid-state reaction method. A stoichiometric amount of La₂O₃ (Shin-Etsu Chemical, 99.99%), LaF₃ (Kojundo Chemical Laboratory, 99.9%), and Mg(NO₃)₂·6H₂O (Wako Pure Chemical Industry, 99.5%), i.e. La₂O₃:LaF₃:Mg(NO₃)₂·6H₂O = (1/3–1/2v): 1/3x, were mixed by an agate mortar and calcined at 800°C for 12 h in synthetic air. The obtained powders were pelletized and sintered at the same condition.

The samples prepared were identified by X-ray powder diffraction (XRD; SmartLab, Rigaku) with Cu-Kα radiation (40 kV, 40 mA) by a step scanning method in the 2θ range between 10 and 70° with step width of 0.04°. The lattice volume of the sample was estimated from the
XRD peak angles with α-Al₂O₃ as an internal standard material.

AC conductivity for the sintered sample with Pt sputtered thin film deposited on both surfaces by means of ion coater (IB-3, Eiko) was measured by complex impedance method in the frequency range from 1 Hz to 13 MHz (1260 Impedance/Gain-Phase Analyzer, Solartron) at the temperatures between 300 and 800°C in atmospheric air.

3. Results and discussion

Figure 1 shows the XRD patterns of the La₁₋ₓMgₓO₁₋ₓF solids calcined at 800°C for 12 h in air. While the samples with x ≤ 0.2 held the single phase of α-LaOF type structure, the samples with x ≥ 0.25 were the two-phase mixture of α-LaOF type solid and MgO. Figure 2 depicts the composition dependence of lattice volume of the α-LaOF type structure for the La₁₋ₓMgₓO₁₋ₓF solids, which was estimated from the XRD peak angles in Fig. 1. For the samples with x ≤ 0.2, the lattice volume decreased with increasing Mg²⁺ ion content (x), suggesting the partial substitution of smaller Mg²⁺ ion [0.130 nm (CN = 8)] for the La³⁺ ion [0.103 nm (CN = 8)] at the La site in the α-LaOF type structure, according to the following reaction:

\[
\frac{1}{3} \text{LaF}_3 + \frac{2 - 3x}{6} \text{La}_2\text{O}_3 + x\text{Mg(NO}_3)_2 \\
\rightarrow \text{La}_{1-x}\text{Mg}_x\text{O}_{1-x}F + 2x\text{NO}_2 + \frac{1}{2}xO_2
\]

From this result, it is regarded that the solids with x ≤ 0.2 are the solid solution. On the other hand, the lattice volume of α-LaOF type structure for the samples with x ≥ 0.25 were larger than that for the mother solid of LaOF, which is unusual tendency expected to the cation-doped crystalline solids; in general, with increasing the doping amount of cation into the solid, the lattice volume linearly changes according to the Vegard’s law and maintain the constant value for the composition exceeded the solid solubility limit. In the case for the present solids, La₁₋ₓMgₓO₁₋ₓF, which were synthesized with controlling the composition by mixing La₂O₃, LaF₃, and Mg(NO₃)₂·6H₂O not for forming the F⁻ vacancy in the solid, high concentration of Mg²⁺ doping causes lattice shrink which cannot hold the single phase of α-LaOF type structure. As a result, the secondary phase of MgO were formed for the samples with x > 0.2, and excess amount of F⁻ over that for the sample with x = 0.2 might be inserted into the interstitial sites of α-LaOF type structure, as the following reaction, which causes the lattice expansion.

\[
\frac{1}{3} \text{LaF}_3 + \frac{2 - 3x}{6} \text{La}_2\text{O}_3 + x\text{Mg(NO}_3)_2 \\
\rightarrow 5x \text{MgO} + 2x\text{NO}_2 + xO_2
\]

The value of n [≡ (5x – 1)/(5 – 3x)] in this formula is the excess amount of F⁻ ion. From these results, it was found that the solid solubility limit composition for the La₁₋ₓMgₓO₁₋ₓF solids was x = 0.2. The existence of phase transition for the La₁₋ₓMgₓO₁₋ₓF solids obtained as the single-phase sample (x ≤ 0.2) was confirmed by thermo gravimetry-differential thermal analyzer (TG–DTA) measurement and in-situ XRD measurement performed at temperatures between 300 and 800°C. While the samples with x ≤ 0.1 were clarified to show the phase transition from α-LaOF (over 500°C) to β-LaOF (below 500°C) by both the TG–DTA and in-situ XRD measurements, the samples with x ≥ 0.15 stably held the α-LaOF type structure without phase transition at temperatures up to 800°C.

Figure 3 displays the temperature dependence of the AC conductivity for the La₁₋ₓMgₓO₁₋ₓF solids with the corresponding data for α- and β-LaOF solids reported in the literature.¹⁰ For the solids (x ≤ 0.1) showing phase transition, a discontinuous temperature dependence in conductivity was clearly observed around 500°C. In contrast, the conductivities for the solids with x ≥ 0.15 linearly changed without showing any discontinuity around 500°C. This result also suggests that the solids with x ≤ 0.1 showed the phase transition around 500°C. Among the samples having single phase of α-LaOF type structure, the La₀.₈Mg₀.₂O₁₋xF (x = 0.2) solids showed the highest con-

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ductivity of $6.9 \times 10^{-3}$ S·cm$^{-1}$ which is ca. 46.5 times higher than that for $\alpha$-LaOF at 800 °C.

4. Conclusion

In conclusion, we have prepared the Mg ion-doped LaOF, $\text{La}_{1-x}\text{Mg}_x\text{O}_{1.5}\text{F}$, for improving the F$^-$ ion conductivity with controlling the crystal structure. With increasing the Mg$^{2+}$ doping amount into the La$^{3+}$ site in LaOF, the phase transition from $\alpha$- to $\beta$-form were gradually suppressed and the stable $\alpha$-LaOF type solid without showing any phase transition was successfully obtained for the solids with $x \geq 0.15$. Among the samples prepared, the $\text{La}_{0.8}\text{Mg}_{0.2}\text{O}_{1.5}\text{F}$ solid having solid solubility limit composition showed the highest F$^-$ ion conductivity which was ca. 46.5 times higher than that for the non-doped $\alpha$-LaOF.

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Fig. 3. Temperature dependence of the ionic conductivity for the $\text{La}_{1-x}\text{Mg}_x\text{O}_{1.5}\text{F}$ ($0 \leq x \leq 0.2$) solids with the corresponding data for the previously reported $\alpha$- and $\beta$-LaOF solids.\(^{10}\)