World Scientific
www.worldscientific.com

EFFECT OF Pb VOLATILIZATION ON DIELECTRIC PROPERTIES OF $0.77PbMg_{1/3}(Nb_{0.9}Ta_{0.1})_{2/3}O_3$-$0.23PbTiO_3$

C. ZHANG and J. T. WANG*

*Department of Physics, Southern University and A&M college
Baton Rouge, LA 70813, USA
Jtwang@grant.phys.subr.edu

M. Q. QIAN

*Institute of Mechanics, Chinese Academia of Science
Beijing, 100080, China*

T. P. CHEN

*Department of Physics, University of North Dakota
Grand Forks, ND 58202, USA*

I. AKUJOBI

*Department of Physics, Southern University and A&M college
Baton Rouge, LA 70813, USA*

R. E. FERRELL

*Department of Geology & Geophysics, Louisiana State University
Baton Rouge, LA 70803*

Lead magnesium niobate-lead titanate (PMN-PT) is an intriguing candidate for applications in many electronic devices such as multi-layer capacitors, electro-mechanical transducers etc. because of its high dielectric constant, low dielectric loss and high strain near the Curie temperature. As an extension of our previous work on Ta-doped PMNT-PT aimed at optimizing the performance and reducing the cost, this paper focuses on the effect of Pb volatilization on the dielectric properties of $0.77Pb(Mg_{1/3}(Nb_{0.9}Ta_{0.1})_{2/3})O_3$-$0.23PbTiO_3$. The dielectric constant and loss of the samples are measured at different frequencies and different temperatures. The phase purity of this compound is determined by X-ray diffraction pattern. It is found that the volatilization during sintering does influence the phase formation and dielectric properties. The best condition is sintering with 0.5 g extra PbO around a 4 g PMNT-PT sample.

*Corresponding author: Department of Physics, Southern University, P. O. Box 10554, Baton Rouge, LA 70813.

1. Introduction

Relaxor ferroelectrics are materials with interesting properties for applications in the area of piezoelectric and electrostrictive actuators, acoustic sensors and pyroelectric detectors. An ultrahigh piezoelectric coefficient, $d_{33} \sim 2500$ pC/N, and high electromechanical coupling factor, $k_{33} > 90\%$, in a $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) crystal and $d_{33} \sim 1200$ pC/N in the textured PMN-PT ceramic near its morphotropic phase boundary (MPB) have been reported.[1−4] A dielectric constant higher than 30000 has been obtained in the PMN-PT ceramic with a MPB composition.[5] Recently, Wang and his co-workers[6,7] have produced a Ta-doped PMNT-PT ceramic with improved dielectric property and lower cost. But in these compounds secondary phases like pyrochlore and a Pb-rich amorphous material appearing in the high temperaturesintered PMN-PT ceramics are detrimental to the dielectric and piezoelectric properties. It is also found that free PbO reacts easily with Nb_2O_5 and other oxides to form a stable pyrochlore phase and it volatilizes as well during high temperature sintering. The columbite precursor method[8] has been used to decrease the formation of the secondary phases. The effect of Pb in the relaxor ferroelectric materials has also been investigated recently.[9−14] Addition of excess PbO during the preparation of PMN-PT is an effective method to compensate for volatilization of Pb and thus to minimize the formation of secondary phases. But this method may promote formation of Pb-rich phase that is even more harmful to the dielectric properties. In this investigation, the effect of extra PbO placed around the samples instead of mixing with specimen during sintering on the phase's present and dielectric properties is studied.

2. Experimental Procedure

Based on the columbite precursor method,[8] adequate amounts of MgO (98.6%), Nb_2O_5 (99.99%), and Ta_2O_5 (99.99%) according to the formula $MgNb_{1.8}Ta_{0.2}O_6$ were thoroughly mixed by grinding, and calcined at 1173 K for 4 h. This precursor was then mixed with PbO (99.9%) and TiO_2 (99.99%) powders stoichiometrically according to the formula $0.77Pb(Mg_{1/3}(Nb_{0.9}Ta_{0.1})_{2/3})O_3$-$0.23PbTiO_3$ (PMNT-PT), and the mixture was cold pressed into disks at 7000 psi. The disks were surrounded by extra PbO powder and placed in an Al_2O_3 crucible well covered by its lip and sintered at 1523 K for 4 h. Five samples having 0, 0.3, 0.5, 0.8, and 1.0 g of extra PbO surrounding them were prepared, and referred as PMNT-PT0, PMNT-PT1, PMNT-PT2, PMNT-PT3, and PMNT-PT4, respectively. The initial weight of PMNT-PT1, PMNT-PT2, PMNT-PT3, and PMNT-PT4 were about 4.0 g, but 1.2 g for PMNT-PT0 for more surface area per unit sample mass and thus more volatilization. Weight loss during sintering was measured by weighing them before and after sintering. After sintering, they were annealed at 1173 K in an oxygen-rich environment for 6 h, and sequentially ground and polished to 0.5 mm thick plates. The plate's surfaces were coated with Pt thin films by Cressington 108 auto Sputter Coater as electrodes and then fired at 873 K for 10 minutes to ensure bonding of

the electrodes to the surfaces. The dielectric response as a function of temperature and frequency was measured with LCR precision meter (Hewlett Packard 4284A) in a frequency range from 100 to 10^6 Hz in a Delta 9039 test chamber with temperatures varying between 298 and 573 K. The crystal structures were analyzed by X-ray diffraction (XRD) (Siemens D5000, Cu-Kα radiation) on the polished surfaces of the plates.

3. Results and Discussion

The effect of the extra PbO on the sample's weight loss during sintering is shown in Table 1. The weight loss decreases with increasing extra PbO. For PMNT-PT0 and PMNT-PT1, the weight loss is significant, 16 wt% and 8.8 wt%, respectively. The PMNT-PT0 plate is brittle and porous. For PMNT-PT2, PMNT-PT3 and PMNT-PT4, the weight loss is smaller, 1–2%.

From the XRD patterns of the polished plates, we detected two phases: perovskite (pero) and pyrochlore (pyro). The percentage (Table 1) of perovskite phase was calculated by

$$\% \, \text{perovskite} = I_{\text{pero}(110)}/(I_{\text{pero}(110)} + I_{\text{pyro}(222)}) \times 100 \,. \tag{1}$$

The relationship between extra PbO and the percentage of perovskite for those samples is illustrated in Fig. 1. PMNT-PT0 and PMNT-PT4 have more pyrochlore than other three plates. We found that in the range of extra PbO from 0.3 to 0.8 g, almost pure perovskite was obtained (94 wt% perovskite). As reported,[9] lead loss due to volatilization of PbO during sintering leads to the formation of a Pb-deficient pyrochlore, and conversely, excess PbO promotes formation of a Pb-rich pyrochlore. Pyrochlore phase mostly occurs at the surface of the plates.[10] The polishing process removed or partially removed it. For PMNT-PT0, the weight loss is larger; the percentage of perovskite is relatively small because the plate still contains pyrochlore. For PMNT-PT1, the weight loss is still large but percentage of perovskite is high because the pyrochlore is largely removed. For PMNT-PT2 and PMNT-PT3, the weight loss is smaller; the percentage of perovskite is high. For PMNT-PT4, however, the weight loss is the smallest but the percentage of perovskite is lower than PMNT-PT2 and PMNT-PT3. We believe that the Pb-rich pyrochlore is formed in PMNT-PT3 and PMNT-PT4 (less weight loss) while Pb-deficient pyrochlore

Table 1.

Notation	Extra PbO (g)	Weight loss (%)	Percentage of perovskite (%)
PMNT-PT0	0	16.6	60*
PMNT-PT1	0.3	8.8	93
PMNT-PT2	0.5	2.4	94
PMNT-PT3	0.8	2.2	94
PMNT-PT4	1.0	1.2	88

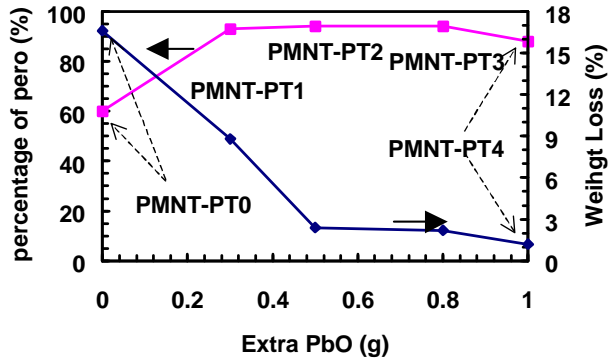*Average over the values from both surfaces of the plate.

Fig. 1.   Percentage of perovskite and weight loss during sintering as a function of the amount of extra PbO.
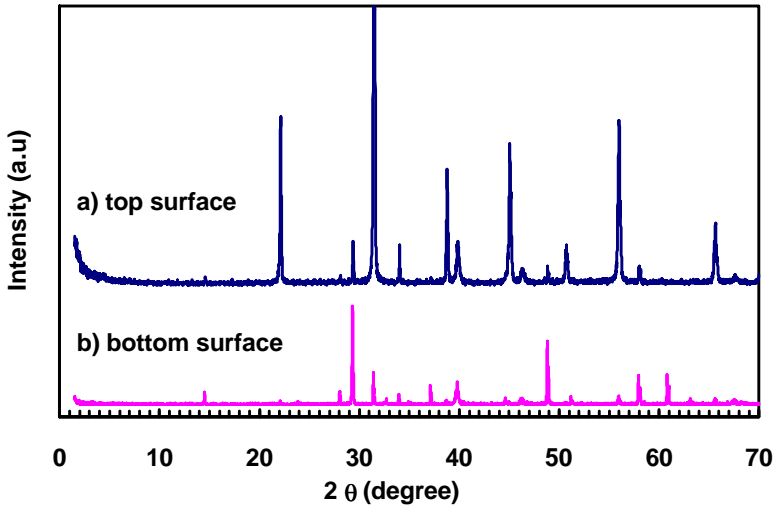

Fig. 2.   X-ray diffraction patterns for both surfaces of PMNT-PT0.

appears in PMNT-PT0 and PMNT-PT1 (more weight loss). The XRD patterns (Fig. 2) of two surfaces of PMNT-PT0 plate show that pyrochlore on the bottom surface is more abundant than that on the top surface. That is, this plate is heterogeneous due to different conditions of Pb volatilization.

Figure 3(a) shows the dielectric constant ε and dielectric loss D as a function of the temperature at frequency of 1 kHz. All plates are typical relaxor ferroelectrics, exhibiting a diffuse phase transition near the temperature $T_m = 368$ K. At T_m, the highest dielectric constant ~ 40000, is obtained in PMN-PT2, close to the value for a single crystal[15,16] and its dielectric loss is low. It corresponds to the largest percentage of perovskite (94 wt%). The high dielectric constant results also from doping of Ta.[6]
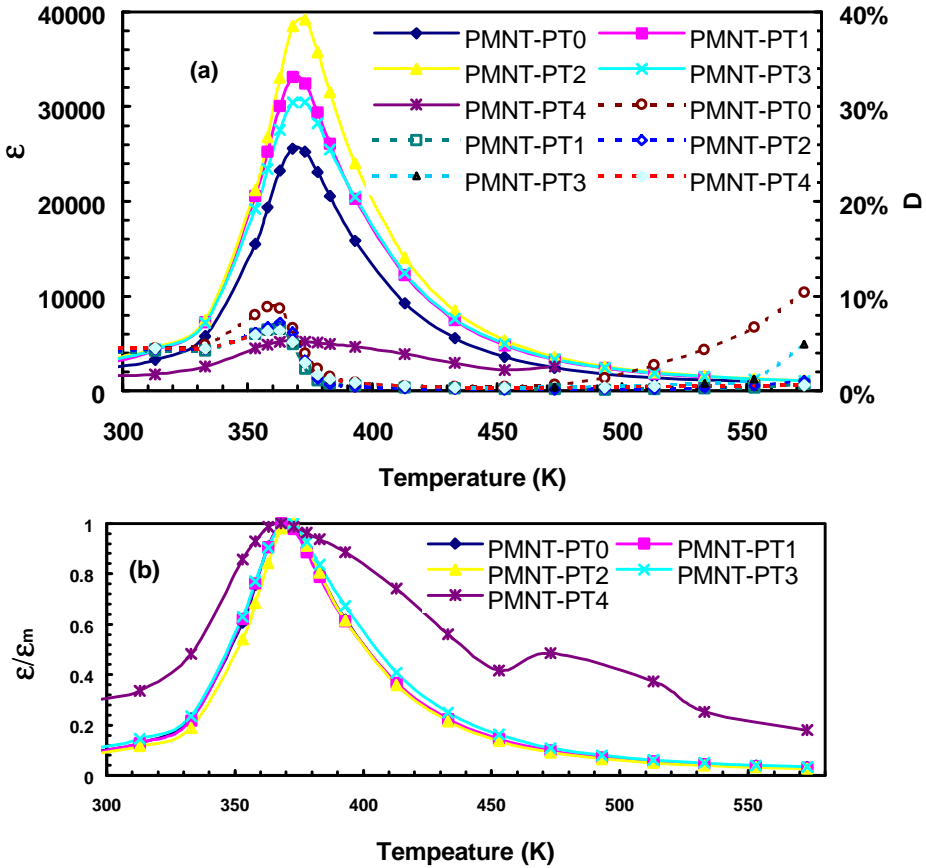
Fig. 3.   (a) Dielectric constant ε (solid) and loss D (dash) as a function of temperature and (b) the normalized ε with ε_m as a function of temperature.

Shown in Fig. 4 is the maximum dielectric constant ε_m as a function of extra PbO. It is seen that if the extra PbO exceeds 0.5 g, the percentage of perovskite decreases due to the formation of Pb-rich second phase and ε_m falls dramatically because Pb-rich secondary phase is more detrimental to the dielectric properties of PMN-PT based ceramics.

Taking into account a theory for diphasic systems,[12,17] the relative dielectric constant of polycrystalline ceramics is expressed as:

$$D/\varepsilon = D_1/\varepsilon_1 + D_2/\varepsilon_2 \,, \qquad (2)$$

where ε is the dielectric constant of the plate, ε_1, ε_2 are the intrinsic dielectric constants of perovskite and pyrochlore, respectively, D_1 the average grain size of the perovskite, D_2 the thickness of the secondary phase, and $D = D_1 + D_2$. Hence, the lower dielectric constant of a secondary phase will reduce the relative dielectric constant significantly.
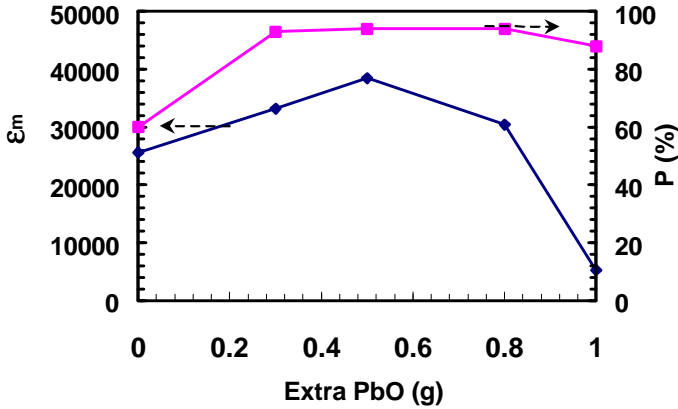
Fig. 4. Maximum dielectric constant (ε_m) and percentage of perovskite (P) as a function of the amount of extra PbO.

Although the temperature of maximum dielectric constant T_m does not clearly depend on amount of extra PbO (Fig. (3a)), the broadness of the dielectric response does. Normalized dielectric constants relative to the maximum dielectric constant as a function of temperature are replotted in Fig. 3(b). The peak is almost the same for PMNT-PT0, PMNT-PT1, and PMNT-PT2 plates, but a little broader for PMNT-PT3 and is much broader for PMNT-PT4. It implys that, the formation of Pb-deficient pyrochlore has no effect on the diffusiveness of the transition, but formation of Pb-rich pyrochlore does. The origin of diffuse phase transition has been explained in Refs. 12 and 18. In $Pb(B'_{1/3}B''_{2/3})O_3$-based perovskite, there are 1:1 (B':B'') short-ranged ordered microdomains and remnant area with B-site compositional fluctuations on a nanometer scale. Although Pb^{2+} occupies an A-location in the perovskite lattice, the formation of Pb-rich pyrochlore leads to the broadening of the size-distribution of polar nanodomains, which, in turn, affects the diffuseness of transition, Pb-deficient pyrochlore phase, on the other hand, does not affect the diffuseness of the transition. Further studies are needed to clarify this finding.

4. Conclusion

Volatilization of Pb during sintering affects perovskite formation, the microstructure and dielectric properties. The volatilization can be controlled by placing extra PbO around the sample in a sealed crucible during sintering. High purity $0.77PbMg_{1/3}(Nb_{0.9}Ta_{0.1})_{2/3}O_3$-$0.23PbTiO_3$ ceramics with high dielectric constant was prepared with 0.5 g of extra PbO around 4 g PMNT-PT. Inadequate or excessive PbO could result in Pb-deficient and Pb-rich secondary phases, respectively. The Pb-rich secondary phase is believed to be more harmful to the dielectric properties of the relaxor ferroelectrics than the Pb-deficient secondary phase to be.

Acknowledgments

References

1. R. E. Service, *Science* **275**, 1878 (1997).
2. S. E. Park and T. R. Shrout, *J. App. Phys.* **82**, 1802 (1997).
3. Y. P. Guo, H. S. Luo, K. P. Chen, H. Q. Xu, X. W. Zhang and Z. W. Yin, *J. Appl. Phys.* **92**, 6134 (2002).
4. E. M. Sabolsky, A. R. James, S. Kwon, S. Trolier-McKinstry and G. L. Messing, *Appl. Phys. Lett.* **78**, 2551 (2002).
5. O. Noblanc, P. Gaucher and G. Calvarin, *J. Appl. Phys.* **79**, 4291 (1996).
6. J. T. Wang and F. Tang, *Materials Chemistry and Physics* **75**, 86 (2002).
7. F. Tang and J. T. Wang, *Adap. Struct. Mater. Syst. AD* **60**, 335 (2000).
8. S. L. Swart and T. R. Shrout, *Mater. Res. Bull.* **17**, 1245 (1982).
9. A. R. James and K. Srinivas, *Mater. Res. Bull.* **34**, 1301 (1999).
10. M. Villegas, A. C. Caballero, M. Koses, C. Moure, P. Durán and J. F. Fernndez, *J. Mater. Res.* **14**, 898 (1999).
11. O. Bidault, E. Husson and A. Morell, *J. Appl. Phys.* **82**, 5674 (1997).
12. M. Villegas, J. F. Fernández, A. C. Caballero, Z. Samardija, G. Drazic and M. Koses, *J. Mater. Res.* **14**, 891 (1999).
13. G. J. Norga, J. Maes, E. Coppye, Laura Fe, D. Wouters and O. Van der Biest, *J. Mater. Res.* **15**, 2309 (2000).
14. D. Saha, A. Sen and H. S. Maiti, *J. Mater. Res.* **11**, 932 (1996).
15. S. Priya, D. Viehland and K. Uchino, *Appl. Phys. Lett.*, **80**, 4217 (2002).
16. D. Viehland, J. Powers, L. E. Cross and J. F. Li, *Appl. Phys. Lett.* **78**, 3508 (2001).
17. H. C. Wang and W. A. Schulze, *J. Am. Ceram. Soc.* **73**, 825 (1990).
18. A. Hilton, C. A. Randall, D. J. Barber and T. R. Shrout, *Ferroelectrics* **93**, 379 (1989).