



Pyroelectricity of BaTiO₃-doped PMNT ferroelectric system for pyroelectric sensor

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Abstract

In this study, an MPB PMNT system containing 0.05 to 0.10 wt.% BaTiO₃ was synthesized using a traditional chemical method and its pyroelectricity was investigated. Pyroelectricity, dielectricity, and ferroelectricity of the synthesized BaTiO₃-PMNT system were analyzed by heat treatment at 1240~1280 °C for 4 hours to evaluate its applicability as a pyroelectric sensor. Unlike the simple ABO₃ ferroelectric, the BaTiO₃-doped PMNT system exhibited phase transition characteristics over a wide temperature range typical of complex perovskite structures. Although no dramatic change could be confirmed depending on the amount of BaTiO₃ added, stable pyroelectricity was maintained near room temperature and over a wide temperature range. When the amount of BaTiO₃ added increased from 0.05BaTiO₃-PMNT to 0.10BaTiO₃-PMNT, the electric field slightly increased from 5.00×10^3 kV/m to 6.75×10^3 kV/m, and the maximum value of remanent polarization slightly increased from 0.223 C/m² to 0.234 C/m². The pyroelectric coefficients of 0.05BaTiO₃-PMNT and 0.10BaTiO₃-PMNT at room temperature were measured to be ~ 0.0084 C/m²K and ~ 0.0043 C/m²K, respectively. The relaxor ferroelectric properties of the BaTiO₃-PMNT system were confirmed by analyzing the plot of K_{\max}/K versus $(T-T_{\max})^\gamma$. The BaTiO₃-doped MPB PMNT system showed a distinct pyroelectric performance index at room temperature, and the values were $F_v \sim 0.0362$ m²/C, $F_d \sim 0.575 \times 10^{-4}$ Pa^{-1/2}.

Keywords : BaTiO₃ ; PMNT ; Ferroelectric hysteresis ; Pyroelectricity.

1. Introduction

The PMNT [Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃] system possesses many excellent properties such as pyroelectricity, piezoelectricity, and ferroelectricity. PMN systems with a centrally asymmetric structure with short-range ordering of Mg²⁺ and Nb⁵⁺ ions do not exhibit long-range ordering and are therefore of great interest in solid-state physics. On the other hand, PbTiO₃, which transitions from

tetragonal to cubic crystals around 490 °C, has normal ferroelectricity. The PMN-PT binary system is very important and exhibits excellent ferroelectric properties when the PT mole fraction is 29 to 34% [1, 2]. For the application of the pyroelectric and piezoelectric properties of ferroelectric materials, in addition to high piezoelectric properties for low-field drives, the reliability and stability of the materials, including minimization of losses in cyclic polarization reversal, are essential [3, 4].

In this study, we closely analyzed the change in pyroelectricity by adding a small amount of BaTiO₃ to PMNT system containing 30% PT in

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the MPB PMNT composition. Based on this, the applicability of the BaTiO₃-PMNT system as a pyroelectric sensor was analyzed.

2. Experimental Procedure

After first synthesizing the MgO+Nb₂O₅→MgNb₂O₆ precursor, BaCO₃ and TiO₂ were finally synthesized and sintered at 1240~1280 °C for 4 hours to produce two BaTiO₃-PMNT compositions.

The phase and crystallinity of the specimens were investigated by XRD, with an XRD scan rate of 2°/min and a step size of 0.02°. To confirm the electrical properties of the BaTiO₃-PMNT system, the pyroelectric current was measured using an electrometer, and the capacitance was measured using an impedance analyzer. Before measuring the pyroelectric current, capacitance, and piezoelectric constant, electrodes were formed using silver and polarized with an electric field of ~15 kV/cm. In order to analyze the polarization characteristics of the BaTiO₃-PMNT system in response to the electric field, a modified S-T circuit was constructed and the ferroelectric hysteresis loop was measured.

3. Results and discussion

Figure 1 shows the XRD patterns at different sintering temperatures for BaTiO₃(x)-doped PMNT systems with x=0.05 and x=0.10. For both compositions, the (222) pyrochlore phase was observed at a sintering temperature of 1240 to 1260 °C, but a single perovskite phase (110) diffraction peak was observed at 1280 °C. This means that the perovskite cubic symmetry of the BaTiO₃-PMNT system requires heat treatment at 1280 °C or higher. In the case of the specimen heat-treated at 1280 °C, approximately

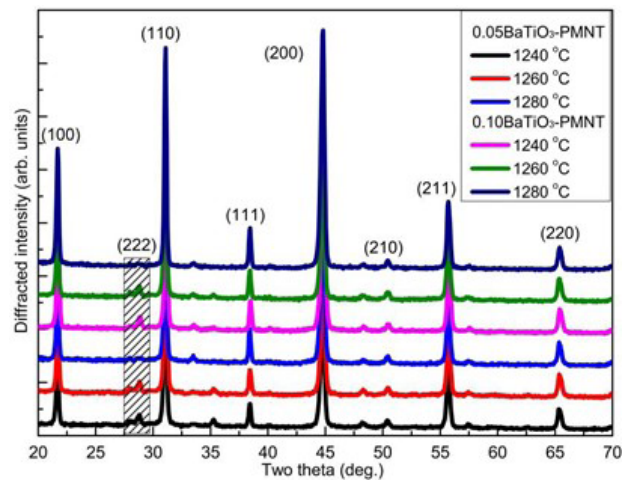


Fig. 1. XRD pattern of the BaTiO₃-doped PMNT system sintered at 1240~1280 °C for 4 hours.

97% of the phases were confirmed as a result of calculation using the equation “perovskite %=I_{perov}/(I_{perov}+I_{pyro})x100” using the XRD measurement intensities of (110) and (222). In XRD studies of the solid solution concentration near the MPB of the PMN-PT system, there is much evidence of a stable monoclinic phase between the rhombohedral and tetragonal phases. Additional analyzes are considered to explain the XRD peak positions and intensities of the BaTiO₃-doped MPB PMNT system, especially the low symmetry phases, i.e. rhombohedral and tetragonal phases.

The best routine to analyze the ferroelectric properties of a dielectric is to check the P-E hysteresis loop. The ferroelectric hysteresis loop can analyze ferroelectricity by changing the electric field versus remanent polarization in a ferroelectric material, and unlike paraelectricity, it has the important property that a remanent polarization value exists even when the electric field is 0 [5, 6]. Figures 2 and 3 show the ferroelectric hysteresis loops according to the sintering conditions of 0.05BaTiO₃-PMNT and 0.10BaTiO₃-PMNT. Figures 2 and 3 clearly show the difference in polarization versus electric field depending on the amount of BaTiO₃ added and especially the sintering conditions. At room temperature, the BaTiO₃-doped PMNT system showed a typically ferroelectric

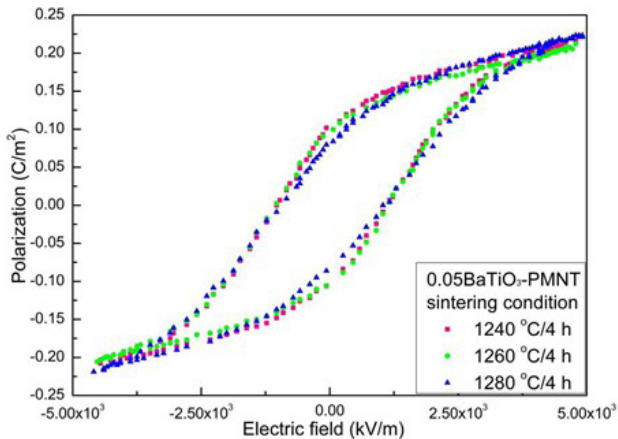


Fig. 2. The hysteresis loop of the 0.05BaTiO₃-doped PMNT system.

loop, and the electric field versus polarization increased with increasing sintering temperature and BaTiO₃ addition amount. When the amount of BaTiO₃ added increased from 0.05 to 0.10 and the electric field increased from 5.00×10^3 kV/m to 6.75×10^3 kV/m, polarization was saturated and the maximum value of polarization increased from 0.223 C/m² to 0.234 C/m². The coercive field of all specimens was 0.75~0.95 kV/m, which increased with the increase in the amount of BaTiO₃ added.

The pyroelectric current of the BaTiO₃-doped PMNT system measured as a function of temperature is $i_p = A_p(dT/dt) = A(dP_s/dT)(dT/dt)$, where A is the effective electrode area of the sample, P_s is the spontaneous polarization, T is the temperature and t is the time. Figure 4 shows the temperature dependence of the pyroelectric coefficient and spontaneous polarization of the BaTiO₃-doped PMNT system depending on the temperature between -50 °C and 150 °C. Analysis of the temperature dependence of the spontaneous polarization in Figure 4 reveals dramatic changes in the ferroelectric-ferroelectric phase transition region, which are closely related to the temperature dependence of the pyroelectric coefficient. As the measurement temperature rises, the dipole is rapidly destroyed, and as a result, the spontaneous polarization at the phase

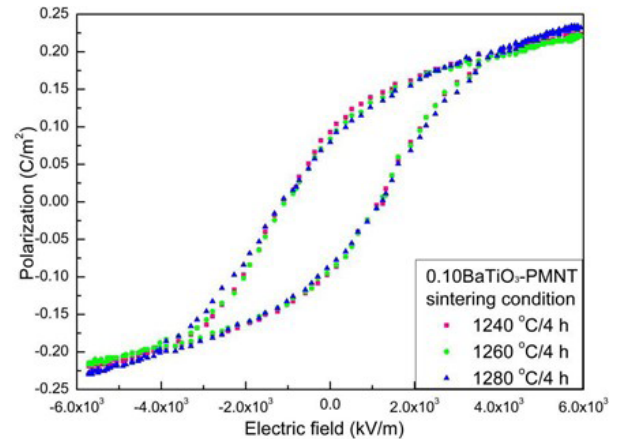


Fig. 3. The hysteresis loop of the 0.10BaTiO₃-doped PMNT system.

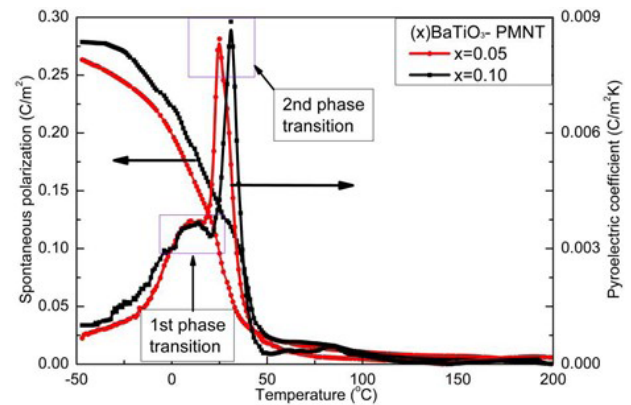


Fig. 4. Pyroelectric coefficient and spontaneous polarization of BaTiO₃-doped PMNT system.

transition temperature rapidly decreases. The spontaneous polarization at room temperature was analyzed to be over 0.12 C/m². The 1st and 2nd phase transitions were confirmed in the composition with BaTiO₃ addition amount, which is in good agreement with the general characteristics of the MPB PMNT system [1]. This phenomenon is because Ba²⁺ ions penetrate the perovskite crystal lattice and greatly affect the ferroelectric-ferroelectric transition temperature. As a result, the addition of Ba²⁺ ions leads to highly unusual pyroelectric properties, and the resulting diffuse pyroelectric properties are probably due to random dipole fields between cluster moments.

The relatively large pyroelectric coefficients of the two compositions reflect their

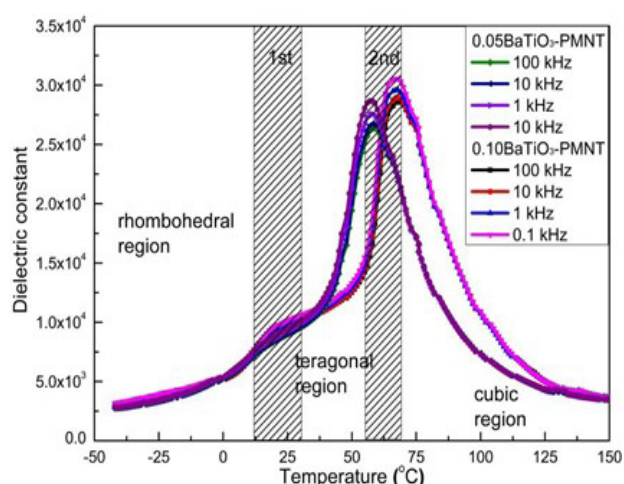


Fig. 5. Dielectric constant as a function of temperature for the BaTiO₃-doped PMNT system.

excellent stoichiometry and crystallization, as can be seen from the XRD data in Figure 1. The maximum pyroelectric coefficient of 0.05BaTiO₃-PMNT was measured to be ~ 0.0073 C/m²K, and that of 0.10BaTiO₃-PMNT was measured to be ~ 0.0032 C/m²K. Pure PMNT complex perovskite Mg²⁺, Nb⁵⁺, Ti⁴⁺ ions and Ba²⁺ ions with different sizes and coordination radii are penetrated to form a ferroelectric polar domain, resulting in a continuous phase transition from rhombohedral to tetragonal and from tetragonal to cubic structure.

Figure 5 shows the temperature dependence of the dielectric constant as the frequency increases from 0.10 to 100 kHz for two compositions: 0.05BaTiO₃-PMNT and 0.10BaTiO₃-PMNT. In relaxor ferroelectrics, as frequency increases, the dielectric constant decreases and the peak temperature increases. Because these ferroelectrics are composed of very heterogeneous materials, observable phase transitions are not clear, so they can be said to be almost independent of temperature. The weak dependence of the dielectric constant on frequency near the peak temperature indicates that nanometer-scale relaxors are not ideal dipole glasses but tend to have ferroelectric ordering of the cluster moments [7, 8]. The big difference between Figures 4 and 5 is that the relaxor depolarizes at a much lower temperature than

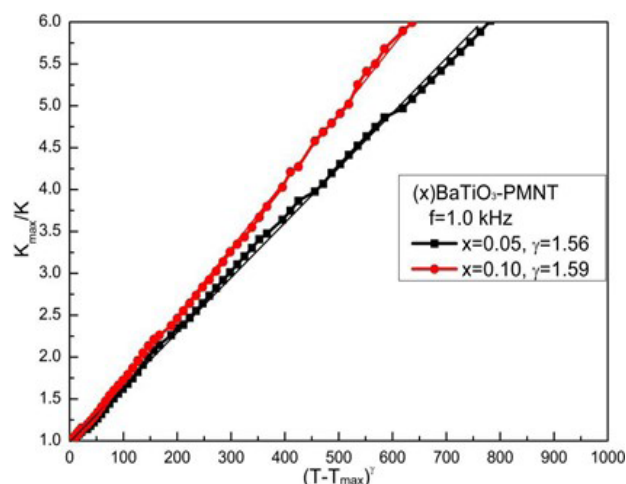


Fig. 6. Plot of K_{\max}/K versus $(T-T_{\max})^{\gamma}$ for the BaTiO₃-doped PMNT system.

the dielectric peak temperature, showing the characteristic that the dielectric peak temperature does not match the pyroelectric peak temperature.

For 0.05BaTiO₃-PMNT and 0.10BaTiO₃-PMNT in Figure 5, there are two phase transition regions in the dielectric constant versus temperature measurements. The peak around 20 °C is a low-temperature anomaly that may correspond to a phase transition from rhombohedral to tetragonal, and the second peak around 60 °C corresponds to a phase transition from tetragonal to cubic. At 25 °C and 1 kHz, the dielectric constants of 0.05BaTiO₃-PMNT and 0.10BaTiO₃-PMNT were measured to be 5847 and 5992, respectively. Meanwhile, the maximum dielectric constants of 0.05BaTiO₃-PMNT and 0.10BaTiO₃-PMNT were measured as 27548 and 29564, respectively.

Figure 6 is a plot of K_{\max}/K versus $(T-T_{\max})^{\gamma}$ of the PMNT system with BaTiO₃ added. From these data, it can be seen that the BaTiO₃-PMNT system exhibits large deviations from the Curie-Weiss law at temperatures well above the maximum dielectric constant. However, it is not easy to determine the temperature at which such deviations from the characteristics of relaxor ferroelectrics actually occur. In the case of Pb(B₁,B₂)O₃, the activation barrier is known to be determined by the dissociation of the

strong Pb-O-B bond to give the material relaxor properties. In atomic-level complex perovskites, ferroelectric active band B cations are dispersed even after the phase transition, and as a result, temperature diffusion characteristics are observed even in the high temperature region. If the local Curie temperature is Gaussian distributed, the reciprocal dielectric constant is “ $1/K = 1/K_{\max} + (T - T_{\max})^\gamma / 2K_{\max}^{\delta^2}$ ”, where K , K_{\max} , T_{\max} , δ and γ are the dielectric constant, maximum dielectric constant and peak temperature, diffuseness parameters and diffuseness component, respectively. γ , obtained from the slope of the $\log(1/K - 1/K_{\max})$ versus $\log(T - T_{\max})$ graph, is slightly higher at 1.56 and 1.59 when the BaTiO_3 addition amount is 0.05 and 0.10, respectively, unlike in the case of the ideal relaxor ferroelectric ($\gamma=2$). This means that the addition of BaTiO_3 , which has a first-order phase transition, slows down the diffusion [9].

When applying pyroelectric materials as detectors and sensors, the electrical properties of the material are determined as the figure of merit. In sensor applications, the required properties include low dissipation factor, specific heat, and high pyroelectric coefficient [10]. The voltage responsivity F_v and detectivity F_d of the 0.10BaTiO_3 -PMNT system were calculated using the two equations $F_v = p / (cV_{\text{erf}})$ and $F_d = p / (C_v \sqrt{\epsilon_r \epsilon_0 \tan \delta})$ were $F_v \sim 0.0362 \text{ m}^2/\text{C}$, $F_d \sim 0.575 \times 10^{-4} \text{ Pa}^{-1/2}$. For precision sensor applications, strict consideration of dopant materials is required in the future.

4. Conclusions

When prepared by the precursor method for compositions BaTiO_3 -doped PMNT, the electrical properties were excellent. Pyroelectric current and spontaneous polarization of BaTiO_3 -doped PMNT was measured as a function of temperature.

BaTiO_3 -doped PMNT is shown the characteristic of the successive phase transition. The pyroelectric coefficient of 0.05BaTiO_3 -PMNT was measured to be $\sim 0.0084 \text{ C/m}^2\text{K}$, and that of 0.10BaTiO_3 -PMNT was measured to be $\sim 0.0043 \text{ C/m}^2\text{K}$ at room temperature or more, which was much greater than LiNbO_3 series, and PZT, PMN-based and exhibited a similar value. The figures of merit ($F_v \sim 0.0362 \text{ m}^2/\text{C}$, $F_d \sim 0.575 \times 10^{-4} \text{ Pa}^{-1/2}$) of composition 0.10BaTiO_3 -PMNT are comparable to the earlier reports on lead-type pyroelectrics.

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