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Development of fast formation process for synthesizing submicron lead magnesium niobate perovskite powder

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Abstract

The characteristics of the solid-state reaction for synthesizing ultrafine $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder using a new percursor, $Mg_4Nb_2O_9$ have been investigated. Quenching the mixtures of $Mg_4Nb_2O_9$ with excess PbO at 850–900°C without further soaking rapidly leads to the complete formation of perovskite phase without pyrochlore phase. Some residual MgO exists in samples; however, MgO is completely eliminated by nitric acid, thereby producing monophasic $Pb(Mg_{1/3}Nb_{2/3})O_3$. This process confirms the feasibility to synthesize $Pb(Mg_{1/3}Nb_{2/3})O_3$ in a fast reaction route. The addition of excess PbO enhances the formation rate of $Pb(Mg_{1/3}Nb_{2/3})O_3$, and also decreases the minimum temperature required for preparing pure perovskite phase. The particle size of obtained $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder is within the range of submicron meter, and increases with the increasing amount of PbO used. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lead magnesium niobate; Powder; Synthesis; Relaxor

1. Introduction

Lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$, a well-known ferroelectric relaxor with perovskite structure, exhibits high permittivity, large electrostrictivity, and diffuse phase transition characteristics. Since its first discovery by Smolenskii and Agranovskaya in 1958 [1], $Pb(Mg_{1/3}Nb_{2/3})O_3$ has been intensively investigated and widely used in dielectric and piezoelectric devices with high quality and reliability [2–8]. In preparation via the solid-state reaction using oxide mixtures, pyrochlore phases with relatively low dielectric constant are inevitably formed with $Pb(Mg_{1/3}Nb_{2/3})O_3$, and these phases significantly reduce the dielectric constant of obtained ceramics. Hence, in order to eliminate the residual pyrochlore phases, Swartz and Shrout developed the columbite process for synthesizing $Pb(Mg_{1/3}Nb_{2/3})O_3$ [9]. In this process, a precursor, $MgNb_2O_6$ with columbite structure is prepared which subsequently reacts with PbO to form around 98% $Pb(Mg_{1/3}Nb_{2/3})O_3$. In the columbite process, an excess amount of MgO has to be added into the reactants for suppressing the formation of pyrochlore phase and to obtain pure perovskite phase. However, excess MgO will exist as discrete particles which in turn deteriorate the dielectric properties [10].

Recently Joy and Sreedhar reported that the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ can be stabilized by adding excess MgO in the precursors [11], and further suggested that use of the precursor $Mg_4Nb_2O_9$ instead of columbite precursor $MgNb_2O_6$ is helpful to prepare the single phase $Pb(Mg_{1/3}Nb_{2/3})O_3$. Hence, it is thought worthwhile to investigate in detail, the reaction processes for the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ using the new precursor — $Mg_4Nb_2O_9$. We report influence of the amount of PbO on the formation of perovskite phase and the microstructure of $Pb(Mg_{1/3}Nb_{2/3})O_3$. Through this study, a fast solid-state synth process for preparing monophasic $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder with submicron size was successfully developed.

2. Experimental procedure

$Mg_4Nb_2O_9$ was prepared from MgO and Nb_2O_5 (the reagent-grade) by solid-state reaction. MgO powder was heated at 800°C for 30 min to eliminate the CO_2

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and H_2O absorbed on the particle surfaces. Nb_2O_5 and MgO were mixed in stoichiometric ratio in ethyl alcohol by ball-milling for 48 h. The mixtures were dried and heated at 1000°C for 2 h to form pure $Mg_4Nb_2O_9$ with a hexagonal unit cell [12]. PbO and the niobate precursor-$Mg_4Nb_2O_9$ were mixed in molar ratios of 3: 1, 3.1: 1, and 3.2: 1 (denoted for systems A–C) by ball-milling for 48 h. For comparing the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ in the process using $Mg_4Nb_2O_9$ and that in the columbite process, PbO and $MgNb_2O_6$ were mixed by the identical ball-milling process in system D. The above four kinds of mixtures were heated at temperature ranging from 600 to 900°C at a ramp rate of 10°C/min. After the set temperature reached, the specimens were subsequently quenched in air without further soaking. The quenched specimens were examined by powder XRD with CuKα radiation to identify the formed phases. The relative content of perovskite phase existing in the specimens was calculated from the following equation:

$$X_{\mathrm{per}}\ (\%) = 100 I_{\mathrm{per}}/(I_{\mathrm{per}} + I_{\mathrm{pyr}} + I_{\mathrm{Mgo}})$$

where I_{per}, I_{pyr} and I_{Mgo} refer to the intensity of the (110) reflection of the perovskite phase, that of the (222) reflection of the pyrochlore phase, that of the (200) of MgO, respectively. The morphology of the obtained powder was examined by scanning electron microscopy (SEM).

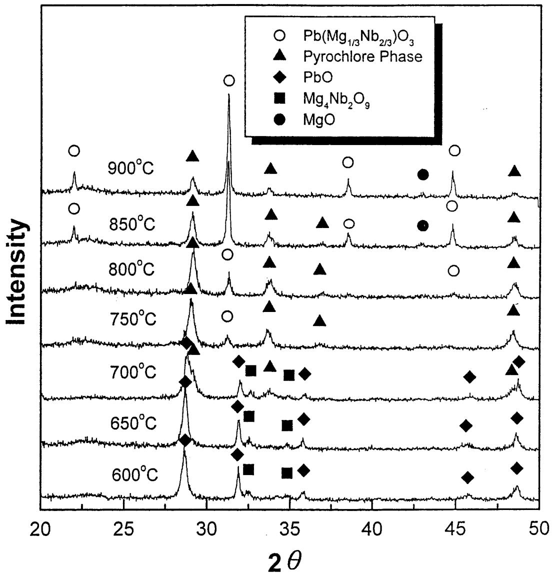

Fig. 1. X-ray diffraction patterns of the mixtures of PbO and $Mg_4Nb_2O_9$ (molar ratio = 3: 1) quenched at various temperatures.

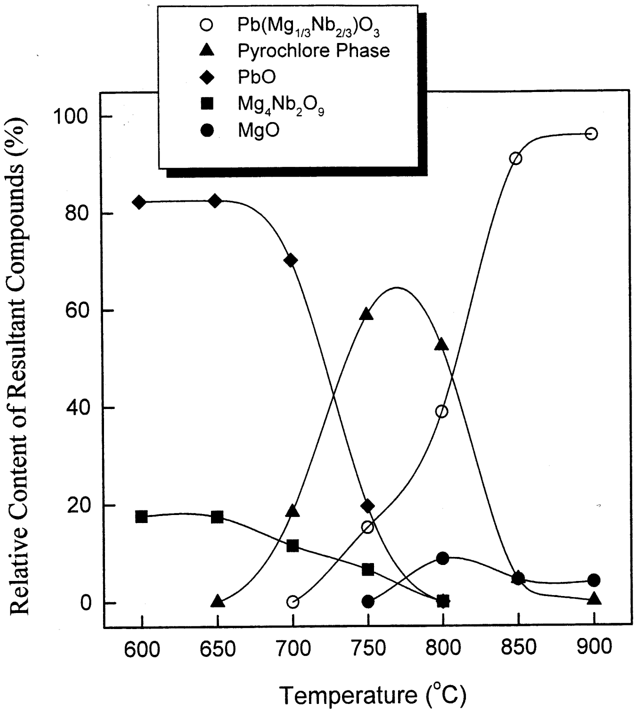

Fig. 2. Relative content of resultant compounds for the mixtures of PbO and $Mg_4Nb_2O_9$ (molar ratio = 3.1: 1) heated at various temperatures.

3. Results and discussion

For realizing the phase development in system A during heating processes, the precursor powder was quenched at elevated temperatures and examined by XRD. The representative XRD patterns for quenched specimens are shown in Fig. 1. After heating at 700°C, pyrochlore phase is formed with unreacted PbO and $Mg_4Nb_2O_9$. Heating up to 750°C, $Pb(Mg_{1/3}Nb_{2/3})O_3$ begins to appear, and PbO and $Mg_4Nb_2O_9$ all disappear. With a rise in the temperature, the amount of $Pb(Mg_{1/3}Nb_{2/3})O_3$ rapidly increases with the correlative decrease in the amount of pyrochlore phase. However, even heating up to 900°C, pyrochlore phase still parasitically coexists with $Pb(Mg_{1/3}Nb_{2/3})O_3$, and no pure perovskite phase can be obtained. In addition, MgO is also found to appear in the products.

For obtaining pure $Pb(Mg_{1/3}Nb_{2/3})O_3$, excess amounts of PbO were added in systems B and C. The relative content of resultant compounds versus quenching temperatures in system B is plotted in Fig. 2. The relative content of the formed compounds was estimated by calculating the ratios of the intensity of the major peak of phase i/Σ intensity of the major peak of phase i for each compound. Fig. 2 indicates that no reactions occur till the temperature reaches 700°C, after which pyrochlore phase begins to appear. In both system A and B, the amount of pyrochlore phase reaches a maximum at 800°C; however, the amount of pyrochlore phase in the latter system is much less than that in the former system. Like system A, the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ initiates at 750°C. After heating up to 900°C without further soaking, $Pb(Mg_{1/3}Nb_{2/3})O_3$

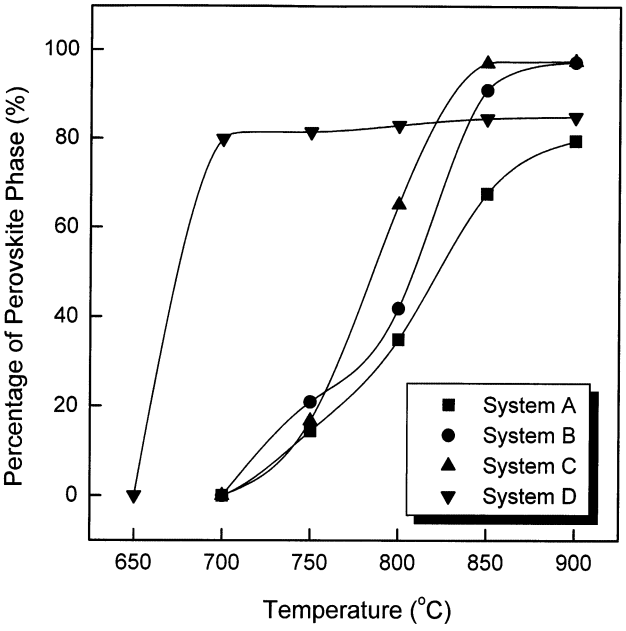

Fig. 3. Content of $Pb(Mg_{1/3}Nb_{2/3})O_3$ perovskite versus the quenching temperature for four different systems.

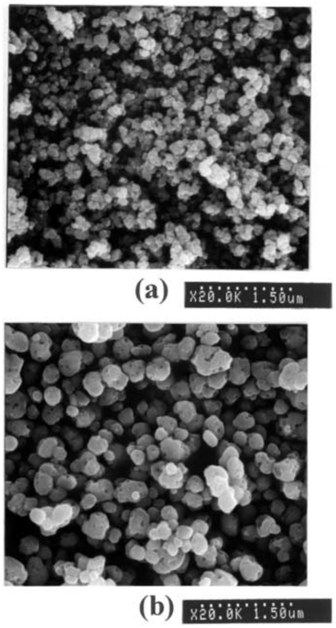

Fig. 4. Scanning electron micrographs of the powders obtained in: (a) system A; and (b) system C by quenching the mixtures at 900°C and leached by nitric acid.

is completely formed without any pyrochlore phase, although some residual MgO exists. The 900°C-quenched powder was then washed by nitric acid (2 M) for 8 h. It is found that all MgO was eliminated by nitric acid, and monophasic $Pb(Mg_{1/3}Nb_{2/3})O_3$ was obtained. The above results confirm that only heating $Mg_4Nb_2O_9$-consisted precursors up to 900°C results in the complete formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$. The reaction processes for the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ is considered as below:

$$PbO + Mg_4Nb_2O_9 \rightarrow \text{Pyrochlore phase}$$

$$\text{Pyrochlore phase} \rightarrow Pb(Mg_{1/3}Nb_{2/3})O_3 + MgO$$

The composition of pyrochlore phase formed in this study is believed to contain excess magnesium species compared with that in the normal columbite process since the magnesium content in $Mg_4Nb_2O_9$ is four times higher than that in $MgNb_2O_6$. The excess magnesium species are driven out from pyrochlore phase to produce MgO when $Pb(Mg_{1/3}Nb_{2/3})O_3$ is formed.

Fig. 3 illustrates the percentage of perovskite phase without residual MgO for systems A–D versus the quenching temperature. The addition of excess PbO significantly enhances the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ at low temperatures. In system A, $Pb(Mg_{1/3}Nb_{2/3})O_3$ coexists with pyrochlore phase after heating up to 900°C. However, pure perovskite phase is formed in systems B and C by quenching the precursors at 900 and 850°C, respectively. It is noted that the required minimum temperature for synthesizing pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ decreases with increasing the amount of excess PbO. The existence of excess PbO is believed to suppress the formation of pyrochlore phase which is produced by the volatilization of PbO and promotes the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ by the liquid phase of PbO [14,15]. On the other hand, although $Pb(Mg_{1/3}Nb_{2/3})O_3$ is rapidly formed at low temperatures in the columbite process (system D), it is not possible to remove the pyrochlore phase by quenching the precursors up to 900°C. Thus, it is revealed that the developed process in this study is more efficient than the columbite process for preparing $Pb(Mg_{1/3}Nb_{2/3})O_3$ with respect to the heating temperature and time [9,13].

The microstructure of the 900°C-quenched powder after the acid-leaching process was examined by SEM. The particle size in systems A–C is within the order of submicron meter. The particle size of the powder in system A (Fig. 4(a)), system B, and system C (Fig. 4(b)) is ~ 0.1, 0.2, and 0.3 μm, respectively. It is found that the particle size greatly increases with increasing the amount of PbO probably due to the liquid-phase sintering of excess PbO. It is also seen that plenty of dimples exist on the obtained powder (Fig. 4(b)). On the other hand, before the acid-leaching process no dimples exist on the powder, and the presence of a lot of tiny MgO particles are observed. Once MgO is leached out by the acid-leaching process, the removal of MgO results in the hollows in the original powder and forms the dimple-like morphology. The particle size of $Pb(Mg_{1/3}Nb_{2/3})O_3$ prepared in this study method is found to be relatively smaller than that prepared via the columbite precursor process [13]. The $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder with fine particle size is regarded to have advantage for lowering sintering temperature.

4. Conclusions

The fast formation process for synthesizing $Pb(Mg_{1/3}Nb_{2/3})O_3$ using a new niobate precursor-$Mg_4Nb_2O_9$ has been developed in this study. Heating the mixtures of $Mg_4Nb_2O_9$ and excess PbO up to 850–900°C without further soaking results in the complete formation of perovskite phase with residual MgO. Leaching the obtained products with dilute nitric acid completely removes residual MgO, thereby producing the monophasic $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder. The amount of PbO plays an important role in synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$. Increasing the amount of PbO not only enhances the formation rate of perovskite phase, but also decreases the required temperature for obtaining pure perovskite phase. The particle size of obtained $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder is within the range of submicron meter, and is increased with the increasing amount of PbO.

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