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Melt synthesis and characterization of complexed oxide perovskites containing rare earths

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Abstract

In order to synthesize various perovskite ABO_3 type compounds and their solid solutions, we have applied a novel “melt synthesis technique” rather than conventional solid-state reaction techniques. In the melt synthesis, the mixture of oxides or their precursors is melted in a short period of time (1–60 s) by a strong light radiation in an arc-imaging furnace. A spherical molten sample where multiple cations were mixed homogeneously was directly solidified on a copper hearth with a rapid cooling of 10^2 K/s. $LaAlO_3$, $GdScO_3$, $ATiO_3$ ($A = Ba$, Sr and Ca) and the solid solutions among them were synthesized in this technique.

Keywords: Perovskite; Synthesis; Solidification; Complex perovskites; Melt synthesis; $GdScO_3$; $BaTiO_3$; $LaAlO_3$

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1. Introduction

Perovskite ABO_3 type compounds have been investigated in wide area of fields like ferroelectrics, magnetics, optics, phosphors, electronics, ionics, superconductors, sensors, catalysts, etc., because they have various but unique properties due to their compositions and structures which are characterized by the various combinations of A and B cations. In order to form the perovskite and/or related structures, A and B ions should have following conditions [1,2]:

(1) A-ion is sufficiently larger than B-ion in size.
(2) The sum of the valences of A-ion and B-ion must be six.
(3) The valence of B-ion is larger than that of A-ion.

Under these conditions, a lot of compounds with the formula of $A^{3+}B^{3+}O_3$, $A^{2+}B^{4+}O_3$, $A^{+}B^{5+}O_3$, even $B^{6+}O_3$ and their solid solutions can be included, that is, “complex perovskites” where multiple A cations and B cations are involved in the lattice. The synthesis of such complex perovskites is not easy by conventional solid-state reaction techniques because the reaction rates among oxides are so slow by solid-state diffusion as to form homogeneous compounds or solid solutions.

Fig. 1 is a schematic comparison of formation mechanism of an intermediate compound by solid-state reaction and liquid-state reaction. As seen in this figure, melt reactions are very fast and homogeneous due to liquid mixing and fast diffusion in the liquid phase in contrasting to conventional solid-state reactions. These melt synthesis techniques are, therefore, suitable for synthesizing multi-components compounds and solid solutions where homogenous cation mixing is essentially required.

The melt synthesis is a high temperature approach for the synthesis which is rather opposite from solid-state syntheses where a low temperature approach to the synthetic temperature. However, the melt synthesis has not widely been studied yet probably because it is not easy to make such a high temperature and to get a non-reactive container to the molten oxides at such a high temperature of 1500–2000 °C. We have succeeded to synthesize series of perovskite-type phases in the systems of $GdScO_3$–$BaTiO_3$, –$SrTiO_3$, –$CaTiO_3$,

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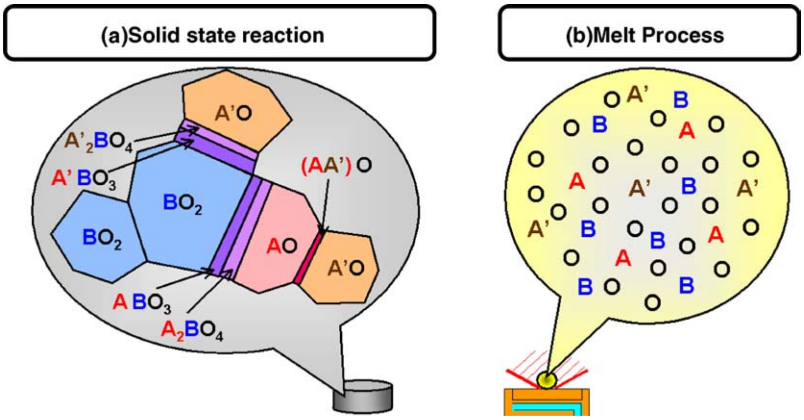

Fig. 1. Comparison of formation mechanism of an intermediate compound (AA′)BO$_3$ in the system AO–A′O–BO$_2$ by (a) solid-state reaction and (b) melt process.

LaAlO$_3$–BaTiO$_3$, –SrTiO$_3$, –CaTiO$_3$, etc., which are the solid solutions in the systems of A^{2+}B^{4+}O$_3$–A^{3+}B^{3+}O$_3$. Their lattice parameters and lattice distortions could be evaluated in the values of sizes and valences in A and B ions. Structural transformations in ABO$_3$ have also been studied as function of temperatures and in relation to kinds of A and B ions. Some of them may have metastable states because of quenching from high temperatures in the melt synthesis. Therefore, we have expected to synthesize metastable perovskite phases.

Combining advantages of melt synthesis and arc-imaging furnace, we studied to prepare perovskite solid solutions rapidly.

2. Experimental

2.1. Arc-imaging furnace

This furnace is designed to heat small-size samples upto very high temperature like above 2000 °C to melt in clean conditions. As shown in the Fig. 2, the light emitted from a 10 KW Xenon Lamp are collected by an ellipsoidal mirror (collector), reflected by a plane mirror and then emitted by another ellipsoidal mirror (Emitter) to the sample. A molded sample with 3–8 mm size of mixed powders was put on a water-cooled Cu hearth. The sample can be heated in various atmospheres in a very short period of time like a few seconds and also cooled down by breaking the light radiation by a shutter or quick removing the sample stage from the focus of the emitter mirror. The brightness temperature can be monitored by a pyrometer. To calibrate this pyrometry system, the solidification temperatures of refractory oxides have been measured as Al$_2$O$_3$ (2054 ± 4 °C), Y$_2$O$_3$ (2433 ± 3 °C), HfO$_2$ (2803 ± 3 °C), and CaO (2899 ± 3 °C) [3,4] Details of the furnace and the pyrometry have been reported previous papers [2–4]. When a sample is melted, it becomes a small molten globule generally with 1–5 mm in size by its surface tension, thus it gives almost point-contract to the Cu hearth, which make minimize the heat loss by the hearth. When the bottom of the sample where unmolten, the sample can be remelted after its turn over.

2.2. Sample preparation

Starting materials were high-purity oxides (TiO$_2$ (99.99%, Kojundo Chemical Laboratory Co. Ltd.), SrCO$_3$ (99.9%,

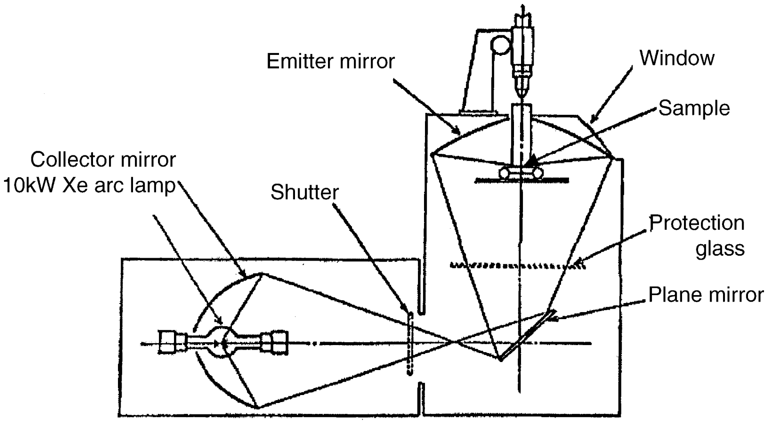

Fig. 2. Optical system of the arc-imaging furnace. The light source is Xenon arc lamp. The light is reflected a collection mirror, plane mirror and emission mirror to heat a sample on a sample stage.

Kojundo Chemical Laboratory Co. Ltd.), $BaCO_3$ (99.95%, Kojundo Chemical Laboratory Co. Ltd.), $CaCO_3$ (99.5%, Kanto Kagaku), Al_2O_3 (99.99%, AKP-30, Sumitomo Chemical Co. Ltd), Gd_2O_3 (99.99%, Shin-Etsu Chemical Co. Ltd.), La_2O_3 (99.99%, Shin-Etsu Chemical Co. Ltd.), and Sc_2O_3 (Mitsubishi Metal Coporation)) powders. They were mixed by dry and wet mixing in a high-purity alumina mortar. The mixed powder or their molded samples were placed on a copper hearth and melted in vacuum using the arc-imaging furnace. It took generally 5–15 s from a molten state at around 2000 °C to a solid-state with dark color at around 600 °C. The cooling rate was, therefore, estimated to be more than 100 K/s.

All the samples were characterized by X-ray diffraction. Powder X-ray diffraction patterns were obtained from arc-melted samples after grinding using an alumina mortar, with Cu Kα radiation in a curved graphite-beam monochrometer (MXP3VA, MAC Science, Tokyo, Japan).

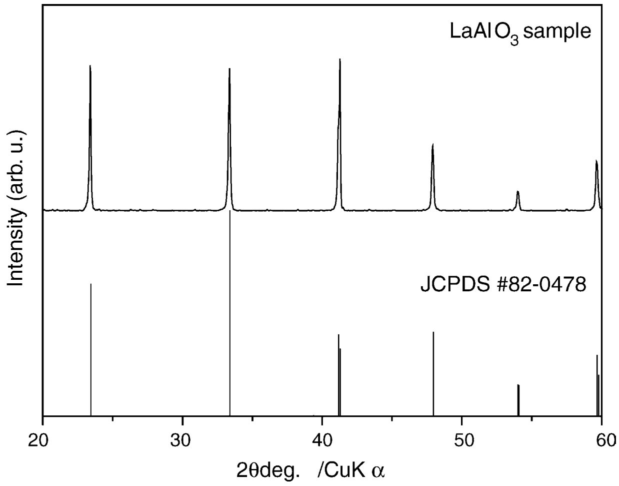

Fig. 3. XRD pattern of the melt synthesized $LaAlO_3$ sample. Lattice parameters obtained: $a = 5.364$, $c = 13.129$ are in good agreement with the reference data (JCPDS #82-0478: $a = 5.364$, $c = 13.11$).

3. Results and discussion

$LaAlO_3$, $GdScO_3$, $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ could be synthesized by the melt method in short periods of time like 5–60 s in a single step from the mixed powders. $GdScO_3$ and $CaTiO_3$ was orthorhombic-perovskites, $LaAlO_3$ was a rhombohedral-perovskite, $BaTiO_3$ was a hexagonal-perovskite and $SrTiO_3$ was a cubic-perovskite. As shown in Fig. 3, a pure $LaAlO_3$ sample could be synthesized by this method in a short period of total 15 s, 5 s × 3 times. It is noticeable merit of the melt synthesis because solid-state synthesis would generally take multi steps: molding to a pellet, heating at high temperatures and grinding, repeatedly. For example, pure sample of $LaAlO_3$ [5] could be synthesized by heating at 1700 °C for 2 h after several intermediate grindings and moldings the calcined sample at 1500 °C. The melt synthesis might prevent the contamination from grinding media and containers during grindings. We have also succeeded to synthesize in a single step multiple series of perovskite type solid solutions for the systems among $LaAlO_3$, $GdScO_3$, $BaTiO_3$, $SrTiO_3$, and $CaTiO_3$.

Except for the $GdScO_3$–$LaAlO_3$ systems, all the samples were the single phases. Fig. 4 shows unit cell volumes

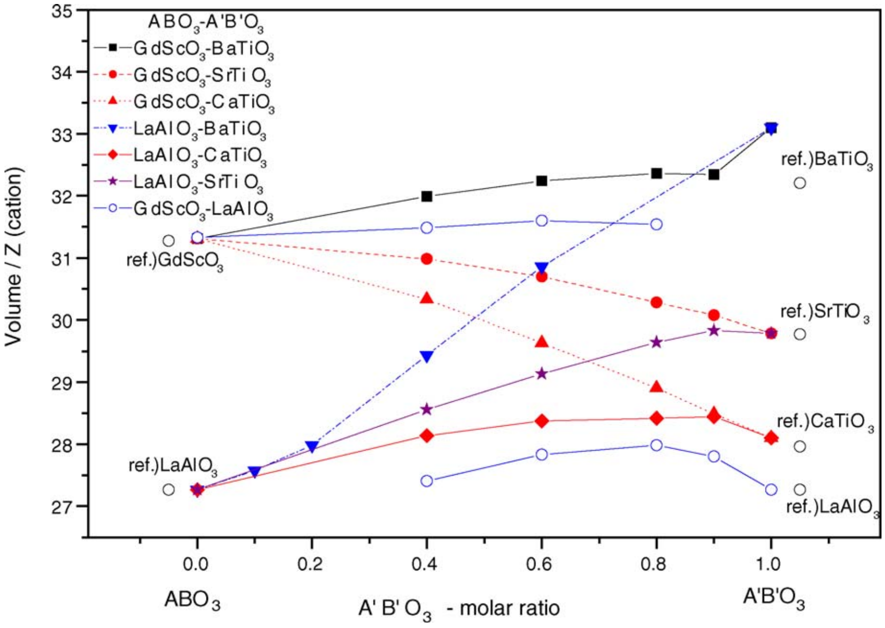

Fig. 4. Unit cell volume per cation of perovskite solid solution phase. $GdScO_3$: JCPDS #27-0220, $LaAlO_3$: JCPDS #82-0478, $BaTiO_3$: JCPDS #05-0626, $SrTiO_3$: JCPDS #35-034, $CaTiO_3$: JCPDS #42-0423.

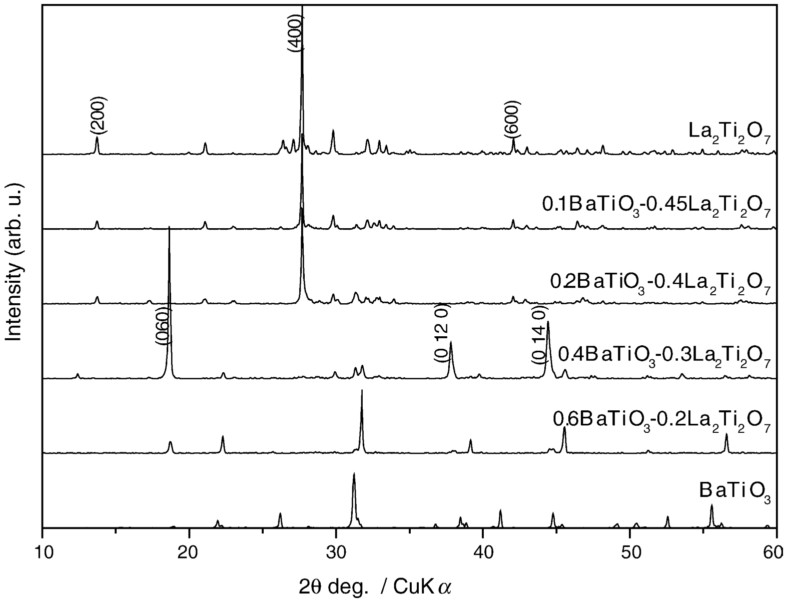

Fig. 5. XRD patterns of $BaTiO_3$–1/2$La_2Ti_2O_7$ system. 1/2$La_2Ti_2O_7$, 0.1$BaTiO_3$–0.45$La_2Ti_2O_7$, and 0.2$BaTiO_3$–0.4$La_2Ti_2O_7$ were Pyrochlore. 0.4$BaTiO_3$–0.3$La_2Ti_2O_7$ was $BaLa_2Ti_3O_{10}$ and 0.6$BaTiO_3$–0.2$La_2Ti_2O_7$ and $BaTiO_3$ was perovskite.

per cation of perovskite solid solution phases. Continuous volume changes suggest continuous solid solutions in spite of different crystal systems in perovskites, that is, $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$. On the other hand, in the system of $GdScO_3$–$LaAlO_3$, continuous solid solutions were not obtained even though $GdScO_3$ and $LaAlO_3$ belonged to the isovalent perovskites of $A^{3+}B^{3+}O_3$. The products were separated into two phases, $LaAlO_3$-rich trigonal and $GdScO_3$-rich orthorhombic phases. The reason is not clear in this moment, but one reason seems to be a large difference between the ionic radius of Sc^{3+} and Al^{3+}, i.e., ionic radius of Sc^{3+} and Al^{3+} is 0.745 and 0.535, respectively [6]. We have tried to expand the melt synthesis technique to study other system $BaTiO_3$–1/2$La_2Ti_2O_7$. ABO_3–perovskite and $A_2B_2O_7$–pyrochlore have similar in cationic composition, where the atomic ratio of A and B is 1:1. Fig. 5 shows X-ray diffraction patterns of the products in the $BaTiO_3$–1/2$La_2Ti_2O_7$ system. In this system, continuous solid solutions have not been formed, but four phases were found, that is, a pyrochlore phase in 1/2$La_2Ti_2O_7$, 0.1$BaTiO_3$–0.45$La_2Ti_2O_7$, and 0.2$BaTiO_3$–0.4$La_2Ti_2O_7$ samples, a tetragonal-perovskite

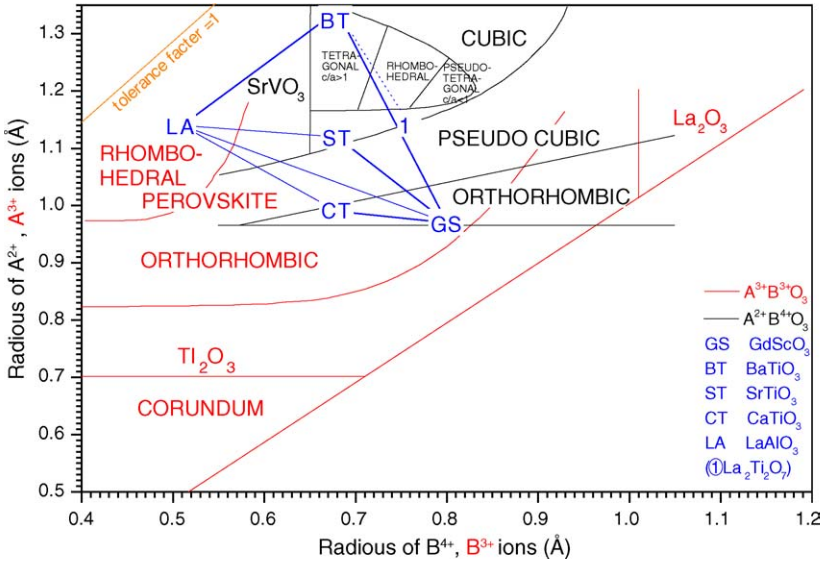

Fig. 6. Studied perovskite solid solutions in ABO_3–$A'B'O_3$ systems, superimposed in the formation diagrams of perovskite type compounds for $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$.

phases in $0.6BaTiO_3$–$0.2La_2Ti_2O_7$ and a hexagonal-$BaTiO_3$ samples, and an intermediate compound of $BaLa_2Ti_3O_{10}$ in the sample ($0.4BaTiO_3$–$0.3La_2Ti_2O_7$). Those Pyrochlore were ($k\,0\,0$)-orientated, $BaLa_2Ti_3O_{10}$ was ($0\,k\,0$)-orientated. The compound of $BaLa_2Ti_3O_{10}$ has been reported by Skapin et al. [7] in the system BaO–La_2O_3–TiO_2. The products formed, therefore, might be the mixture of the compound $BaLa_2Ti_3O_{10}$ and $BaTiO_3$ because of $La_{0.6}Ba_{0.4}Ti_{0.4+0.6}O_{1.2+2.1} = 0.4(BaLa_{1.5}Ti_{2.5}O_{3.3/4}) = 0.4\{0.75(BaLa_2Ti_3O_{10}) + 0.25BaTiO_3\}$. In fact, we can observe the diffraction peaks corresponding to $BaTiO_3$ in the XRD pattern for the sample with this composition. Those results seem to indicate that the melt synthesis is useful to study for the systems including multiple phases. The formation of continuous solid solution requires the similarity in crystal structures between two end members. The systems studied were plotted in Roth's perovskite formation map [8], for comparison as shown in Fig. 6. Although the studied systems pass across the many structural areas, the formation of complete solid solutions was confirmed for all systems except for $GdScO_3$–$LaAlO_3$ by the melt synthesis. These results suggest that the formation of continuous solid solutions probably could be enhanced by melting at a high temperature and rapid cooling during the melt synthesis methods. In addition, Roth's map may be applicable to predict new perovskite solid solutions by the melt synthesis.

4. Conclusion

From a scientific and engineering point of view, melt-solidification method is suitable for material researches in high temperature syntheses.

Various perovskite compounds and their solid solutions in the systems of ABO_3–$A'B'O_3$ perovskite were prepared by the rapid synthesis via melt-solidification methods using the arc-imaging furnace. On the other hand, the single phase of solid solutions were not formed in the system of ABO_3–$1/2A'_2B'_2O_7$. The intermediate compound $BaLa_2Ti_3O_{10}$ was formed in the system $BaTiO_3$–$1/2La_2Ti_2O_7$.

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