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Crystal chemistry of new brownmillerite-type compounds

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In the $Ba_2(M,M')_2O_5$ (M=Al, Ga, Sc, M'=Lu, Yb, Tm, Er, Y) systems, some new brownmillerite-type compounds were successfully synthesized when M=Sc, M'=Lu, Yb, Tm and Er. It was found that the larger ion strongly influences the lattice size of the new compounds and the compounds having the larger unit cell free volume can uptake the larger amount of H_2O.
Key words: brownmillerite structure, unit cell free volume, absorption of H_2O, electrical conductivity

1. INTRODUCTION

The perovskite-type oxides which exhibit high ionic conduction were attracted for solid electrolyte materials. Particularly, the electrolytes which have high oxide-ion conductivity are needed in the application of the solid oxide fuel cells (SOFCs). Recently, it has been reported that $Ba_2In_2O_5$ which exhibits a phase transition around 1173 K due to disordering of the oxide ion in the defect perovskite-type structure is attracted for the ionic conductor of the next generation. [1]

Kakinuma et al. [2] have reported that $(Ba_{0.3}Sr_{0.2}La_{0.5})InO_{2.75}$, which was derived from $Ba_2In_2O_5$ having a brownmillerite structure, exhibits higher oxide-ion conductivity than that of yttria-stabilized zirconia (8YSZ). Moreover, the conductivity decreased when $(Ba_{0.3}Sr_{0.2}La_{0.5})InO_{2.75}$ was doped with Sc or Yb in the In site.

In present study, we tried to synthesize new brownmillerite compound by combination of two kinds of three valent elements, of which the average ionic radius agrees with In^{3+} in $Ba_2In_2O_5$. The results obtained were discussed from the view point of ionic radius and unit cell free volume in the relation with $Ba_2In_2O_5$.

2. EXPERIMENTAL

Powder sample of $Ba_2In_2O_5$ and $Ba_2(M,M')_2O_5$ system were synthesized by a solid-state reaction, using $BaCO_3$ (99.9%, Wako Pure Chemical Industries) Al_2O_3 (99.9%), Ga_2O_3 (99.9%), Sc_2O_3 (99.99%), In_2O_3 (99.99%), Lu_2O_3 (99.9%), Yb_2O_3 (99.9%), Tm_2O_3 (99.9%), Er_2O_3 (99.9%) and Y_2O_3 (99.9%, Kojund Chemical Lab.) as starting materials.

Weighed powders were wet ball-milled for 24 h using a milling pot made of synthetic resin and resin-coated balls, and ethanol as a dispersion reagent. The dried powder mixtures were calcined at 1273 K for 10 h in air. After sieving with a mesh size of 53 μm, the powder samples were uniaxially molded at 5 MPa and then subjected to rubber pressing at 200 MPa. Compacts thus obtained were sintered at 1573 K for 10 h in air.

The powder samples were characterized by X-ray diffraction (XRD) analysis (model : MultiFlex, Rigaku) with monochromated CuKα radiation. The lattice constant was determined from XRD peaks by least-squares method and the unit cell free volumes were calculated. The unit cell free volume, which means a "free space" in the crystal structure, was estimated using the lattice constant and the component ionic radii.

Moreover, the thermal properties of the samples were measured by TG-DTA method (model : TG8192, Rigaku) and TG-MS method (model : M-200QA) with the program (model : Quand Vision ver.3, Anerupa).

3. RSULT&DISCUSSION

XRD experiments confirmed that $Ba_2(M,M')_2O_5$ were single phases of the orthorhombic brownmillerite structure when M=Sc, M'=Lu, Yb, Tm and Er. Figure 1 typically shows XRD pattern of $Ba_2(Sc,Lu)_2O_5$, where most of the peaks could be indexed according to the orthorhombic lattice, but a few unknown peaks is remained. Table 1 lists the lattice constants of $Ba_2In_2O_5$ and $Ba_2(M,M')_2O_5$, which were abtained as single phase. Although the average ionic radii of the all samples were fixed to be 0.08 nm by the appropricate combination of M and M', the single phase was obtained only when the

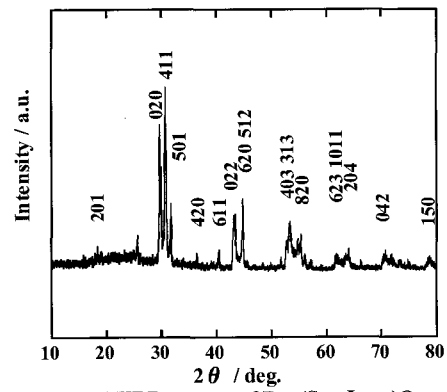

Fig.1 XRD pattern of $Ba_2(Sc_{1.1}Lu_{0.9})O_5$.

Table1 Lattice constant of $Ba_2In_2O_5$ and $Ba_2(M,M')_2O_5$ system

B site	a(nm)	b(nm)	c(nm)	V(nm^3)
In	1.672	0.610	0.596	7.588
Sc-Lu	1.615	0.608	0.571	7.012
Sc-Yb	1.628	0.607	0.572	7.073
Sc-Tm	1.603	0.618	0.585	7.239
Sc-Er	1.705	0.593	0.605	7.642

composition ratio of M and M' is nearly 1:1. Therefore, it can be speculated that the small M ions may occupy the tetrahedral site and the large M' ions the octahedral one in the brownmillerite structure, where the tetrahedral and the octahedral sites are alternatively arranged. Whether the new compounds can be successfully synthesized may be closely related to the ionic radius ratio. However, the unit cell volumes of the new compounds increased with increasing M' ion radius, although the average ionic radius was fixed, as shown in Fig.2. These results suggest that the cell size is not decided by the average ionic radius, but did by the larger ion in the B site. The temperature dependence of crystal structure of the new compounds was investigated using high temperature XRD, because $Ba_2In_2O_5$ exhibited phase transition at high temperature region. These new brownmillerite samples exhibited the phase transition from orthorhombic brownmillerite structure to orthorhombic perovskite one. The transition temperature has a tendency to increase with increasing the M' ion radius.

The new brownmillerite phases showed large weight loss in the TG-DTA experiments. As shown in Fig.3, most of weight loss was due to the desorption of H_2O and the remainder was due to that of CO_2 by TG-MS analysis. The desorption amount of CO_2 was almost constant independent on the unit cell free volume, while the H_2O content increased with increasing the free volume. Figure 4 shows H_2O in mole per chemical formula as a function of unit cell free volume.

It has been reported that the oxide-ion conductivity of $Ba_2In_2O_5$ remarkably increase at the phase transition temperature. However, the present samples failed to measure the electric conductivity, because their relative

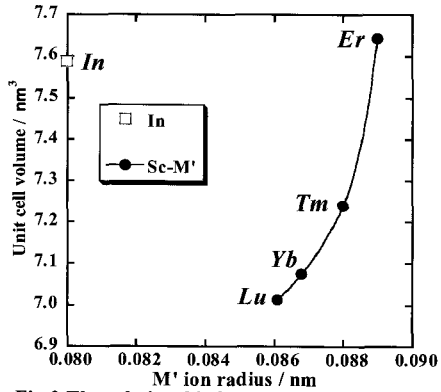

Fig.2 The relationship between unit cell volume and M' ion radius.

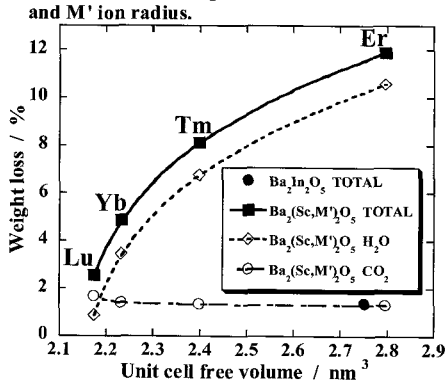

Fig.3 The relationship between unit cell free volume and weight loss up to 1473K.

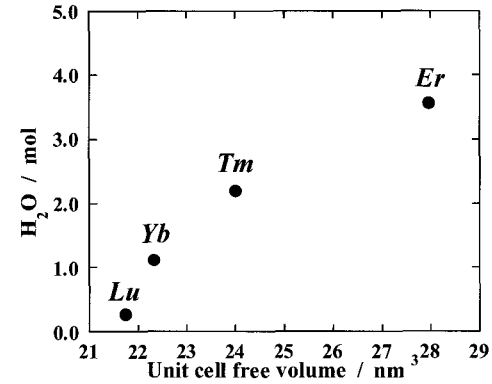

Fig.4 The relationship between unit cell free volume and x in $Ba_2(Sc,M')_2O_5 \cdot xH_2O$.

density was too low to obtain the bulk conductivity. Then, in order to increase the relative density, $Ba_2In_{2-x}(Sc_{1.1}Lu_{0.9})_xO_{5.5}$ system was newly prepared. The sample with x=0.2 exhibited a single phase of perovskite-type structure with orthorhonmib symmetry. Figure 5 represents Arrhenius plots of the conductivity of $Ba_2In_{1.8}(Sc_{1.1}Lu_{0.9})_{0.2}O_5$ in addition to 8YSZ and $Ba_2In_2O_5$. The conductivity at x=0.2 in the low temperature region exhibited higher than that of 8YSZ, which is widely used as an electrolyte of SOFC. (Fig.5) These results are expected to contribute for low temperature operation of SOFC.

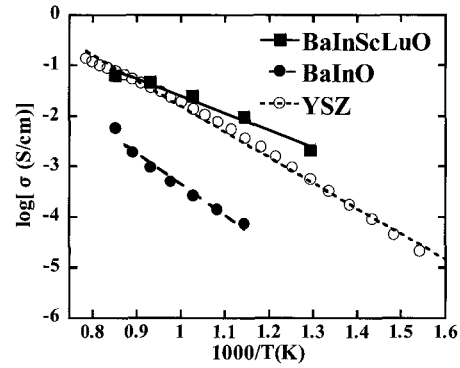

Fig.5 Arrhenius plots of $Ba_2In_{1.8}(Sc_{1.1}Lu_{0.9})_{0.2}O_5$, $Ba_2In_2O_5$ and 8YSZ.

4. CONCLUSION

(1) New orthorhombic brownmillerite-type compounds were successfully synthesized when M=Sc, M'=Lu, Yb, Tm and Er and these samples transformed to the orthorhombic perovskite-type structure at high temperature.

(2) The unit cell free volume of new compounds were influenced by the larger ions among the small (M) and large (M') ions in the B site, and the H_2O amount in the crystal increased with increasing the unit cell free volume.

(3) $Ba_2In_{2-x}(Sc_{1.1}Lu_{0.9})_xO_{5.5}$ system showed orthorhomibic perovskite structure at x=0.2, and it exhibited higher conductivity than that of yttria-stabilized zirconia in the low temperature region.

Acknowledgment

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References
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