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Synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(In_{1/2}Nb_{1/2})O_3$ ceramics by b-site precursor method

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Abstract

$Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(In_{1/2}Nb_{1/2})O_3$ ceramics were synthesized by b-site precursor method which is widely used for making Pb-related complex perovskite materials. The intermediate phases formed during the heating process were analyzed, and the mechanism of the perovskite formation was discussed. The cubic pyrochlore phase ($Pb_3Nb_4O_{13}$) was formed at approximately 600 °C but had almost disappeared at temperature over 650 °C in the case of $3PbO–MgNb_2O_6$ mixture. In contrast, it was formed around 600 °C without the formation of the perovskite phase and remained even at temperature as high as 900 °C in the case of the $2PbO–InNbO_4$ mixture. These differences were attributed to the shorter bond length and the small electronegativity difference in the In–O bond in $InNbO_4$ than those of the Mg–O bond in $MgNb_2O_6$, which means that $InNbO_4$ has a relatively lower structural stability.

Keywords: D. Perovskite; $Pb(Mg_{1/3}Nb_{2/3})O_3$; $Pb(In_{1/2}Nb_{1/2})O_3$; Relaxor ferroelectric material; Columbite; Wolframite

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$, one of the most popular Pb-related relaxor ferroelectric materials, first reported by Smolensky in 1960, has been widely investigated due to its high dielectric constant and low sintering temperature [1,2]. Because the conventional mixed-oxide method has not succeeded in removing all the cubic pyrochlore ($Pb_3Nb_4O_{13}$), which degrades the dielectric properties, the reaction mechanism and the kinetics of the perovskite formation have attracted special interest from researchers, and many types of synthetic methods (repeated calcination, addition of excess PbO and/or MgO, control of the increasing temperature rate, sol–gel process, etc.) has been reported [3–6]. However, these methods have some disadvantages such as a difficulty in obtaining a stoichiometric composition, the high cost of raw materials, etc.

After it was reported that the formation of the cubic pyrochlore phase in $Pb(Mb_{1/3}Nb_{2/3})O_3$ is due to the low reactivity of MgO, Swartz and Shrout suggested the b-site precursor ($MgNb_2O_6$) method where the perovskite phase was successfully synthesized suppressing the cubic pyrochlore phase [7–9]. This method has two advantages: one is that MgO and Nb_2O_5 are well-dispersed in $MgNb_2O_6$, and the other is that the low decomposition rate of $MgNb_2O_6$ prevents the formation of the cubic pyrochlore phase [10]. The b-site precursor method is also successful in synthesizing other various complex perovskites such as $Pb(Mg_{1/3}Ta_{2/3})O_3$, $Pb(Ni_{1/3}Nb_{2/3})O_3$, $Pb(Sc_{1/2}Ta_{1/2})O_3$, etc. However, it was partially successful in synthesizing $Pb(In_{1/2}Nb_{1/2})O_3$ and unsuccessful in the $Pb(Zn_{1/3}Nb_{2/3})O_3$, $Pb(Cd_{1/2}Nb_{1/2})O_3$, and $Pb(Zn_{1/3}Ta_{2/3})O_3$ systems.

In order to obtain the pure perovskite phase of $Pb(In_{1/2}Nb_{1/2})O_3$, Park et al. suggested the two-step calcination method with the addition of 2 wt.% excess In_2O_3, and Alberta et al. reported that calcination under oxygen atmosphere with the addition of Li_2CO_3 and excess In_2O_3 enhanced the formation of the perovskite phase [11,12]. According to Cho et al. [13], Ba is the most effective substituent for Pb in perovskite formation. However, the reason why the pure $Pb(In_{1/2}Nb_{1/2})O_3$ cannot be obtained by the b-site precursor method is unclear.

This study was highlighted on the reason why pure $Pb(In_{1/2}Nb_{1/2})O_3$ was difficult to be obtained by b-site

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precursor method. The intermediate phases during the heating of $3PbO–MgNb_2O_6$ and $2PbO–InNbO_4$ were compared, and the differences in their reaction sequences were explained in view of the crystal structure and bond strength of the b-site precursors.

2. Experimental procedure

2.1. Synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(In_{1/2}Nb_{1/2})O_3$

PbO (99.9%, Aldrich, USA), MgO (99.99%, High Purity Chem. Co., Japan), Nb_2O_5 (99.9%, Aldrich) and In_2O_3 (99.9%, High Purity Chem. Co.) were used to synthesize $Pb(In_{1/2}Nb_{1/2})O_3$. The weight loss of In_2O_3 and MgO (0.4 and 2.2 wt.%, respectively, at 900 °C, which were measured by thermogravitational analysis) were taken into account when they were weighed. In order to prepare the $MgNb_2O_6$ and $InNbO_4$ precursors, the $MgO–Nb_2O_5$ and $In_2O_3–Nb_2O_5$ mixtures were ball-milled in ethyl alcohol for 24 h and heat treated at 1000 °C for 24 h. Subsequently, the mixture of PbO and the b-site precursor was ball-milled again, and reacted at various temperatures at a heating rate of 5 °C/min.

2.2. Measurements

The expansion/shrinkage behavior of the disk-type pellets of $3PbO–MgNb_2O_6$ and $2PbO–InNbO_4$ was measured using dilatometry (DIL 402C; Netsch, Germany). The temperature at which the perovskite phase began to appear was measured using differential temperature analysis (DTA, DSC 910S; Du Pont, USA). In addition, the reaction sequences were investigated with the heat-treated samples using X-ray diffractometer (XRD; M18XHF-SRA; MacScience, Japan).

3. Results and discussion

3.1. Synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$

Swartz et al. [9] reported the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ using the b-site precursor (columbite) method as follows:

$$3PbO + MgNb_2O_6 \rightarrow 3Pb(Mg_{1/3}Nb_{2/3})O_3 \qquad (1)$$

According to this reaction, the almost pure perovskite phase was obtained without the remaining cubic pyrochlore phase, while only the 70% perovskite phase was obtained using the conventional oxide mixing method. However, Sreedhar and Mitra [14] showed that the intermediate cubic pyrochlore phase appeared around 600 °C, and this study obtained the same results, as shown in Fig. 1. This means that a small portion of $MgNb_2O_6$ was decomposed and reacted with PbO to form cubic pyrochlore.

Fig. 2 shows the thermal linear expansion/shrinkage behavior of the disk-type pellet of the $3PbO–MgNb_2O_6$ mixture that expanded rapidly at 600–700 °C and then shrank slowly over 700 °C. The maximum linear expansion rate was approximately 14%, i.e. approximately 50% of the volume expansion. The dotted curve of the differentiated expansion/shrinkage curve showed that the temperature of the most rapid expansion was about 650 °C. Compared to the XRD results shown in Fig. 1, this temperature implies that of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ formation. Shrout et al. [15] also observed the linear expansion behavior in the formation of the other perovskite systems, e.g. $PbTiO_3$, $PbZrO_3$, $Pb(Ti, Zr)O_3$, which was attributed to PbO diffusion into the other oxide particles uniaxially with the original PbO sites vacant with the formed layer having a different molar volume to that of the starting powders.

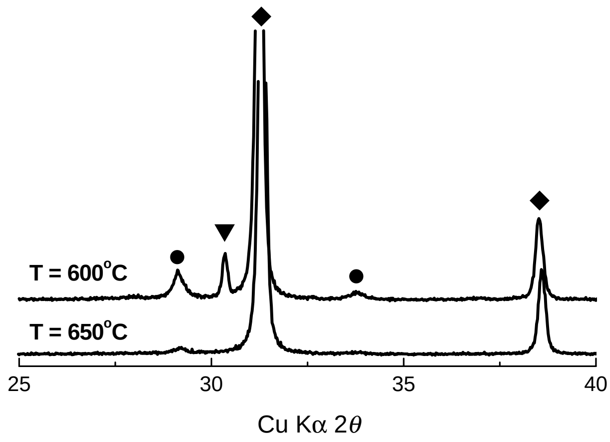

Fig. 1. XRD patterns of the powders calcined at each temperature using $3PbO–MgNb_2O_6$ mixture: (◆) $Pb(Mg_{1/3}Nb_{2/3})O_3$, (●) $Pb_3Nb_4O_{13}$, and (▼) $MgNb_2O_6$.

3.2. Synthesis of $Pb(In_{1/2}Nb_{1/2})O_3$

According to Fig. 3, which shows the DTA result of the $2PbO–InNbO_4$ mixture, the shape of the curve was similar to that of the $3PbO–MgNb_2O_6$ mixture [9]. The exothermal peak around 295 °C means the combustion of the remaining

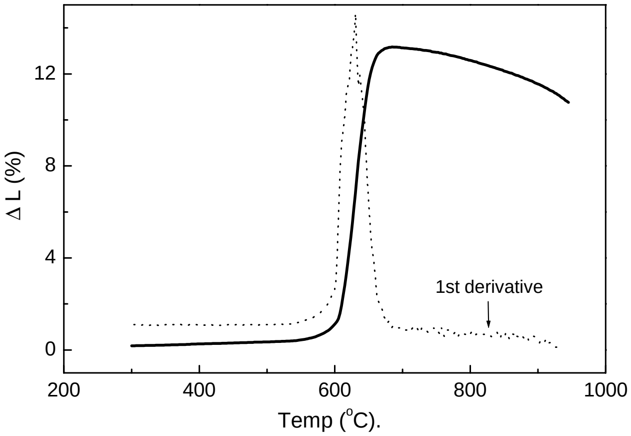

Fig. 2. Linear expansion/shrinkage behavior of the $3PbO–MgNb_2O_6$ mixture as a function of temperature (heating rate: 5 °C/min).

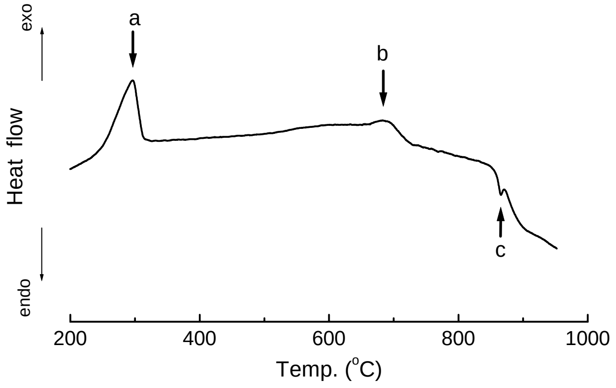

Fig. 3. DTA curve of 2PbO–$InNbO_4$ mixture for the $Pb(In_{1/2}Nb_{1/2})O_3$ preparation (a) 270 °C, (b) 858 °C, and (c) 868 °C.

ethyl alcohol and organics, and the endothermic peak at approximately 870 °C indicates the fusion temperature of $Pb(In_{1/2}Nb_{1/2})O_3$ has been reached. The broad exothermal peak of the perovskite formation is found at about 680 °C.

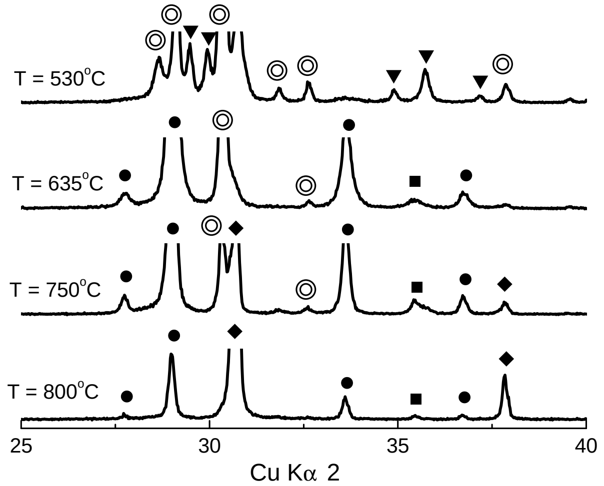

Fig. 4. XRD patterns of the powders calcined at each temperature using the 2PbO–$InNbO_4$ mixture: (◆) $Pb(In_{1/2}Nb_{1/2})O_3$, (●) $Pb_3Nb_4O_{13}$, and (▼) $InNbO_4$, (◎) PbO, (×) Pb_3O_4 and (■) In_2O_3.

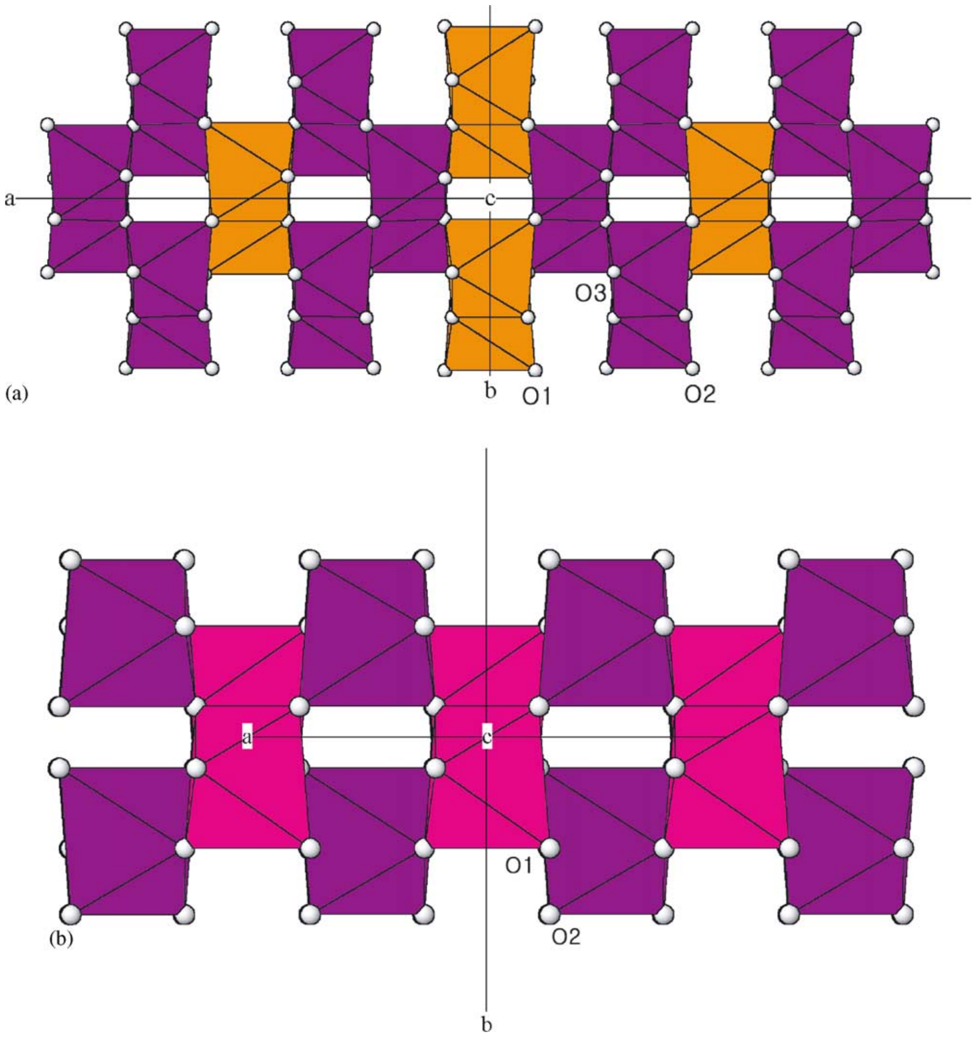

Fig. 5. Crystal structure of (a) $MgNb_2O_6$ and (b) $InNbO_4$.

The XRD results of the heat-treated samples at the various temperatures are shown in Fig. 4. At 530 °C, PbO and $InNbO_4$ were still observed, but a small portion of the PbO was oxidized to Pb_3O_4. As the temperature was increased to 635 °C, PbO and $InNbO_4$ were reacted to form the cubic pyrochlore phase, and a small amount of In_2O_3 existed, which ensures the decomposition of $InNbO_4$. In addition, the main phase at 635 °C was the cubic pyrochlore phase with a small amount of perovskite, which is differently from the case of $3PbO–MgNb_2O_6$ where the main phase at 600 °C was the perovskite phase. The perovskite phase began to form at 750 °C where PbO and In_2O_3 were still present, and became the main phase at 800 °C. However, a considerable amount of cubic pyrochlore still remained even at 800 °C. Based on these reaction sequences, the $Pb(In_{1/2}Nb_{1/2})O_3$ appeared to form from the reaction between PbO, In_2O_3 and cubic pyrochlore, and the remaining of cubic pyrochlore was attributed to the small diffusivity of In_2O_3.

The difficulty in obtaining pure $Pb(In_{1/2}Nb_{1/2})O_3$ has been explained simply by its small tolerance factor and electronegativity difference, which lowers the phase stability of $Pb(In_{1/2}Nb_{1/2})O_3$. However, according to Fig. 4, the decomposition of $InNbO_4$ enhanced the formation of the cubic pyrochlore phase, of which the reason should be found in the structural properties of the b-site precursor, $InNbO_4$, rather than those of $Pb(In_{1/2}Nb_{1/2})O_3$. In addition, a comparison with $Pb(Mg_{1/3}Nb_{2/3})O_3$ suggests that the degree of decomposition can be explained by the structural differences between $MgNb_2O_6$ and $InNbO_4$.

Fig. 5 shows the crystal structure of $MgNb_2O_6$ and $InNbO_4$ [16,17]. For the formation of cubic pyrochloro phase, the bonds of O1 and O2 that connect the NbO_6 and MgO_6 octahedra or the NbO_6 and InO_6 octahedra should be broken. The average bonding length of Mg–O in the Mg–O–Nb bond, 2.12 Å, is shorter than that of In–O in the In–O–Nb bond, 2.16 Å. Moreover, $MgNb_2O_6$ has the Nb–O–Nb bond, which is stronger than the Mg–O–Nb bond, and is believed to prevent decomposition, while $InNbO_6$ does not have the Nb–O–Nb bond. The electronegativity difference, which is a measure of the covalent bonding and the force on the electron pair, of the Mg–O bond is 2.3, which is greater than that of the In–O bond is 1.9. This means that the In–O–Nb bond is relatively easier to be broken and the cubic pyrochlore phase easily forms.

Fig. 6 shows the linear expansion/shrinkage behavior in the disk-type pellet of the $2PbO–InNbO_4$ mixture. At the temperature range of 600–700 °C, the expansion rate was approximately 15%, which is due to the uniaxial diffusion of PbO. However, the results of the diffusion between $3PbO–MgNb_2O_6$ and $2PbO–InNb_2O_6$ were different resulting in the formation of the perovskite and cubic pyrochlore phase, respectively. The $2PbO–InNbO_4$ sample rapidly shrank at temperatures over 800 °C, which is attributed to the perovskite formation of $Pb(In_{1/2}Nb_{1/2})O_3$.

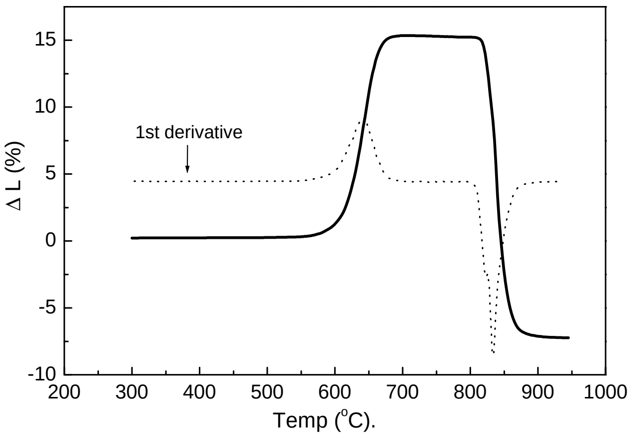

Fig. 6. Linear expansion/shrinkage behavior of the $2PbO–InNbO_4$ mixture as a function of temperature (heating rate: 5 °C/min).

4. Conclusion

The reaction sequences of $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(In_{1/2}Nb_{1/2})O_3$ formation were investigated. $Pb(Mg_{1/3}Nb_{2/3})O_3$ was synthesized by a reaction between PbO and $MgNb_2O_6$, while $Pb(In_{1/2}Nb_{1/2})O_3$ was synthesized by a reaction between PbO, In_2O_3 and cubic pyrochlore, which had been formed by the decomposition of $InNbO_4$. The easy decomposition behavior of $InNbO_4$ can be explained by the structural differences between $MgNb_2O_6$ and $InNbO_4$: the longer bond length and the smaller electronegativity difference in the In–O bond than those of the Nb–O bond.

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