

PREPARATION OF $Ba_{1-x}Ln_xFeO_{3-\delta}$ and $BaFe_{1-x}Ln_xO_{3-\delta}$ (Ln : TRIVALENT ION) WITH CUBIC PEROVSKITE STRUCTURE AND RANDOM DISTRIBUTION OF OXIDE ION VACANCY

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Oxides with perovskite structure and random arrangement of oxide ion, such as $Ba_{0.5}Sr_{0.5}Fe_{0.2}Co_{0.8}O_{3-\delta}$, attract much interest as oxygen permeation material. For wide spread of oxygen permeation devices, development of new material without Co is highly desired because of high cost of Co. Recently, we reported that arrangement of oxide ion vacancy in monoclinic $BaFeO_{2.5-\delta}$ changes from ordered to random by partial La^{3+} substitution for Ba^{2+} site, resulting in cubic perovskite structure and improvement of electrical conductivity [1, 2]. Fujishiro reported preparation of $BaFe_{1-x}Ln_xO_{3-\delta}$ with cubic perovskite structure and enhancement of electrical conductivity with In substitution [3]. It is expected that material with higher property may be developed by substitution of other trivalent ion, such as lanthanoid or Y, for Ba- or Fe- site in $BaFeO_{2.5-\delta}$. In this work, preparation of various $Ba_{1-x}Ln_xFeO_{3-\delta}$ and $BaFe_{1-x}Ln_xO_{3-\delta}$ (Ln : trivalent ion) was examined and factors determining substitution site and crystal structure were investigated.

The samples of $Ba_{1-x}Ln_xFeO_{3-\delta}$ and $BaFe_{1-x}Ln_xO_{3-\delta}$ were prepared with Pechini method. Each solution of Ba^{2+} , Ln^{3+} and Fe^{3+} was mixed with nominal cation composition. After addition of citric acid and ethylene glycol, the solution was heated at about 450 °C, resulting in precursor. The precursor was calcined at 700 °C for 24 h in air, followed by 1300 °C for 10 h in air twice. The crystal structure and lattice constants of the specimens were investigated with X-ray diffraction. The chemical state of Fe and oxygen content of the specimens were evaluated with iodometric titration.

Single phase of $Ba_{1-x}La_xFeO_{3-\delta}$ and $Ba_{1-x}Nd_xFeO_{3-\delta}$ with cubic perovskite structure was obtained for $0.1 \leq x \leq 0.6$ and $0.1 \leq x \leq 0.5$, respectively. Cubic perovskite $Ba_{1-x}Ln_xFeO_{3-\delta}$ was also obtained for $Ln=Sm, Eu$ and Gd despite that $BaFe_2O_4$ was observed as second phase and that compositional range where the cubic perovskite phase was obtained decreased with decreasing ionic radius of Ln . It was revealed that the cubic perovskite phase was obtained where tolerance factor was more than 0.98. For Ln with smaller ionic radius such as Y, Ho, Yb , $Ba_{1-x}Ln_xFeO_{3-\delta}$ with cubic perovskite structure was never prepared.

For $Ln=Nd, Sm, Gd, Ho, Yb$ and Y , single phase of $BaFe_{1-x}Ln_xO_{3-\delta}$ with cubic perovskite structure was successfully prepared although compositional range of x was narrow such as $0.075 \leq x \leq 0.1 \sim 0.2$. The x range where single cubic perovskite phase was obtained spread with decreasing ionic radius. The generation of $BaFe_2O_4$ in $Ba_{1-x}Ln_xFeO_{3-\delta}$ with $Ln=Sm, Eu$ and Gd was attributed to compositional deviation due to partial Fe-site substitution of Sm, Eu and Gd .

Figure 1 shows difference of ionic radius of 12-coordinated Ln^{3+} and Ba^{2+} . Difference of ionic radius of 6-coordinated Ln^{3+} and Fe^{3+} are also shown in Fig. 1. The smaller difference of ionic radius of La^{3+} and Ba^{2+} than that of La^{3+} and Fe^{3+} is suggested to be an origin of substitution of La for Ba site instead of Fe -site. For Ho, Y and Yb , no substitution for Ba -site but Fe -site is ascribed to smaller difference of ionic radius of Ln^{3+} and Fe^{3+} . For Nd, Sm and Gd , the difference between Ln^{3+} and Ba^{2+} and Ln^{3+} and Fe^{3+} was similar, resulting in capability of substitution for both Ba - and Fe - site.

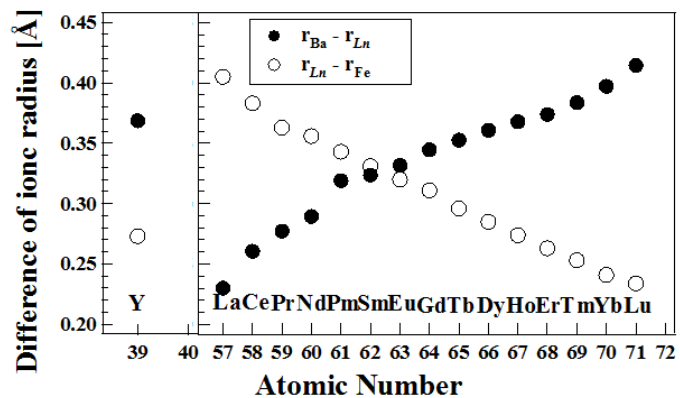


Figure 1 – Difference of ionic radius of 12-coordinated Ln^{3+} and Ba^{2+} and 6-coordinated Ln^{3+} and Fe^{3+} .

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