

## Research Paper

# Improvement of the Figure of Merit in $\text{Pb}[(\text{Mg}_{1/3}\text{Ta}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3$ Systems

Yeon Jung Kim\*

Center for Innovative Engineering Education, Dankook University, Yongin 16890, Korea

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**Abstract** The  $\text{Pb}[(\text{Mg}_{1/3}\text{Ta}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3+x\text{wt}\%\text{PbO}$  systems at temperature of 1250°C for 4 hours was successful synthesized. In this study, PbO-doped  $\text{Pb}[(\text{Mg}_{1/3}\text{Ta}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3$  systems with non-linear behaviors showed ordering-degree dependence at the low temperature range were prepared using the columbite precursor method. And the characteristic of remnant polarization vs. electric field were analyzed. The pyroelectric, dielectric and piezoelectric properties of partially disordered  $\text{Pb}[(\text{Mg}_{1/3}\text{Ta}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3+x\text{wt}\%\text{PbO}$  solid solutions were studied as a function of temperature, frequency, and electric field. It showed distinct features of temperature dependent of pyroelectric coefficient, spontaneous polarization and dielectric constant at about 50°C. The figure of merit was calculated as pyroelectric coefficient, dielectric constant and dissipation factor. It was found that the high voltage responsivity  $F_V$ , high detectivity  $F_D$  were 0.0373  $\text{m}^2/\text{C}$  and  $0.6735 \times 10^{-4} \text{ Pa}^{-1/2}$ , respectively, in the  $\text{Pb}[(\text{Mg}_{1/3}\text{Ta}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3+3.0 \text{ wt}\%\text{PbO}$  system.

**Keywords:**  $\text{Pb}[(\text{Mg}_{1/3}\text{Ta}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3$ , Hysteresis, Successive phase transition, Figures of merit

## I. Introduction

Complex perovskite relaxors with the general formula  $\text{Pb}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$ , are of high interest due to their excellent piezoelectric and pyroelectric properties [1]. Relaxor ferroelectrics, exhibit unusual strong frequency-dependent properties because of the chemical inhomogeneity of the nano-scale in the B-site sub-lattice. Lead magnesium tantalate [ $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ , PMT], is a well-known relaxor ferroelectrics, analogous to  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  and  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ . Lead titanate [ $\text{PbTiO}_3$ , PT] is also historic ferroelectrics. Crystal PMT, PT appears to have the ideal structure of perovskite only above  $-98^\circ\text{C}$ ,  $490^\circ\text{C}$ , respectively. When these materials form a solid solution, the phase transition temperature is expected to vary with the composition. To date, few papers have reported on the relaxor, ferroelectric, pyroelectric properties and morphotropic phase boundary (MPB) of PMT and its solid solutions. But, material scientists are very interested in infrared detector (IR) applications of PMT crystal, until before the powerful development lead-free materials. Despite extensive studies of the PMT ceramics, development of PMT with an excellent performance is insufficient. As detailed in [2~5], with the addition of PT, the  $(1-x)\text{PMT}-x\text{PT}$  (PMTT) composition exhibits a MPB at a between 25 and 35 mole% of PT, even though many researchers have published a slightly different MPB system. These MPB compositions have been found to exhibit potential

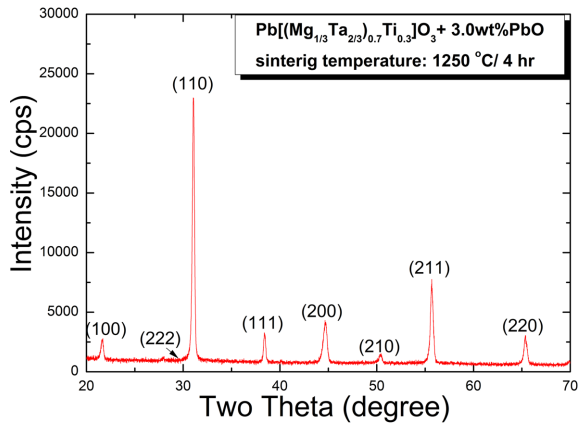
applications.

Therefore, this experiment is intended to improve the pyroelectric material applications in particular  $\text{Pb}[(\text{Mg}_{1/3}\text{Ta}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3$  [PMTT] composition in the MPB. To understand the pyroelectric application of the PbO-doped  $\text{Pb}[(\text{Mg}_{1/3}\text{Ta}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3$  [PMTT+xwt%PbO] is discussed by carefully analyzing the experimental data. Also it analyzed the high voltage responsivity and high detectivity quality of the PMTT+xwt%PbO series ( $x=1.0\sim 4.0$ ). The purpose of the investigation was to obtain ceramics having lower dielectric constant, dissipation factor, and higher pyroelectric coefficient than those of a base material and to develop a material having a high pyroelectric figure of merit at room temperature.

## II. Experimental Procedure

Compositions PMTT+xwt%PbO ( $x=1.0\sim 4.0$ ) were prepared using the columbite precursor method as described by Swartz and Shrout [6]. The PMTT+xwt%PbO green pellet was calcined at  $900^\circ\text{C}$  for 4 hours and the PMTT+xwt%PbO pellet were sintered at  $1250^\circ\text{C}$  for 4 hours. The XRD pattern of the PMTT+3.0wt%PbO samples are shown in Fig. 1. X-ray diffraction patterns obtained on a laboratory diffractometer with  $\text{CuK}\alpha$  radiation confirmed the formation of perovskite phases with no evidence of any impurities. The ferroelectric hysteresis loops were monitored using a modified Sawyer-Tower method [7]. The pyroelectric current and polarization were measured by the modified static Byer-Roundy method [8] as the samples were heated, again at a rate of  $4^\circ\text{C}/\text{min}$ , though the phase transition region. Pyroelectric coefficient

\*Corresponding author  
E-mail: yjkim80@dankook.ac.kr



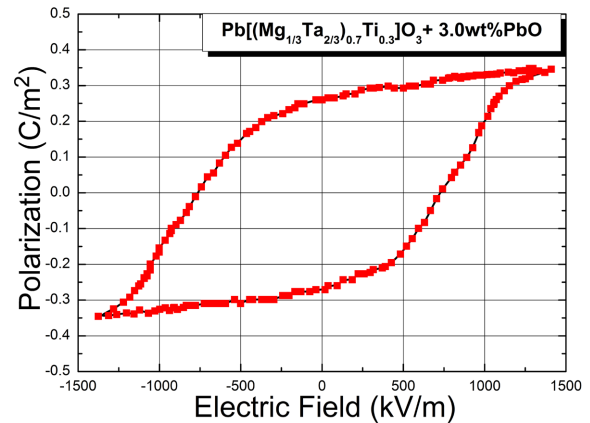
**Figure 1.** XRD patterns for sintered sample of the PMTT+3.0 wt%PbO system.

is routinely calculated from the well-known equation follows  $i_p = Ap \frac{dT}{dt}$ , where  $i_p$  is the pyroelectric current,  $A$  is the area of sample,  $p$  is the pyroelectric coefficient, and  $dT/dt$  is the heating rate. The capacitance and dissipation factor of sintered PMTT+xwt%PbO were examined at various temperature ( $-50$ – $150^\circ\text{C}$ ) and frequency ( $0.1$ – $100$  kHz) with a heating rate of  $4^\circ\text{C}/\text{min}$  using a HP 4284A impedance analyzer. Piezoelectric properties were measured by modified resonance-antiresonance method and  $d_{33}$  meter [9].

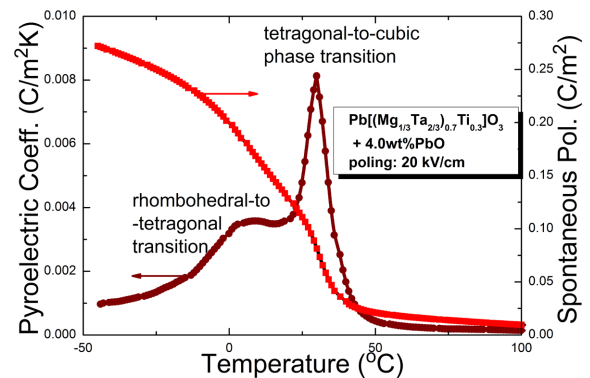
### III. Results and Discussion

Fig. 2 shows the ferroelectric hysteresis loop of the PMTT+3.0 wt%PbO system, which were taken from sintered at  $1250^\circ\text{C}$  for 4 hours. Shape of the measured hysteresis loop at room temperature showed a rectangular loop of relaxor ferroelectrics. In general, the value of both the remnant polarization and the coercive field decreased in the MPB of binary and ternary complex systems. As shown in Fig. 2, hysteresis property of the PMTT+3.0 wt%PbO system showed the characteristics of a typical ferroelectric solid solution. Occurrence of maximum remnant polarization in the PMTT+3.0 wt%PbO system were comparable to the values published for the binary complex perovskites can be attributed to the increase in pseudo-cubic domains transformation into tetragonal domains. Values of remnant polarization and coercive field of the PMTT+3.0 wt%PbO system at the room temperature were  $0.2598 \text{ C}/\text{m}^2$  and  $741.9 \text{ kV}/\text{m}$ , respectively.

Fig. 3 shows the pyroelectric coefficient and the spontaneous polarization as a function of temperature of the PMTT+4.0 wt%PbO system. Most of the complex perovskite ferroelectrics have several phase transition regions. Therefore, Fig. 3 shows two pyroelectric peaks corresponding to rhombohedral-to-tetragonal and tetragonal-to-cubic transitions are observed in the composition of PMTT+4.0 wt%PbO. The first peak region represents the abrupt change in  $0$ – $20^\circ\text{C}$ . That is, the phase transition region of the ferroelectric-to-ferroelectric means in the PMTT+4.0 wt%PbO. The



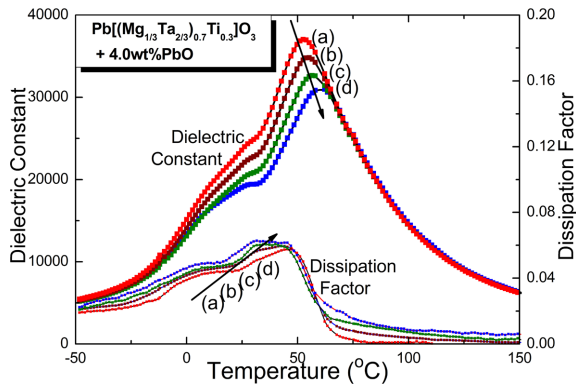
**Figure 2.** The hysteresis loop of the PMTT+3.0wt%PbO system.



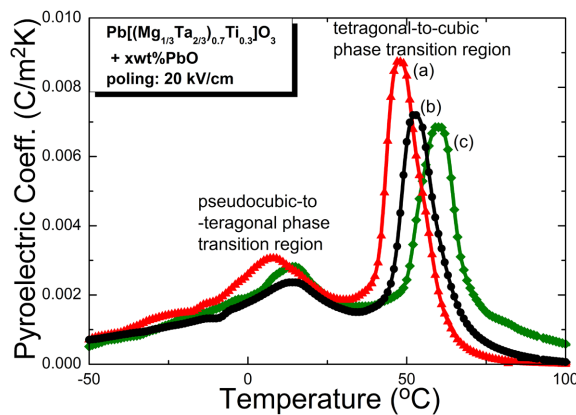
**Figure 3.** The pyroelectric coefficient and spontaneous polarization vs. temperature for the PMTT+4.0wt%PbO system.

second peak region illustrates the pyroelectric coefficient increases initially at  $25^\circ\text{C}$  and then decreases rapidly with increasing temperature. Sure, the phase transition region of the ferroelectric-to-paraelectric means in the PMTT +4.0 wt%PbO. The spontaneous polarization decreases gradually with increasing temperature, but does not vanish at the transition temperature ( $\sim 30^\circ\text{C}$ ) of the PMTT+4.0 wt%PbO system, as shown in Fig. 3. It is clear that the temperature characteristics of spontaneous polarization show a typical diffuse phase transition. The reason for this is not yet clear. But, it is expected that the micro-regions of tetragonal and cubic phases coexist in the transition region near the second phase transition. The origin the fact that a successive phase transition of Fig. 3 can be retained for a wide range of conventional manufacturing conditions has real practical advantages. Therefore, the ferroelectric relaxor can be synthesized having excellent pyroelectric applications with careful selection of the various dopants.

Fig. 4 shows plot of the dielectric constant and the dissipation factor vs. temperature at various frequencies ( $0.1$ – $100$  kHz) of the PMTT+4.0wt%PbO system. Dielectric responses of relaxor ferroelectrics are due to the motion of domain walls and their interaction with the lattice defects [10]. The dielectric constant and dissipation factor as a function temperature at heating process measurements in the PMTT+4.0 wt%PbO system. The



**Figure 4.** Temperature dependence of dielectric constant and dissipation factor at various frequency for the PMTT+4.0 wt%PbO system. (a) 0.1 kHz, (b) 1 kHz, (c) 10 kHz, (d) 100 kHz.



**Figure 5.** The pyroelectric coefficient as a function of temperature for the PMTT+xwt%PbO systems. (a)  $x=0.3$ , (b)  $x=0.2$ , (c)  $x=0.1$ .

dielectric constant of well-sintered solid solutions is excellent, but dissipation factor is stable. Thus, the dielectric constant of PMTT+4.0 wt%PbO system was the highest (34812 at 1 kHz). Fig. 4 shows the maximum dielectric constant (37035 at 0.1 kHz to 30974 at 100 kHz) decreased with increasing frequency, and the dielectric transition temperatures (74°C at 0.1 kHz to 79°C at 100 kHz) also increased in the PMTT+4.0 wt%PbO system. Relatively large dielectric dispersion is observed at temperatures near the phase transition region. The PMTT+xwt%PbO systems were pseudo-cubic (rhombohedral) and tetragonal phases in ferroelectric state. The phase transition temperature corresponds to the transition from the non-polarized state into a polarized state. As a result of the above, the measured dielectric constant showed typical relaxor ferroelectric material properties. The PMTT+3.0 wt%PbO composition exhibited frequency dispersion behavior of both dielectric constant and dissipation factor, which is a characteristic of relaxor ferroelectrics. The dielectric constant is gradually decreased with an increase in frequency, and dissipation factor increased. This is the most typical characteristics of diffuse phase transition due to compositional fluctuations and micro-inhomogeneity. It

**Table 1.** The piezoelectric and pyroelectric properties of the PMTT+xwt%PbO systems.

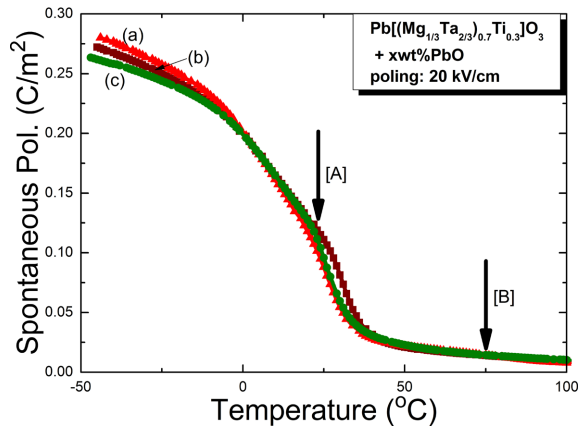
Compositions (xwt%PbO)	Piezoelectric constant		Figure of merit	
	$d_{33}$ (pC/N)	$k_p$ (%)	$F_V$ (m <sup>2</sup> /C)	$F_D$ (x10 <sup>-4</sup> Pa <sup>-1/2</sup> )
1.0	333.63	0.362	0.0127	0.1659
2.0	349.91	0.356	0.0128	0.2706
3.0	374.48	0.383	0.0373	0.6735
4.0	362.54	0.379	0.0356	0.6523

$d_{33}$ : the piezoelectric constant,  $k_p$ : the planar electromechanical coupling factor,  $F_V$ : the high voltage responsivity,  $F_D$ : the high detectivity.

is clear that, as the frequency increases, since these properties seem to need a lot of energy required for the rotation of the dipole. Such behaviors coincides with a freezing of nano-cluster occurs at temperature in the vicinity of room temperature. The transformation of a well-ordered sample into a disordered one is correlated with a significant change in the dielectric properties as a function of temperature and frequency [11]. These characteristics are in good agreement with the pyroelectric coefficient and spontaneous polarization properties of Fig. 3. The mechanism of phase transition in the PMTT+4.0 wt%PbO is different from the Curie-Weiss law, as shown in Fig. 4. Due to low symmetry of tetragonal phase at approximately phase transition region, ferroelectric domains are formed. Therefore, it deviation from the Curie-Weiss law in PMTT+4.0 wt%PbO system indicates the increase of the short range ferroelectric order. Finally, the PMTT+xwt%PbO systems were determined to exhibit a typical diffuse phase transition characteristics.

Fig. 5 shows the pyroelectric coefficient for various compositions in the PMTT+xwt%PbO systems as a function of temperature. The maximum pyroelectric coefficient about 0.00873 C/m<sup>2</sup>K at transition temperature increases with additions of PbO up to 3.0wt% and then decreases about 0.00813 C/m<sup>2</sup>K with further additions of 4.0 wt%PbO. As the PbO concentration increases, the phase transition temperature gradually decreases. The decrease in the phase transition temperature indicates that PbO is incorporated into PMTT sub-lattice. It can be seen that the increase in the small amount of PbO obviously affected phase transition temperature, which decreased approximately linearly. These phenomena may be resulted in the distribution of ions having different ionic radii in the same sub-lattice of a complex perovskite structure, but they cannot be fully explained at present. The PbO adding results in a shifting of phase transition temperature by about 6°C/wt%PbO downward in PMTT+xwt%PbO systems. Therefore, with an addition of PbO, the phase transition temperature of the PMTT can be suitably adjusted for the room temperature pyroelectric applications.

Table 1 summarized the piezoelectric and pyroelectric properties of PMTT+xwt%PbO systems with the piezoelectric constant ( $d_{33}$ ), planar electromechanical coupling factor ( $k_p$ ),



**Figure 6.** The spontaneous polarization as a function of temperature for the PMTT+xwt%PbO systems.

high voltage responsivity ( $F_V$ ) and high detectivity ( $F_D$ ). Table I shows the  $d_{33}$  was found to be about 333–374 pC/N for the PMTT+xwt%PbO systems. And the  $k_p$  was found to be about 0.356–0.368, as shown Table I. Recently, the pyroelectric effect of ferroelectrics has attracted considerable attention for application to infrared detectors (IR) [12,13]. This IR application required in such large pyroelectric coefficient, low dielectric constant and low dissipation factor at room temperature. Achieving stabilization of energy loss, and will be able to improve the applicability of pyroelectric sensor by adding an impurity which can improve the pyroelectric properties. The pyroelectric response of a material is generally related to device application by the figures of merit  $F_V = \frac{p}{c_v \epsilon_r \epsilon_0}$  and  $F_D = \frac{p}{c_v \sqrt{\epsilon_r \epsilon_0} \tan \delta}$ , where  $C_V$  is the volume specific heat,  $\epsilon_r$  is a relative dielectric constant,  $\epsilon_0$  is a permittivity of free space, and  $\tan \delta$  is the dissipation factor. Thus, the important properties to look for in sensors are high pyroelectric coefficient, low volume specific heat, low dielectric constant and low dissipation factor. The  $F_V$  and  $F_D$  of PMTT+xwt%PbO compositions were comparable to the values published for the binary and ternary Pb-based materials [13–16]. Table 1 shows the  $F_V$  was found to be about 0.0127–0.0373  $\text{m}^2/\text{C}$  for the PMTT+xwt%PbO systems. And the  $F_D$  were about 0.1659–0.6735  $\times 10^{-4} \text{ Pa}^{-1/2}$ , as shown Table 1.

Fig. 6 shows the spontaneous polarization vs. temperature in the PMTT+xwt%PbO systems. Pyroelectric depolarization studies showed that the spontaneous polarization of relaxor ferroelectric drops down more smoothly, while first-order ferroelectric depolarize abruptly within the phase transition region. Spontaneous polarization, indicating the destruction of the other dipole in temperature increase, showed a value of 0.0879  $\text{C}/\text{m}^2$  at 25°C in the composition was PMTT+3.0 wt% PbO. The spontaneous polarization decreases gradually with increasing temperature, but does not vanish at transition temperature [A] region of the PMTT+xwt%PbO systems, as shown in Fig. 6. In particular, the spontaneous polarization in

the temperature region [B] after the phase transition is not completely destroyed. This is the most typical characteristics of relaxor ferroelectrics. Value of this degree is great compared to the level of spontaneous polarization value of ferroelectric relaxor other.

#### IV. Conclusions

X-ray diffraction patterns obtained on a laboratory diffractometer with  $\text{CuK}\alpha$  radiation confirmed the formation of perovskite phases with no evidence of any impurities. Values of remnant polarization and coercive field at the room temperature were 0.2598  $\text{C}/\text{m}^2$  and 741.9  $\text{kV}/\text{m}$ . Hysteresis property of the PMTT+3.0 wt%PbO system showed the characteristics of a typical ferroelectric ceramic. The spontaneous polarization decreases gradually with increasing temperature, but does not vanish at the transition temperature of the PMTT+xwt%PbO systems. All of samples show two pyroelectric peaks corresponding to rhombohedral-to-tetragonal and tetragonal-to-cubic transitions are observed in the composition of PMTT+xwt%PbO. The dielectric constant is gradually decreased with an increase in frequency, and dissipation factor increased. Maximum dielectric constant of PMTT+4.0 wt%PbO system was value of 34812 at 1 kHz. The mechanism of phase transition in the PMTT+xwt%PbO is different from the Curie-Weiss law. The maximum pyroelectric coefficient about 0.00873  $\text{C}/\text{m}^2\text{K}$  at transition temperature increases with additions of PbO up to 3.0 wt% and then decreases about 0.00813  $\text{C}/\text{m}^2\text{K}$  with further additions of 4.0 wt%PbO. Spontaneous polarization showed a value of 0.0879  $\text{C}/\text{m}^2$  at 25°C in the composition was PMTT+3.0 wt%PbO. Maximum values of  $F_V$  and  $F_D$  were found to be 0.0373  $\text{m}^2/\text{C}$  and 0.6735  $\times 10^{-4} \text{ Pa}^{-1/2}$  for the PMTT+3.0 wt%PbO system. The high voltage responsivity  $F_V$  and the high detectivity  $F_D$  of these solid solutions is comparable to the values published for the complex perovskites.

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