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Short communication

Simultaneous synthesis and sintering of lead magnesium niobate ferroelectric ceramics

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Abstract

Lead magnesium niobate ($Pb(Mg_{1/3}Nb_{2/3})O_3$) ceramics have been synthesized and sintered simultaneously by a newly developed reaction sintering process. During the formation of pyrochlore phase, the specimens expand at first. When $Pb(Mg_{1/3}Nb_{2/3})O_3$ begins to form at elevated temperatures, the specimens rapidly shrink, indicating the occurrence of reaction sintering. After sintering at 1000°C, monophasic perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with high sintering density (> 96%) are obtained. Adding 5 mol% excess MgO further enhances the densification of $Pb(Mg_{1/3}Nb_{2/3})O_3$. However, when 20 mol% excess MgO is added, MgO particles distribute on the grain boundary of $Pb(Mg_{1/3}Nb_{2/3})O_3$, thereby impeding the densification process. The 5 mol% MgO-added $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics exhibit high density as well as high dielectric permittivity.

Keywords: Lead magnesium niobate ceramics; Sintering; High density; High diaelectric permittivity

1. Introduction

Relaxor ferroelectric ceramics are important materials for the application to dielectric and piezoelectric devices. Among the relaxor ferroelectrics, lead magnesium niobate ($Pb(Mg_{1/3}Nb_{2/3})O_3$) has been intensively investigated because of its high permittivity, high electric resistivity, and diffuse phase transition characteristics. $Pb(Mg_{1/3}Nb_{2/3})O_3$ has been recognized as one of the most potential materials used in multilayer ceramic capacitors and actuators [1–5]. In the conventional process for preparing $Pb(Mg_{1/3}Nb_{2/3})O_3$, one often encounters the difficulty in fabricating pure perovskite phase because of the existence of residual pyrochlore phase [6]. The other problem is that high-temperature sintering is required for densifying $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder prepared by the conventional process. The high-temperature treatment causes compositional variation and results in thermal decomposition of the perovskite phase [7,8].

For solving the problems of the conventional process, a new reaction sintering process is developed to simultaneously prepare monophasic $Pb(Mg_{1/3}Nb_{2/3})O_3$ phase and achieve densified ceramics. Reaction sintering has been successfully applied to synthesize ceramics containing single or multiple components [9–12]. However, the study concerning the reaction sintering of $Pb(Mg_{1/3}Nb_{2/3})O_3$ has not yet been investigated in detail so far. In this study, excess amounts of Pb_3O_4 are added in the starting materials of $Pb(Mg_{1/3}Nb_{2/3})O_3$ to enhance the formation of perovskite phase as well as the sintering process. The effects of the addition of MgO on the sintering and microstructure of ceramics are examined. The temperature and frequency dependencies of dielectric permittivity of densified $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics are also analyzed.

2. Experimental

Reagent-grade Pb_3O_4, MgO, and Nb_2O_5 were used for preparing $Pb(Mg_{1/3}Nb_{2/3})O_3$. For enhancing the sin-

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tering process of specimens, 10 mol% excess Pb_3O_4 with respect to the stoichiometric ratio of lead species in $Pb(Mg_{1/3}Nb_{2/3})O_3$ was added. Three kinds of starting materials were prepared. PMN0 contained the stoichiometric content of MgO, while PMN5 and PMN20 contained 5 and 20 mol% excess MgO, respectively. The weighed 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 pressed into pellets under 196 MPa. The pressed pellets were covered by $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder to prevent the evaporation of PbO, and heated at temperature ranging from 700 to 1050°C for 2 h. The phase evolution of sintered specimens was analyzed by X-ray powder diffraction (XRD) using Cu–K_α radiation. The sintering behavior of the pressed specimens was examined by a dilatometer. After reaction sintering, the densities of sintered specimens were measured, and the microstructures were investigated by scanning electron microscopy (SEM). The dielectric permittivity of sintered $Pb(Mg_{1/3}Nb_{2/3})O_3$ was examined by an impedance analyzer from -50 to 100°C.

3. Results and discussion

The linear change percentage and differential coefficient of expansion curves of the starting materials of PMN0, PMN5, and PMN20 are illustrated in Fig. 1a, b and c, respectively. It is found that the specimens of all three systems begin to expand from around 500°C, and

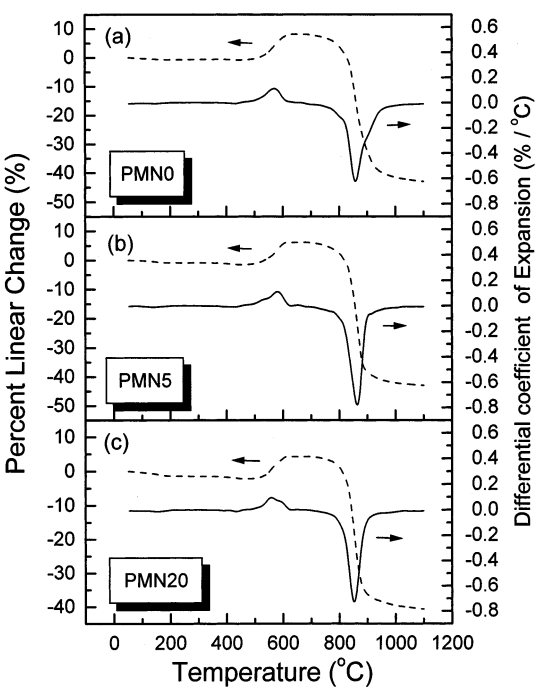

Fig. 1. Percent linear change and differential coefficient of expansion of the starting materials of (a) PMN0; (b) PMN5; and (c) PMN20.

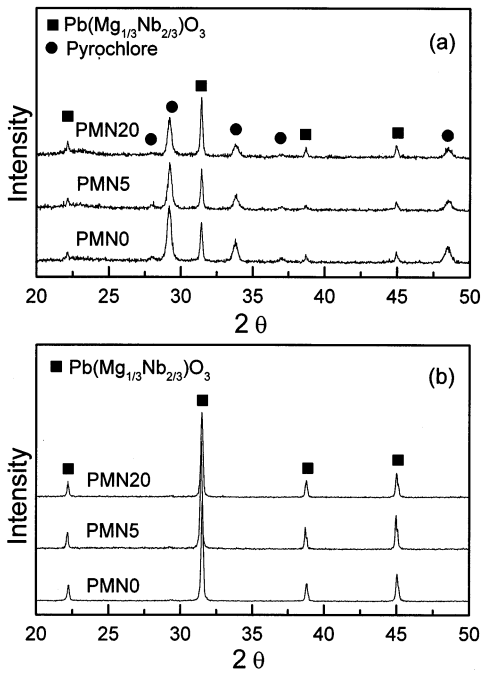

Fig. 2. X-ray diffraction patterns of (a) 700°C and (b) 800°C-heated specimens.

the linear expansion percentage reaches a plateau at around 600°C. While after heating up to 800°C, all specimens start to shrink rapidly. From the curves of the differential coefficient of expansion for each specimen, two distinct peaks are observed which indicate the expansion and shrinkage stages during the heating process. The peak temperatures of all three specimens are almost the same. The temperatures of the first and the second peaks are around 550 and 850°C, respectively. It is noted that the second peak of PMN5 and PMN20 is sharper than that of PMN0, implying that the former two specimens exhibit a greater shrinkage rate.

Based on the XRD results of quenched specimens, it is found that pyrochlore phase begins to appear from 500°C, and its content increases with increasing temperature up to 800°C. The formation of pyrochlore phase results in the expansion of specimens as shown in Fig. 1. At higher temperatures, $Pb(Mg_{1/3}Nb_{2/3})O_3$ begins to form, associated with a corresponding decrease in the content of pyrochlore phase. Once $Pb(Mg_{1/3}Nb_{2/3})O_3$ is formed, the specimens begin to shrink, implying that formation and sintering of $Pb(Mg_{1/3}Nb_{2/3})O_3$ happen simultaneously. The occurrence of reaction sintering of $Pb(Mg_{1/3}Nb_{2/3})O_3$ is attributed to the presence of excess of Pb_3O_4 which induces the liquid phase sintering at elevated temperatures.

The specimens were reaction-sintered at elevated temperatures for 2 h. The XRD patterns of 700°C-heated specimens are shown in Fig. 2a. Pyrochlore phase and $Pb(Mg_{1/3}Nb_{2/3})O_3$ coexist in all specimens. It is found that the addition of MgO enhances the formation of

$Pb(Mg_{1/3}Nb_{2/3})O_3$, and the content of $Pb(Mg_{1/3}Nb_{2/3})O_3$ increases with greater amount of added MgO. These results are similar to the MgO effect on the formation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ reported in literature [13,14]. After heating at temperature higher than 800°C, pure perovskite phase of $Pb(Mg_{1/3}Nb_{2/3})O_3$ is obtained in all three systems. The XRD patterns of 800°C-heated specimens are shown in Fig. 2b. The density of reaction-sintered specimens versus the sintering temperature is illustrated in Fig. 3. This figure indicates that the density of specimens increases monotonously with temperature up to 1000°C. After heating at 1050°C, the density of specimens slightly drops, which is due to the partial decomposition of $Pb(Mg_{1/3}Nb_{2/3})O_3$ at elevated temperatures [15]. In addition, at all sintering temperatures, the sequence of the density of specimens is as follows: PMN5 > PMN0 > PMN20. After sintering at 1000°C, the densities of PMN0, PMN5, and PMN20 are 7.88, 7.91, 7.86 g cm^{-3}, respectively. The densities of these three specimens are all greater than 96% of the theoretical value. Therefore, densified $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics are successfully achieved through the reaction sintering process.

The fractured surface of 1000°C-sintered specimens is shown in Fig. 4. It is found that the addition of MgO decreases the grain size of $Pb(Mg_{1/3}Nb_{2/3})O_3$. The grain size of pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN0) ranges from 7 to 15 μm, while that of PMN10 reduces to 6–10 μm. In the MgO-doped specimens, MgO particles are found to distribute on the grain boundary of $Pb(Mg_{1/3}Nb_{2/3})O_3$, and more MgO particles are observed in PMN20 than in PMN5. When 5 mol% excess MgO is added, the grain growth of $Pb(Mg_{1/3}Nb_{2/3})O_3$ is suppressed, and the sintering process is enhanced. However, when the addition amount reaches 20 mol%, MgO particles significantly hinder the diffusion process and the migration of grain boundary, thereby decreasing the density of specimens.

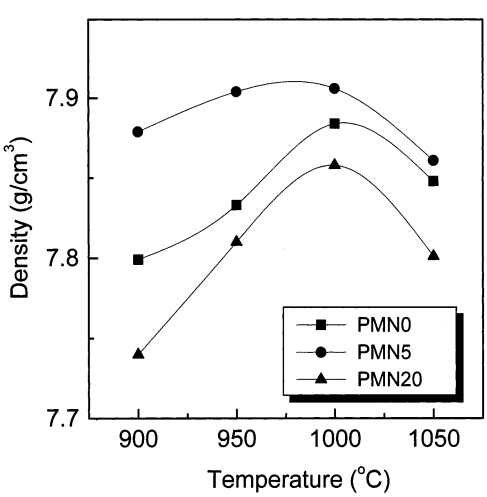

Fig. 3. Density of $Pb(Mg_{1/3}Nb_{2/3})O_3$ versus sintering temperature for specimens containing various amounts of excess MgO.

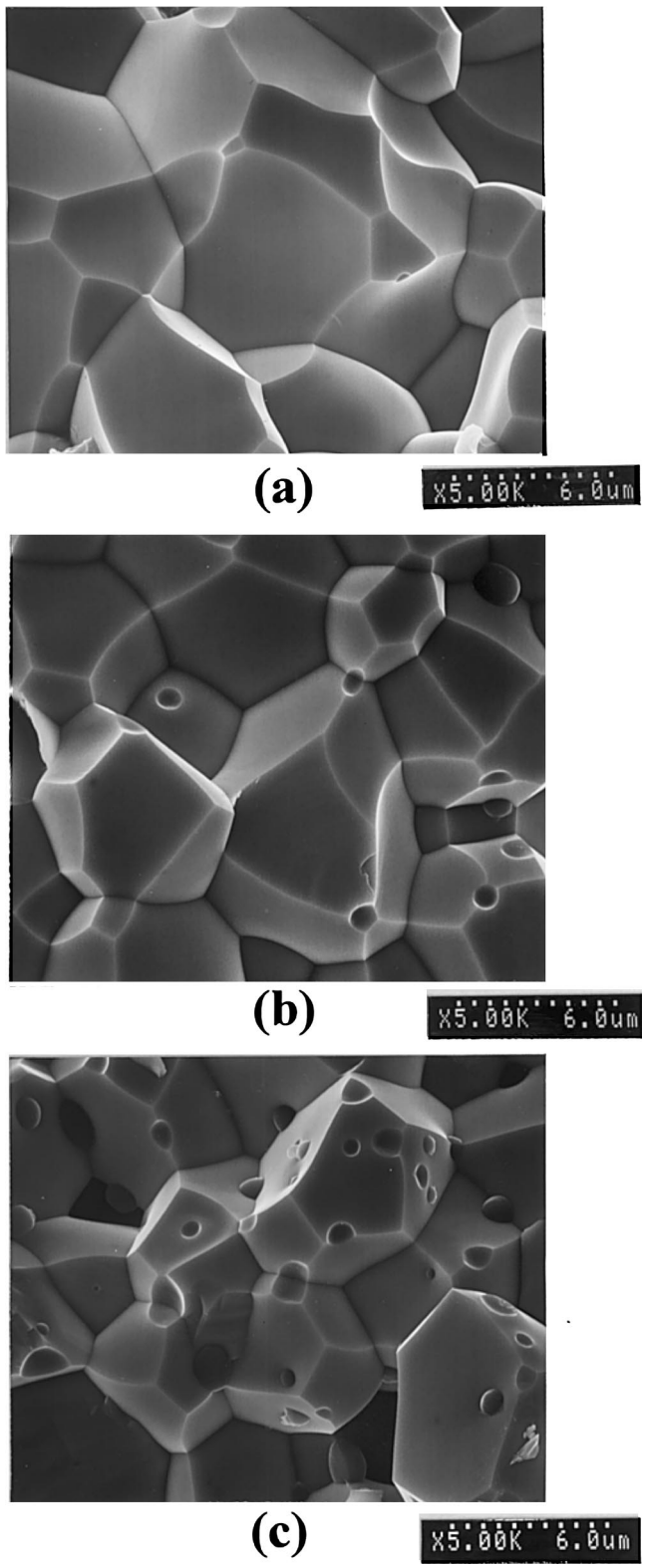

Fig. 4. Scanning electron micrographs of the fractured surface for 1000°C sintered (a) PMN0; (b) PMN5; and (c) PMN20.

The dielectric permittivity of 1000°C-sintered specimens were measured. All specimens are found to exhibit typical relaxor ferroelectric characteristics. The

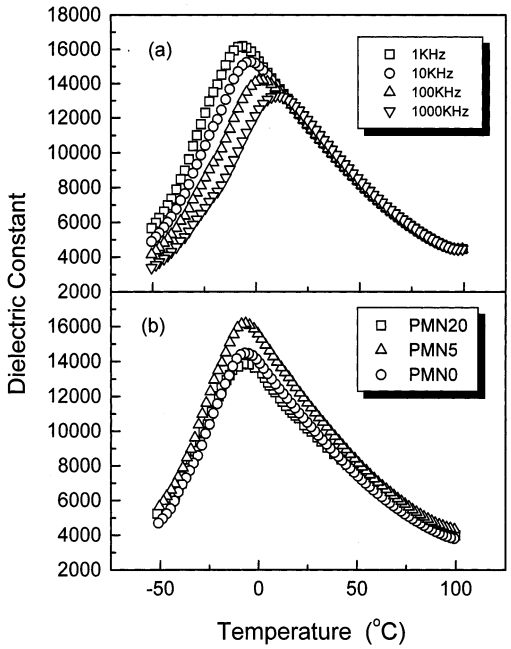

Fig. 5. (a) Dielectric permittivity of 1000°C-sintered PMN5 at various frequency and (b) dielectric permittivity of 1000°C-sintered PMN0, PMN5, and PMN20 at 1 kHz.

temperature and frequency dependence of dielectric permittivity for PMN5 is shown in Fig. 5a. With a decrease in temperature, a broad dielectric permittivity maximum appears, and dielectric permittivity substantially varies with frequency in low temperature region. Upon reducing the field frequency from 1 MHz to 1 kHz, the apparent Curie temperature decreases from 10 to -5°C. The dielectric permittivities of all three systems at 1 kHz are compared in Fig. 5b. All three systems have a broad dielectric maximum. In addition, it is found that PMN5 exhibits a largest maximum dielectric permittivity (16 200), and PMN20 has the smallest one (13 900). The variation in the magnitude of dielectric permittivity is attributed to the change in sintering density as well as composition. From the results in Figs. 3 and 5, it is revealed that the sintering density of specimens plays a more important role in affecting the dielectric permittivity.

4. Conclusions

The simultaneous synthesis and sintering of $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics have been investigated. During heating, the specimens expand at first while pyrochlore phase is formed. From temperature higher than 800°C, the formation and rapid sintering of $Pb(Mg_{1/3}Nb_{2/3})O_3$ occur simultaneously. After reaction sintering at 1000°C, pure perovskite phase of $Pb(Mg_{1/3}Nb_{2/3})O_3$ with high sintering density is achieved. The addition of 5 mol% excess MgO further enhances the densification process of $Pb(Mg_{1/3}Nb_{2/3})O_3$. However, when 20 mol% excess MgO is added, the presence of abundant MgO particles on the grain boundary hinders the densification process of $Pb(Mg_{1/3}Nb_{2/3})O_3$, thereby lowering the density. Due to high sintering density, the 5 mol% MgO-doped $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics exhibit high dielectric permittivity.

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