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Preparation of pyrochlore-free lead magnesium niobate via adding excess constituent compounds

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Abstract

Pyrochlore-free $Pb(Mg_{1/3}Nb_{2/3})O_3$ was successfully synthesized in the mixed-oxide process without using columbite precursors. Adding excess amounts (5–20 mol%) of MgO and PbO in starting materials effectively resulted in the complete formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ after 1000°C calcination. The more the excess amount of MgO was added, the less the minimum excess amount of PbO was required for fabricating monophasic $Pb(Mg_{1/3}Nb_{2/3})O_3$. The morphology of calcined specimens markedly depended on the purity of $Pb(Mg_{1/3}Nb_{2/3})O_3$. The grain size of $Pb(Mg_{1/3}Nb_{2/3})O_3$ in the specimens containing the pyrochlore phase was 1.0–1.5 μm, whereas that of $Pb(Mg_{1/3}Nb_{2/3})O_3$ in the pure specimens increased considerably to 6.0–10.0 μm. The above phenomena suggested that the coarsening of $Pb(Mg_{1/3}Nb_{2/3})O_3$ was hindered by the presence of the pyrochlore phase.

Keywords: Lead magnesium niobate; Ferroelectric; Perovskite; Pyrochlore phase; Preparation; Microstructure; Solid-state reaction

1. Introduction

Lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$, a ferroelectric ceramic exhibiting a perovskite structure, has been intensively studied recently. Because of its high permittivity and diffuse phase transition characteristics, $Pb(Mg_{1/3}Nb_{2/3})O_3$ has been recognized as one of the most potential materials for possible use in multilayer capacitors [1–3]. It is also an important material used in actuators in view of its large electrostrictivity [4,5]. However, the major problem in the fabrication of $Pb(Mg_{1/3}Nb_{2/3})O_3$ is that the pure perovskite compound is difficult to obtain. The parasitic pyrochlore phases are often formed with $Pb(Mg_{1/3}Nb_{2/3})O_3$. Due to the low dielectric permittivities of the pyrochlore phases, the dielectric permittivities of ceramics are greatly reduced by the presence of the pyrochlore phases.

In order to eliminate the pyrochlore phases, several synthesis processes have been investigated. The columbite process [6,7], using pre-reacted $MgNb_2O_6$ precursors, has been known to be an effective solid-state reaction process for synthesizing $Pb(Mg_{1/3}Nb_{2/3})O_3$. Other solution routes such as precipitation [8,9], sol–gel [10,11], molten-salt [12,13], and hydrothermal [14] processes have also been studied. The composition in the starting materials has been found to significantly affect the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$. Adding excess MgO in the columbite process [6,15], and adding excess PbO in the mixed-oxide process [16] and the molten-salt

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process [12], can increase the yield of $Pb(Mg_{1/3}Nb_{2/3})O_3$. Varying the ratio of all constituent species to a specific region can also facilitate the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ [17]. Although the nearly pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ can be obtained through the above processes, the effects of adding excess MgO and PbO on the phase formation and microstructure in the mixed-oxide process have not been thoroughly investigated. Furthermore, considering the mass production in industry, it is necessary to develop an alternative method without employing environment-sensitive materials and complicated operation processes such as in solution routes.

The main purpose of this study was to prepare monophasic $Pb(Mg_{1/3}Nb_{2/3})O_3$ via the conventional mixed-oxide process without using $MgNb_2O_6$ precursors. For enhancing the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$, excess MgO and PbO (up to 20 mol%) were added in starting materials. The effects of both excess MgO and PbO on the phase formation were systematically investigated, and the compositional region for forming pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ was determined. Furthermore, the effect of the $Pb(Mg_{1/3}Nb_{2/3})O_3$ purity on microstructure was examined.

2. Experimental

Reagent-grade PbO, MgO and Nb_2O_5 were used as raw materials. For accurately calculating the weight of MgO, the purchased MgO powder was pre-heated at 800°C for 30 min to eliminate CO_2 and H_2O absorbed on particle surfaces. 5–20 mol% excess PbO and MgO were added in the starting materials. Weighed according to the designed composition, the starting materials were ball-milled for 48 h with ethyl alcohol using zirconia balls. Following drying in a rotary evaporator under reduced pressure, the mixed powder was uniaxially pressed into pellets under 196 MPa. The average packing density of the pellets was around 4.1 g/cm^3. Then the pressed pellets were heated at temperatures ranging from 900 to 1100°C for 4 h. X-ray powder diffraction (XRD) analysis was used to identify the compounds present in the specimens. Scanning electron microscopy (SEM) was utilized to analyze the microstructural evolution of perovskite and pyrochlore phases. The content of $Pb(Mg_{1/3}Nb_{2/3})O_3$ was calculated from the intensity of the XRD peaks according to the following formula:

$$\text{Content of } Pb(Mg_{1/3}Nb_{2/3})O_3(\%) = \frac{I_{Pb(Mg_{1/3}Nb_{2/3})O_3(110)}}{I_{Pb(Mg_{1/3}Nb_{2/3})O_3(110)} + I_{\text{pyrochlore}(222)}}.$$

3. Results and discussion

Fig. 1 shows the contents of $Pb(Mg_{1/3}Nb_{2/3})O_3$ at various calcination temperatures when 5–20 mol% excess MgO was added in the starting materials. At 900°C, a large amount of $Pb(Mg_{1/3}Nb_{2/3})O_3$ was formed with pyrochlore phase. The content of $Pb(Mg_{1/3}Nb_{2/3})O_3$ for all compositions increased after 1000°C calcination. However, the content of $Pb(Mg_{1/3}Nb_{2/3})O_3$ dropped at 1100°C, indicating that the decomposition of $Pb(Mg_{1/3}Nb_{2/3})O_3$ occurred at elevated temperatures. The amount of MgO was found to significantly influence the formation and decomposition processes of $Pb(Mg_{1/3}Nb_{2/3})O_3$. At temperatures lower than 1000°C, increasing the amount of excess MgO tended to facilitate the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$. However, at elevated temperatures, the more excess MgO was added, the

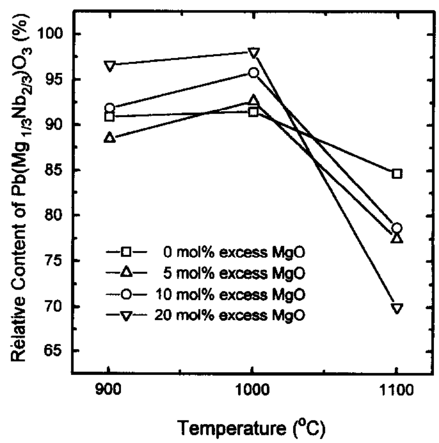

Fig. 1. Relative content of $Pb(Mg_{1/3}Nb_{2/3})O_3$ versus calcination temperature for the specimens with various amounts of excess MgO.

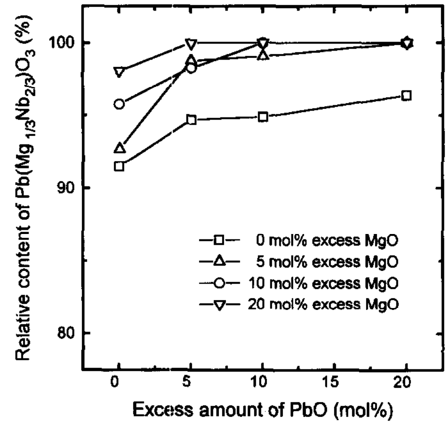

Fig. 2. The relation between the content of $Pb(Mg_{1/3}Nb_{2/3})O_3$ and various amounts of excess PbO and MgO.

less $Pb(Mg_{1/3}Nb_{2/3})O_3$ was formed, implying that the thermal stability of $Pb(Mg_{1/3}Nb_{2/3})O_3$ was reduced.

As shown in Fig. 1, the calcination at 1000°C was found to be the optimum condition for $Pb(Mg_{1/3}Nb_{2/3})O_3$ to form. However, pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ could not be synthesized by merely adding excess MgO. Therefore the effects of both excess MgO and PbO on the phase formation were examined. The relation between the content of $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the amounts of excess MgO and PbO is indicated in Fig. 2. The contents of the $Pb(Mg_{1/3}Nb_{2/3})O_3$ for each designed composition are listed in Table 1. When a fixed amount of excess PbO was added in the starting materials, increasing the MgO amount significantly raised the amount of $Pb(Mg_{1/3}Nb_{2/3})O_3$ formed. As for a fixed amount of MgO in the starting materials, increasing the PbO amount also increased the yield of $Pb(Mg_{1/3}Nb_{2/3})O_3$. As seen in Table 1, the suitable conditions for pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ to form lie in the region where both excess MgO and PbO were

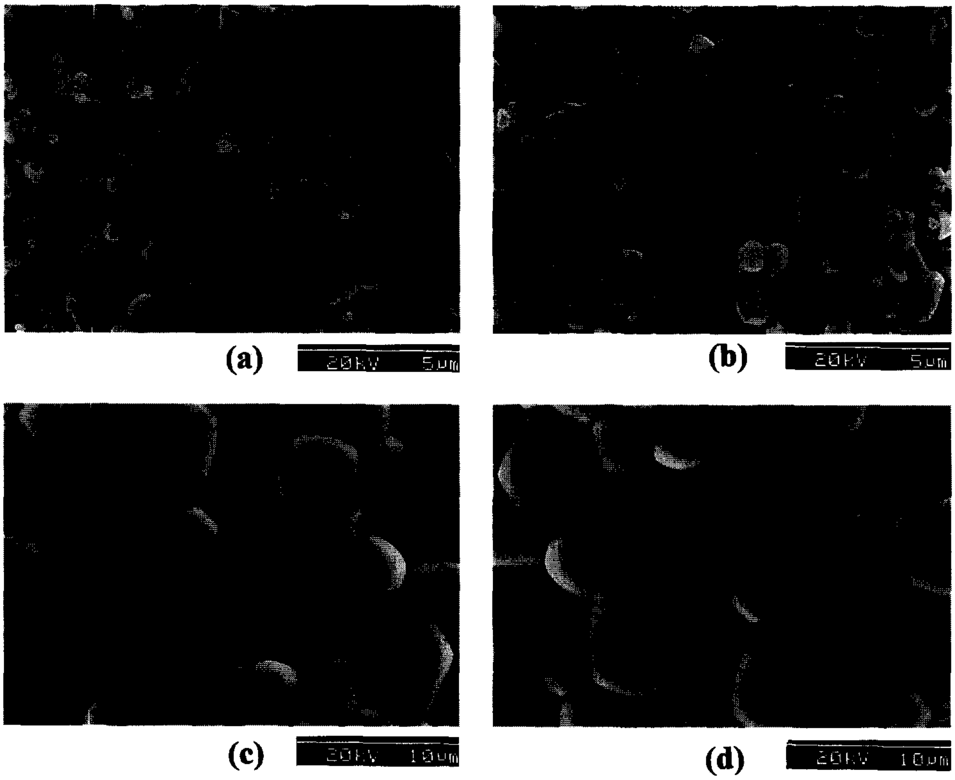

Fig. 3. Microstructures of 1000°C calcined specimens containing excess amounts of constituent compounds for (a) 5 mol% PbO and 0 mol% MgO, (b) 5 mol% PbO and 5 mol% MgO, (c) 10 mol% PbO and 10 mol% MgO, and (d) 20 mol% PbO and 5 mol% MgO.

Table 1
Relative content (in %) of $Pb(Mg_{1/3}Nb_{2/3})O_3$ versus various amounts of excess MgO and PbO after 1000°C calcination

Excess amount of MgO (mol%)	Excess amount of PbO (mol%)			
	0	5	10	20
0	91.5	94.7	94.9	96.4
5	92.7	98.8	99.1	100.0
10	95.8	98.3	100.0	100.0
20	98.1	100.0	100.0	100.0

added. When the excess amount of MgO was 5, 10 and 20 mol%, the minimum excess amount of PbO required for synthesizing pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ was 20, 10 and 5 mol%, respectively. The results indicate that as more MgO was added, less PbO was needed for the synthesis of monophasic $Pb(Mg_{1/3}Nb_{2/3})O_3$, and vice versa.

For realizing the formation reaction of $Pb(Mg_{1/3}Nb_{2/3})O_3$, three kinds of specimens were quenched at various temperatures during heating. The amounts of excess PbO in specimens A, B and C were 0, 10, and 20 mol%, respectively, and the amount of excess MgO in all specimens was 10 mol%. At 800°C unreacted PbO was found to coexist with the pyrochlore phase and a small amount of $Pb(Mg_{1/3}Nb_{2/3})O_3$ in all specimens. When the temperature reached 900°C, the content of $Pb(Mg_{1/3}Nb_{2/3})O_3$ increased rapidly, and all unreacted PbO disappeared. On further heating to 1000°C, the formation rate of $Pb(Mg_{1/3}Nb_{2/3})O_3$ levelled off. Compared with specimen A, specimens B and C had a larger amount of unreacted PbO at 800°C, and a larger amount of $Pb(Mg_{1/3}Nb_{2/3})O_3$ after 900°C heating. Considering that the melting of PbO occurs at 888°C, the formation process of $Pb(Mg_{1/3}Nb_{2/3})O_3$ seems to be accelerated by the melting of the unreacted PbO on heating from 800 to 900°C. Without the presence of the molten PbO, the conversion of the pyrochlore phase to the perovskite phase becomes slow on further heating from 900 to 1000°C.

The microstructures of the 1000°C-calcined specimens were found to strongly depend on the purity of $Pb(Mg_{1/3}Nb_{2/3})O_3$. When $Pb(Mg_{1/3}Nb_{2/3})O_3$ coexisted with the pyrochlore phase, two kinds of grains with different morphology were observed. These specimens contained the rounded $Pb(Mg_{1/3}Nb_{2/3})O_3$ grains with a size of 1.0–1.5 μm and the polyhedral pyrochlore grains with submicron size (as seen in Fig. 3a and 3b). On the other hand, when pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ was formed, all polyhedral grains disappeared, and the grain size of $Pb(Mg_{1/3}Nb_{2/3})O_3$ markedly increased to 6.0–10.0 μm (as seen in Fig. 3c and 3d). From the above microstructural evolution, it is considered that the coarsening of $Pb(Mg_{1/3}Nb_{2/3})O_3$ grains seems to be retarded by the presence of the pyrochlore phase in the matrix. As a result, the addition of excess MgO and PbO in the mixed-oxide process significantly affects not only the formation reaction, but also the microstructure of $Pb(Mg_{1/3}Nb_{2/3})O_3$.

4. Conclusion

(i) Pyrochlore-free $Pb(Mg_{1/3}Nb_{2/3})O_3$ was successfully synthesized by the mixed-oxide process via adding both excess MgO and PbO. When the excess amount of MgO was increased, the minimum excess amount of PbO required for fabricating pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ was reduced.

(ii) The optimum calcination temperature for the $Pb(Mg_{1/3}Nb_{2/3})O_3$ formation was found to be 1000°C. Heating at higher temperatures caused $Pb(Mg_{1/3}Nb_{2/3})O_3$ to decompose.

(iii) In the biphasic specimens, the $Pb(Mg_{1/3}Nb_{2/3})O_3$ grains, 1.0–1.5 μm in size, coexist with the polyhedral pyrochlore-phase grains. As for pure $Pb(Mg_{1/3}Nb_{2/3})O_3$, the grain size of it was markedly increased to 6.0–10.0 μm. The above phenomena imply that the presence of the pyrochlore phase could hinder the coarsening of the $Pb(Mg_{1/3}Nb_{2/3})O_3$ grains.

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