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Fig. 1 Schematic illustration of the apparatus.

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Table 1Schematic illustration of the apparatus.

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Table 2Schematic illustration of the

Table

References

[1] M. Takashima and G. Kano, Solid State Ionics 23 (1987), p. 99.

[2] M. Takashima, S. Yonezawa, K. Horita, K. Ohwaki and H. Takahashi, J. Mater. Chem. 6 (1996), p. 795.

Fluoride Compounds Containing Rare Earth Elements as Functional Materials

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Because of the similar ionic size of fluoride and oxide ion, fluoride ion can substitute or incorporate for oxide ion or vacant site in the metal oxides. Therefore, the bond character and the coordination in the crystal structure must be controlled by introducing of F^- into the metal oxides with partially covalent M-O bond. From this concept, the binary rare-earth oxide fluorides, Ln₂Ln²O₃F₆ in which Ln and Ln' are different rare earths, have been investigated as oxide ionconducting solid electrolytes with much higher conductivity than that of stabilized zirconia ¹⁻⁴. Here, Ln₂Eu₂O₃F₆ were synthesized by the solid-state reaction between 1 mol Ln₂O₃ (Ln: La, Nd) and 2 mol EuF₃ at 1000–1200 °C in a highly dry atmosphere. Nd₂Eu₂O₃F₆ exhibits the oxide ion conductivity of 2.0 S m⁻¹ at 500 °C under $P_{O2} = 0.4$ Pa, and the transport numbers τO^{2-} was 0.9 at a temperature ranging from 500 to 700 °C. X-ray diffraction Rietveld analysis revealed Nd₂Eu₂O₃F₆ was the monoclinic lattice (Fig.1) with the crystal parameters $a_0 = 0.396$ nm, $b_0 = 1.13$ nm, $c_0 = 0.562$ nm, $b = 134.8^\circ$, Z = 1. The structures of Nd_{2.1}Eu_{1.9}O₃F₆ and La₂Eu₂O₃F₆ were also analyzed as the monoclinic structure ($a_0 = 0.397 \text{ nm}$, $b_0 = 1.13 \text{ nm}$, $c_0 = 0.561 \text{ nm}$, $\beta = 135.0^\circ$, Z = 1for Nd_{2.1}Eu_{1.9}O₃F₆ and $a_0 = 0.404$ nm, $b_0 = 1.14$ nm, $c_0 = 0.574$ nm, $\beta = 135.3^\circ$, Z = 1 for La₂Eu₂O₃F₆). The ionic arrangement was suggested to be not a little disordered in the crystal lattice of Nd_{2,1}Eu_{1,9}O₃F₆ and La₂Eu₂O₃F₆ in contrast to that in the Nd₂Eu₂O₃F₆. The disorder of anionic

arrangement in $Nd_{2.1}Eu_{1.9}O_3F_6$ and $La_2Eu_2O_3F_6$ lattice was assumed to result in the lower oxide ion conductivity $Nd_{2.1}Eu_{1.9}O_3F_6$ ($\sigma = 1.0$ S m⁻¹, $\tau O^{2-} = 0.9$) and $La_2Eu_2O_3F_6$ ($\sigma = 0.8$ S m⁻¹, $\tau O^{2-} = 0.7$).

On the way to prepare the binary rare earth oxide fluorides mentioned above, some glasses have been obtained. The obtained glass was a new oxide fluoride glass containing a large amount of rare earth element. Several reports have described preparation of glasses containing rare earth elements for use as optical or magneto-optical materials ⁵⁻⁸. Every rare earth element has unique optical properties because of its arrangement of electrons in the 4f orbital. It is very interesting to study the preparation processes and characteristics of these glasses to develop new functional materials. Figure 2 shows fluorescence spectra of 20TbF₃- $20BaF_2-10AlF_3-50GeO_2/mol\%+x/wt\%$ SmF₃



Fig.1 Unit lattice of Nd₂Eu₂O₃F₆.

Example

glasses (x=0.01-1.00). The intensity of fluorescence was measured about Sm-only doped glass and Tb–Sm co-doped glass where x=0.05. The intensities of fluorescence at 600 nm of Sm-only glass and Tb–Sm co-doped glass, were 6.7×10^1 and 8.5×10^3 cps, respectively. From the results, the emission originated from Sm³⁺ was enhanced by the presence of Tb³⁺ about 130 times.



Fig.2 Fluorescence spectra of $20\text{TbF}_3-20\text{BaF}_2-10\text{AlF}_3-50\text{GeO}_2/\text{mol}\%+x/\text{wt}\%$ SmF₃ glasses, (a) x=0.01, (b) x=0.08, (c) x=0.1, (d) x=0.5, (e) x=1.0. (f) and (g) respectively show the fluorescence spectra of $20\text{TbF}_3-20\text{BaF}_2-10\text{AlF}_3-50\text{GeO}_2$ and $20\text{BaF}_2-20\text{AlF}_3-60\text{GeO}_2+0.05/\text{wt}\%$ SmF₃ glasses.

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