Ionic Conductivity of $Ln_{1-x}Ae_xF_{3-x}$ (Ln=Tb, Dy, Ho, and Ae=Ca, Sr) Tysonite-type Fluoride for Ion Conductive Solid-state Electrolyte

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[Introduction] All-solid-state fluoride batteries are highly expected as a next-generation rechargeable battery that can replace Li-ion batteries. Fluorides used in all-solid-state fluoride batteries are more adequate in resources compared to Li, and since all components are solid, they have the advantages of high volumetric energy density and safety. The electrolyte of All-solid-state fluoride batteries must have high ionic conductivity and a large potential window, which LaF_3 and CeF_3 tysonite-type fluorides are expected to be practical [1,2]. Rare earth metals like La and Ce are generally produced from minerals that include other rare earth metals, and it requires a lot of cost to purify. So it is important to achieve high-performance electrolytes using low-purity ingredients, which include other rare earth metals. In this study, we gave attention to the rare earth fluorides other than LaF_3 and CeF_3, such as TbF_3, DyF_3, and HoF_3. Those fluorides are known to transform to tysonite-type structure from β-YF_3-type structure corresponding to the addition of alkaline earth metal ions, but there are few reports on the ionic conductivity of these tysonite-type fluorides [3,4]. In this study, we fabricated $Ln_{1-x}Ae_xF_{3-x}$ (Ln=Tb, Dy, Ho, and Ae=Ca, Sr) tysonite-type fluorides and investigated the effect of alkaline earth metal ions addition on the ionic conductivity. [Experimental] $Tb_{0.8}Ca_{0.2}F_{2.8}$, $Dy_{0.77}Ca_{0.23}F_{2.77}$, $Ho_{0.77}Ca_{0.23}F_{2.77}$, $Tb_{0.76}Sr_{0.24}F_{2.76}$, $Dy_{0.76}Sr_{0.24}F_{2.76}$, and $Ho_{0.76}Sr_{0.24}F_{2.76}$, which are congruent compositions, were prepared from TbF_3, DyF_3, HoF_3, CaF_2, and SrF_2 raw materials. Ingredients were installed in a graphite crucible and melted by induction heating, then it was cooled down for 12 hours. Each phase of the samples was identified using powder XRD analysis. The ionic conductivity was measured by the electrochemical impedance method. [Results] The samples were all transparent single crystals, and XRD analysis showed that all samples were a tysonite-type structure. $Tb_{0.8}Ca_{0.2}F_{2.8}$, $Dy_{0.77}Ca_{0.23}F_{2.77}$, $Ho_{0.77}Ca_{0.23}F_{2.77}$, $Tb_{0.76}Sr_{0.24}F_{2.76}$, $Dy_{0.76}Sr_{0.24}F_{2.76}$, and $Ho_{0.76}Sr_{0.24}F_{2.76}$ had ionic conductivity of 1.69×10^{-6}, 1.16×10^{-6}, 1.56×10^{-6}, 1.16×10^{-6}, 7.22×10^{-7}, and 1.13×10^{-6} S/cm at room temperature, respectively. As a comparison, 1.7% Tb-doped TbF_3, which is a β-YF_3-type fluoride, was also tested; however, the ionic conductivity was so bad that we were not able to measure it properly, which explains the transition to the tysonite-type structure contributed to the improvement in ionic conductivity.

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