

Research Paper

Pyroelectricity of Ni-doped PMNT Ferroelectric for Pyroelectric Detector

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Abstract A pyroelectric properties of Ni(x)-doped PMNT systems were analyzed. Modified PMNT samples were prepared using the columbite structure method. Pyroelectric current, polarization, dielectric constant and dissipation factor of Ni-doped PMNT samples were measured as a function of temperature. By adding a small amount of NiO, pyroelectricity of PMNT is increased. Unlike the normal ABO_3 ferroelectric, Ni-doped PMNT showed properties for relaxor ferroelectric of causing the successive phase transition over a wide temperature. The optimum conditions for obtaining compositions with improvement ferroelectric properties are a nominal addition of 0.02 mole% Ni. Also, Ni-doped PMNT ferroelectric showed excellent pyroelectric figures of merit in the vicinity of room temperature. The pyroelectric coefficient ($0.00524 \text{ C/m}^2\text{K}$ at 25°C) and figures of merit ($F_v \sim 0.039 \text{ m}^2/\text{C}$ and $F_d \sim 0.664 \times 10^{-4} \text{ Pa}^{-1/2}$) of composition PMNT with 0.02 mole% Ni are comparable to the earlier reports on lead-type pyroelectrics.

Keywords: PMNT, Pyroelectricity, Responsivity, Detectivity

I. Introduction

Some lead-based ferroelectrics have long been employed as single or multi-element passive infrared (IR) devices for fire detectors and un-cooled thermal images [1]. Historically, $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) has a great advantage, which exhibits a good electrical. PMN appears to have the noncentro-symmetry structure only below -15°C . When Mg^{2+} and Nb^{5+} ions of the PMN structure have short range ordering, it becomes a diffuse phase transition. PMN relaxor compared with other complex perovskites has attracted a strong interest in solid state physics for which no long-range order emerges. Normal ferroelectric PbTiO_3 (PT) shows a cubic crystal structure above the phase transition temperature ($\sim 490^\circ\text{C}$). With the addition of PT, the PMN-PT (PMNT) system exhibits a morphotropic phase boundary (MPB) at between 29 and 35 mole% PT [2]. The composition near the MPB between the rhombohedral and tetragonal phases exhibits excellent ferroelectric properties. These PMNT MPB compositions remain the subject of intense research, while the pyroelectric properties of the material depend on the small dopants, such as Bi, Fe, La, Mn and Ni. Many studies for PMNT have been conducted, but got a great result there was limited improvement of the pyroelectric properties of PMN. Therefore, in this study, $\text{Pb}[(\text{Mg},\text{Nb})_{0.7}\text{Ti}_{0.3}]$ with 30 mole% PT (which is close to the MPB) was chosen in the PMN-PT systems. Also, the

aim of the study was to examine the effect of the addition of Ni on the electrical properties of the PMNT system.

II. Experimental Procedure

The Ni(x)-doped $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3$ with concentrations where $x=0-0.04$ mole% were prepared using the B-site columbite MgNb_2O_6 precursor method. This process basically involves the pre-reaction of MgO and Nb_2O_5 to form the MgNb_2O_6 prior to reaction with PbCO_3 , TiO_2 and NiO. The calcining and sintering were carried out at 900°C for 4 hours and at 1200°C for 1.5 hours, respectively. To measure the electrical properties of the PMNT, a silver (99.9%) electrode was coated on both sides of the specimens using a thermal evaporator. Before measurement electrical quantities, applying an electric field to the sample at room temperature of about 20 kV/cm was treated with the poled. Electrical quantities, such as pyroelectric current, polarization, capacitance, and dissipation factor of sintered PMNT were examined at various temperature between R.T. and 200°C using an electrometer, an impedance analyzer, an environment chamber, and a control unit as the interface. Especially, the pyroelectric currents were measured by the modified Byer-Roundy method [3] as the samples were heated at a rate of $2^\circ\text{C}/\text{min}$ through the phase transition.

III. Discussion

Ni(x)-doped PMNT were completely prepared using a solid

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state reaction at 1200°C for 1.5 hours. The pyroelectric characteristic of the ferroelectrics can be found by analysis of the pyroelectric current and polarization measurements as a function of temperature. The pyroelectric coefficient is one of the most important parameters for pyroelectric effects to manifest themselves. Therefore, the pyroelectric coefficient (p) can be calculated via Eqs. (1) and (2), where i_p is the pyroelectric current, P_s is the spontaneous polarization, A is the area of the electrodes, and dT/dt is the rate of heating:

$$i_p = Ap \frac{dT}{dt} \quad (1)$$

and

$$p = \frac{dP_s}{dT} \quad (2)$$

The figure of merit of pyroelectric materials is a very important factor in sensor and detector applications. The figure of merit can be calculated from Eqs. (3) and (4):

$$F_v = \frac{p}{C_v \epsilon_r \epsilon_0} \quad (3)$$

and

$$F_d = \frac{p}{C_v \sqrt{\epsilon_r \epsilon_0} \tan \delta} \quad (4)$$

where F_v and F_d are figures of merit for the high voltage responsivity and the high detectivity, respectively, C_v is the volume specific heat, ϵ_r is a relative dielectric constant, ϵ_0 is a permittivity of free space, and $\tan \delta$ is the dissipation factor of the PMNT system [4].

Fig. 1(a) shows 1st phase transition of the pyroelectric coefficient versus temperature between 40°C to 120°C for the base composition modified with Ni(x) as a function of the amount additive, from 0 to 0.04 mole% Ni. In all compositions, a broad phase transition in the vicinity low temperature region was observed with the increasing of the mole fraction of Ni, the pyroelectric coefficient decreases in magnitude and the maxima shifts to a lower temperature. This effect may be associated with NiO incorporation into the perovskite lattice; that is, Ni²⁺ ions enter the lattice, affecting the 1st transition temperature. The glassy property of relaxor ferroelectric in un-electrified states probably arises due to the random dipole fields between electric domains. Of course, relaxor ferroelectric material is very inhomogeneous components. The pyroelectric coefficient at room temperature of all compositions was 0.0028 pC/m²K or more, which was much greater than LiNbO₃ series, and PZT, PMN-based and exhibited a similar value. Fig. 1(b) shows 2nd phase transition of the pyroelectric coefficient versus temperature between 100°C to 180°C for Ni-doped PMNT systems. In all compositions, a sharp phase transition unlike the 1st phase transition was observed, the pyroelectric coefficient increases in magnitude

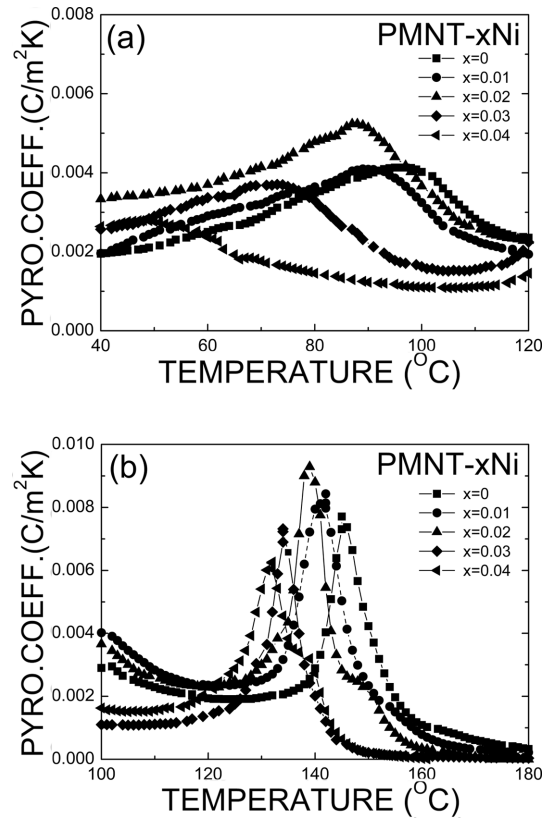


Figure 1. Pyroelectric coefficient as a function of temperature for Ni-doped PMNT in the vicinity of 1st and 2nd phase transition regions.

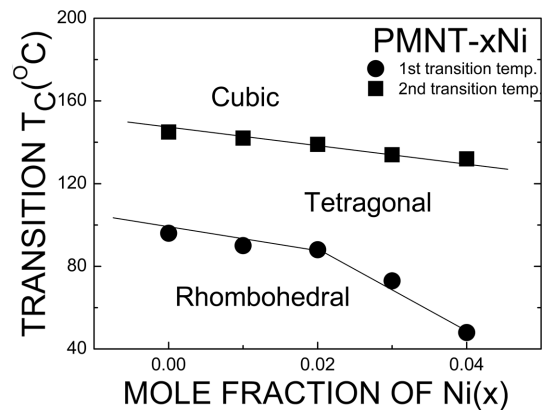


Figure 2. Variation of the transition temperature versus mole fraction of Ni(x) for Ni-doped PMNT.

and the maxima shifts to a lower temperature with the increasing of the mole fraction of Ni(x). Pyroelectric coefficient was increased with the increase of ~0.02 mole% Ni. The higher pyroelectric coefficient of the samples reflects the good stoichiometry and crystallization. The maximum pyroelectric coefficient (~0.0093 pC/m²K) was observed at 0.02 mole% Ni content. However, for Ni(x) more than ~0.02, the pyroelectric coefficient slightly was decreased. Fig. 2 shows variation of the peak temperature of pyroelectric coefficient as a mole fraction of Ni(x) in the PMNT systems. The 1st and 2nd transition temperature of pyroelectric coefficient increases almost linearly as amount

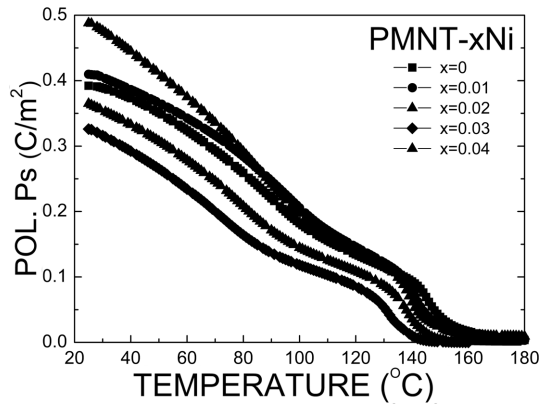


Figure 3. Spontaneous polarization as a function of temperature for Ni-doped PMNT.

Table 1. Dielectric properties of the Ni-doped PMNT systems at 1 kHz.

Compositions [Ni(x) mole%]	Dielectric constant (K)		Dissipation factor $\tan\delta_{25^\circ\text{C}}$
	$K_{25^\circ\text{C}}$	K_T	
0	2492	25740	0.0165
0.01	2556	26565	0.0091
0.02	2574	27455	0.0082
0.03	2655	23220	0.0112
0.04	2620	22355	0.0074

of Ni(x) in the composition increases. Mg^{2+} , Nb^{5+} and Ti^{4+} ions of B-site must have a radius of different size and coordination, due to 1st phase transition from rhombohedral to tetragonal and 2nd phase transition from tetragonal to cubic structure at near peak temperature in PMNT, ferroelectric polar domains are formed. In most cases, as in the pyroelectric data, two major anomalies corresponding to the rhombohedral→tetragonal→cubic phase transitions were observed. Therefore, Ni-doped PMNT systems are clearly showed the characteristic of the successive phase transition.

Fig. 3 shows the spontaneous polarization versus temperature in the Ni-doped PMNT systems. Spontaneous polarization, indicating the destruction of the other dipole in temperature increase, showed a value of 0.47 C/m^2 in the composition was added to 0.02 mole% Ni. The value of this degree is great compared to the level of the spontaneous polarization value of ferroelectric relaxor other. Table 1 shows the dielectric properties. Fig. 4 shows the figures of merit responsivity F_v and detectivity F_d as a function composition of Ni(x) in the PMNT systems. The optimum conditions for obtaining compositions with improvement ferroelectric properties are a nominal addition of 0.02 mole% Ni. Also, Ni-doped PMNT ferroelectric showed excellent pyroelectric figures of merit in the vicinity of room temperature. The figures of merit ($F_v \sim 0.039 \text{ m}^2/\text{C}$, $F_d \sim 0.664 \times 10^{-4} \text{ Pa}^{-1/2}$) of composition PMNT with 0.02 mole% Ni are comparable to the earlier reports on lead-type pyroelectrics [5-8]. Achieving stabilization of energy loss,

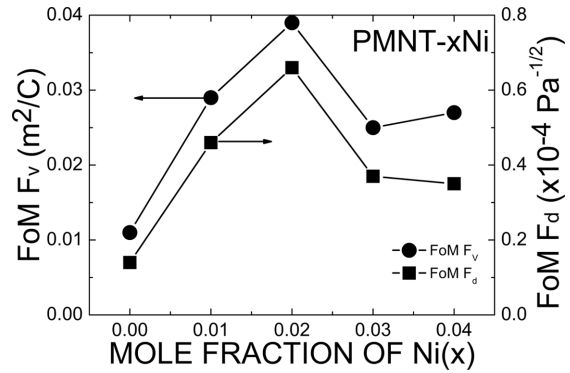


Figure 4. Responsivity F_v and detectivity F_d versus mole fraction of Ni(x) for Ni-doped PMNT.

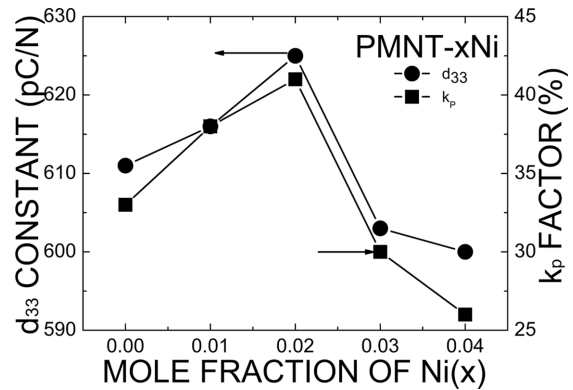


Figure 5. Piezoelectric constant d_{33} and electromechanical coupling factor k_p versus mole fraction of Ni(x) for Ni-doped PMNT.

and will be able to improve the applicability of a pyroelectric sensor by adding an impurity which can improve the pyroelectric properties. Thus, the important properties to look for in sensors are low dissipation factor and specific heat, and high pyroelectric coefficient. The piezoelectric constant (d_{33}) was found to be about 500-600 pC/N for Ni-doped PMNT systems. Also, the electromechanical coupling factor (k_p) was found to be 0.274-0.342 (as shown in Fig. 5). However, piezoelectric properties did not show any significant improvement as expected. It is necessary to ensure a more precise addition of dopant materials in the future.

IV. Conclusions

When prepared by the precursor method for Ni-doped PMNT compositions, the electrical properties were excellent. Pyroelectric current and spontaneous polarization of Ni-doped PMNT was measured as a function of temperature. Ni-doped PMNT is shown the characteristic of the successive phase transition. The pyroelectric coefficient at room temperature of all compositions was $0.0028 \text{ pC/m}^2\text{K}$ or more, which was much greater than LiNbO_3 series, and PZT, PMN-based and exhibited a similar value. The pyroelectric coefficient at peak temperature of Ni-doped PMNT composition was $0.006 \text{ pC/m}^2\text{K}$ or more. The

figures of merit ($F_v \sim 0.039 \text{ m}^2/\text{C}$, $F_d \sim 0.664 \times 10^{-4} \text{ Pa}^{-1/2}$) of composition PMNT with 0.02 mole% Ni are comparable to the earlier reports on lead-type pyroelectrics.

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