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# Research on dielectric and piezoelectric properties of Ta-doped $0.68Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.32PbTiO_3$ ceramics

Linhong Cao*, Xi Yao, Zhuo Xu, Yajun Feng

*Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China*

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## Abstract

Pure perovskite 0.68Pb $[Mg_{1/3}(Nb_{(1-x)}Ta_x)_{2/3}]O_3$–$0.32PbTiO_3$ (0.68PMNTa–0.32PT) ceramics were prepared by one-step calcination method using $Mg(NO_3)_2$ instead of MgO as starting chemical. The dielectric properties as a function of temperature and $P$–$E$ and $\varepsilon$–$E$ loops were investigated in this work. The $T_m$ and $T_c$ shift down for ∼13 °C with Ta addition. The $\varepsilon_m$ with Ta-doping is higher than that without doping. Both of the diffusion phase transition and frequency dispersion are weak, but the relaxor feature with Ta-doping is more apparent than that without doping. Both of the values of $P_r$ and $E_c$ decrease with Ta addition, and the values of remnant and maximum strain increase with Ta-doping.

*Keywords:* C. Dielectric properties; C. Piezoelectric properties; PMN–PT; Ta-doped; One-step calcination method

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## 1. Introduction

Lead magnesium niobate–lead titanate (PMN–PT) is a solid solution of relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and normal ferroelectric $PbTiO_3$ (PT) [1]. PMN–PT materials with composition near the morphotropic phase boundary (MPB) exhibit unusual high dielectric permittivity, low dielectric loss and high strain, it is a very promising material for the applications of multilayer ceramic capacitors as well as ceramic electrostrictive actuators and electro-mechanical transducers [1–3]. So far, the PMN–PT system has been extensively investigated. Most of the results, however, have concentrated on the processing parameters, microstructure, dielectric, and electrostrictive properties, especially the compositions at 0.90PMN–0.10PT and near the morphotropic phase boundary (MPB). Many alternative techniques to synthesis pyrochlore-free PMN–PT have been developed, such as the two-stage columbite [3], sol–gel [4], and high-energy ball milling [5]. These approaches, however, require either two-step calcination or expensive processes. Therefore, efforts were made to develop a simple, economic and reproducible fabrication technique. A modified oxide method using highly reactive starting materials would be a good choice. Since $Mg(NO_3)_2$ is soluble in water as well as in alcohol. It is a better precursor of MgO than $MgCO_3$. The PMN ceramic with a perovskite phase has been prepared by one-step calcination method using $Mg(NO_3)_2$ instead of MgO [6]. For the tantalum (Ta) is analogous of niobium (Nb), the tantalum impurity is difficult to separate from niobium oxide ($Nb_2O_5$), which is one of the components for preparing PMN–PT ceramics. The dielectric properties of $(1-y)Pb[Mg_{1/3}(Nb_{(1-x)}Ta_x)_{2/3}]O_3$–$yPbTiO_3$ ($y = 0.1, 0.30, 0.35$; $x = 0, 0.1$) ceramics prepared by the columbite precursor method have been studied by Wang and Tang [7].

In the present study, $0.68Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.32PbTiO_3$ (0.68PMN–0.32PT) was selected as the starting composition, and Nb substituted by Ta with 0 and 10 mol.%. The 0.68PMNTa–0.32PT ceramics were prepared by the one-step calcination method using $Mg(NO_3)_2$ instead of MgO as starting chemical. The phase composition and dielectric/piezoelectric properties of 0.68PMNTa–0.32PT ceramics were studied.

## 2. Experimental

The compositions of the specimens were calculated according to the general formula $0.68Pb[Mg_{1/3}(Nb_{(1-x)}Ta_x)_{2/3}]$

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* Corresponding author. Fax: +86-29-82668794.
*E-mail address:* caolh@mailst.xjtu.edu.cn (L. Cao).

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$O_3$–$0.32PbTiO_3$, with $x = 0$, 0.1. Starting chemicals were PbO (purity >99.9%), $Nb_2O_5$ (>99.9%), $Ta_2O_5$(>99.9%), $TiO_2$(>99.0%), and $Mg(NO_3)\cdot 6H_2O$(>98.0%). The one-step calcination method [6] was used to prepare 0.68PMNTa–0.32PT ceramics. Starting materials in stoichiometric ratio (without any addition of excess amount) were placed with alcohol in a polypropylene bottle and milled with zirconia balls for 5 h, dried in an infrared chamber and calcined at 850 °C for 2 h, then the perovskite precursors were prepared. The precursor powders added with 1 wt.% of polyvinyl alcohol (PVA) were dry ground using an agate mortar, passed through 60-mesh sieves and pressed into disks (12 mm in diameter and 1–2 mm thick) by die pressing at 100 MPa. The binder was burnt-out by heating up to 600 °C for 2 h, then the disks were supported on $Al_2O_3$ setters and sintered at 1230 °C for 2 h in a multiple-enclosure crucible setup sealed with perovskite powders of identical composition to minimize the PbO volatilization. The precursor powders and ceramics were analyzed using X-ray diffraction (XRD). The relative amount of perovskite and pyrochlore phase was determined using the formula [6]:

$$\text{perovskite (\%)} = \frac{I_{\text{perov}(1\,1\,0)}}{I_{\text{pyrov}(2\,2\,2)} + I_{\text{perov}(1\,1\,0)}} \times 100 \qquad (1)$$

Both sides of the specimens were polished and electroded, then fired in air at 550 °C for 30 min to form silver electrode for electrical measurements. A HP4284A impedance analyzer was used to measure the dielectric constants as a function of temperature on heating at frequencies of 1 Hz to 100 kHz. The samples were poled by applying a dc field of 3 kV/mm at 60 °C for 20 min. $d_{33}$ was measured using a $d_{33}$-meter. The $P$–$E$ and $\varepsilon$–$E$ was measured using a modified Swayer–Tower circuit and DGS-6 displacement sensor at the frequency of 0.1 Hz. The 0.1 Hz sine wave voltage was supplied using a Trek 610 high voltage dc amplifier. Strain measurements were performed under mechanically "free" conditions.

## 3. Results and discussions

### 3.1. XRD analysis

The XRD profiles of the precursors and ceramics of 0.68PMNTa–0.32PT are presented in Fig. 1. In the precursors, which were calcined at 850 °C for 2 h, except perovskite phase small trace of cubic pyrochlore was detected. The relative amount of perovskite and pyrochlore phase was calculated by Eq. (1). It showed 86 and 89% perovskite phase for the powder with 0 and 10 mol.% Ta-doping, respectively. The Ta-doping has little effect on the formation of perovskite. In the ceramics, however, pure perovskite phase was identified. Effectiveness of the one-step calcination method with $Mg(NO_3)_2$ instead of MgO in suppression of the pyrochlore formation during perovskite development has thus been proven again in the present study. Meanwhile, the reflection angles decrease after sintering, this may be attributed to grain growth after sintering at 1230 °C. The reflection angles of the Ta-doped sample are smaller than that of the pure sample. This is undoubtedly due to the incorporation of Ta (10 mol.%) during the solid solution formation.

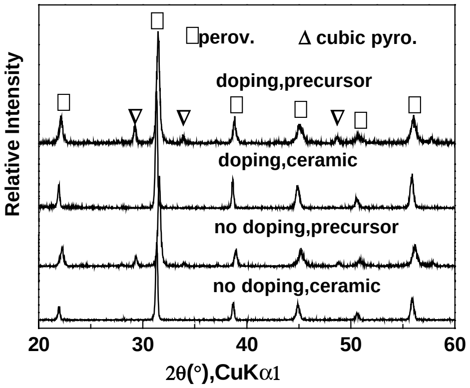

Fig. 1. The XRD patterns of 0.68PMNTa–0.32PT.

### 3.2. Dielectric properties

Fig. 2 shows the dielectric properties as a function of temperature at 1 kHz for 0.68PMNTa–0.32PT. The dielectric constant ($\varepsilon$) for Ta-doped 0.68PMN–0.32PT ceramic has a sharp peak near $T_m = 155.3\,^\circ C$ for FE–PE phase transition at 1 kHz, corresponding to the curves of $\tan\delta$ versus $T$, where sharp peaks exist at $T_c = 151.5\,^\circ C$, while these values of pure 0.68PMN–0.32PT ceramic are $T_m = 142.2\,^\circ C$ and $T_c = 138.6\,^\circ C$, respectively. The $T_m$ and $T_c$ shift down for about 13 °C with Ta addition. The value of $\varepsilon_m$ with Ta-doping ($\varepsilon_m \sim 25{,}000$) is higher than that without doping ($\varepsilon_m \sim 24{,}000$).

The temperature dependence of $\varepsilon$ and $\tan\delta$ at different frequencies for 0.68PMNTa–0.32PT are presented in Fig. 3. $\Delta T = T_{m/100\,\text{kHz}} - T_{m/1\,\text{kHz}}$, where $\Delta T$ can be used to figure frequency dispersion. The value of $\Delta T$ without Ta-doping is 0.6 °C, and that with Ta-doping is 2.1 °C. The sample with Ta addition, thus, has more apparent frequency dispersion than

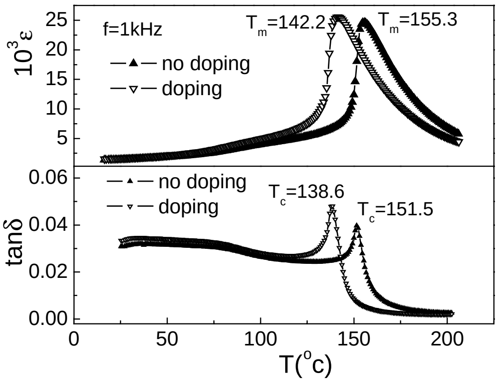

Fig. 2. Temperature dependence of $\varepsilon$ and $\tan\delta$ at 1 kHz for 0.68PMNTa–0.32PT ceramic.

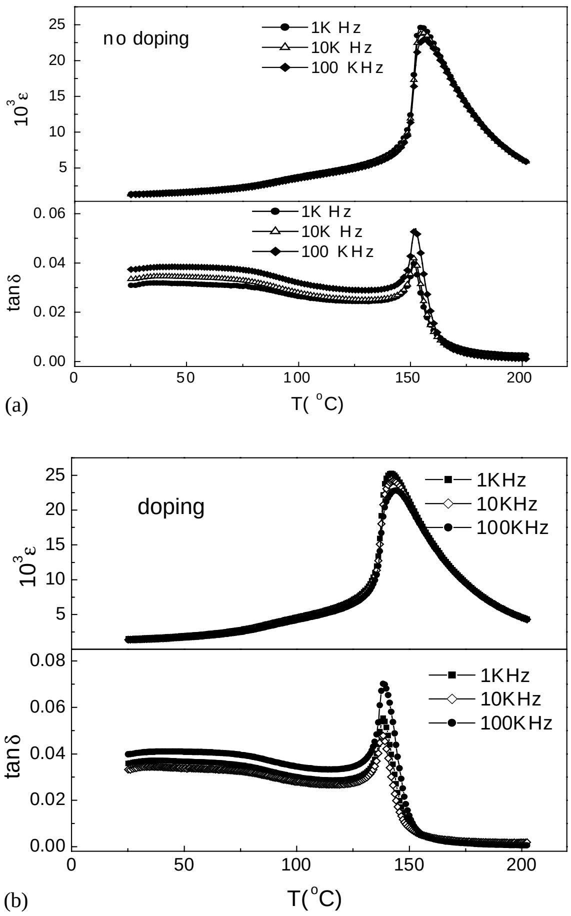

Fig. 3. Temperature dependence of $\varepsilon$ and $\tan\delta$ at different frequencies for pure 0.68PMNTa–0.32PT ceramic.

that without Ta addition. This result is consistent with that in 0.65PMNTa–0.35PT and 0.70PMNTa–0.30PT ceramics by Wang [7]. From Figs. 2 and 3, both of the diffusion phase transition (DPT) and frequency dispersion are weak.

In order to examine the relaxor character, the relationship between $\varepsilon$ and $T$ above $T_m$ (temperature corresponding to the maximum dielectric constant $\varepsilon_m$) can be expressed as [8]:

$$\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}=\frac{1}{\varepsilon_m}\left(\frac{T-T_m}{\delta_4}\right)^{\eta} \qquad (2)$$

where, $\varepsilon_m$ corresponds to the maximum value of dielectric constant at $T_m$, $\eta$, and $\delta_4$ are constants for all the frequencies. $\eta$ is called as diffuseness exponent, and can be used to scale the degree of dielectric relaxation in a relaxor FE. When $\eta = 1$, Eq. (2) is Curie–Weiss law for normal ferroelectrics, and in this situation, $\delta_4$ is proportional to the Curie constant. When $\eta = 2$, Eq. (2) represents a typical relaxor ferroelectric, in this case, $\delta_4$ has the dimension of a temperature and indicates the range of temperature extension for DPT. For many ferroelectrics, $\eta$ is between 1 and 2 [8]. The relationship between $\varepsilon$ and $T$ above $T_m$ for 0.68PMNTa–0.32PT ceramics was fitted to Eq. (2). Fig. 4 is the plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T - T_m)$, which shows a linear relationship, the value of $\eta$ is 1.53 and 1.61 and the corresponding value of $\delta_4$ is 23 and 24 °C for 0.68PMN–0.32PT ceramics with 0 and 10 mol.% Ta concentration, respectively. According to our results, the dielectric behavior of 0.68PMNTa–0.32PT has relaxor feature in the range of $T > T_m$. The value of $\eta$ with Ta-doping is distinctly larger than that without doping, this means the relaxor feature with Ta-doping is more apparent than without doping.

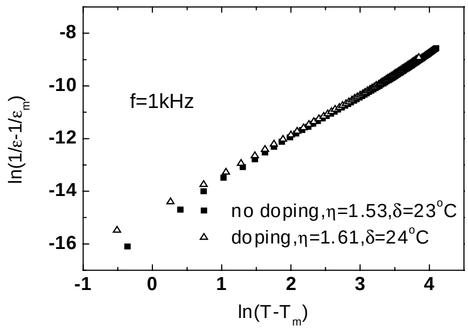

Fig. 4. The relationship between $\ln(1/\varepsilon - 1/\varepsilon_m)$ and $\ln(T - T_m)$ for 0.68PMNTa–0.32PT ceramics.

### 3.3. Piezoelectric properties

The $P$–$E$ hysteresis loops of 0.68PMNTa–0.32PT ceramics are shown in Fig. 5. The remnant polarization $P_r$ is 31.1 μC/cm$^2$ and the coercive field $E_c$ is 4.7 kV/cm for Ta-doped 0.68PMN–0.32PT ceramic, while these values are 26.2 μC/cm$^2$ and 4.1 kV/cm for pure 0.68PMN–0.32PT ceramic, respectively. The $P_r$ value is about the same as the spontaneous polarization $P_s$ defined as the intercept at zero field of the straight-line portion of the hysteresis loop. Both of the $P_r$ and $E_c$ decrease with Ta addition. The hysteresis loop is square-like. Fig. 6 shows the electric field–strain behavior of 0.68PMNTa–0.32PT ceramics. The strain curves are typical butterfly shaped. Strong hysteretic strain behavior was observed. For the sample with 0 and 10 mol.% Ta concentration, the remnant strain is ~0.22 and 0.34%, while the magnitude of the maximum electrically induced shape change are ~0.3 and 0.55% under an electric field of

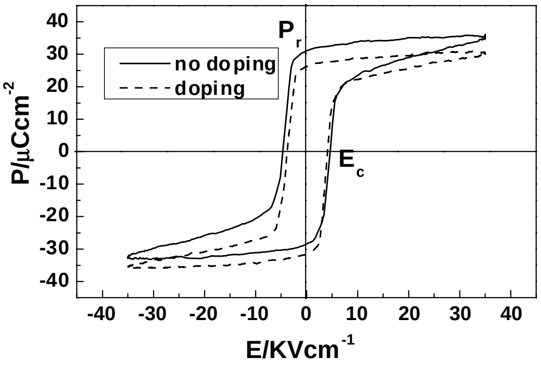

Fig. 5. $P$–$E$ hysteresis loops of 0.68PMNTa–0.32PT ceramics.

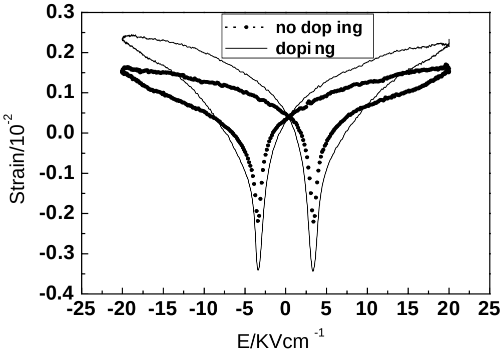

Fig. 6. $\varepsilon$–$E$ responses for 0.68PMNTa–0.32PT ceramics in a bipolar electric field.

~20 kV/cm, respectively. Meanwhile, both of the remnant and maximum strain with Ta-doping are found to be distinctly larger than that without doping. The maximum strain with Ta-doping (0.55% under $E = 20$ kV/cm) is equivalent that of the 0.7PMN–0.3PT single crystal (0.45% under $E = 15$ kV/cm) [9]. The piezoelectric constant $d_{33}$ are 458 and 465 pC/N for 0.68PMN–0.32PT ceramics with 0 and 10 mol.% Ta concentration, respectively. It is obvious that the piezoelectric constant with Ta-doping is larger than that without doping, this explains that both of the remnant and maximum strain with Ta-doping is higher than that without doping.

## 4. Summary

In the present study, the perovskite solid solutions 0.68PMNTa–0.32PT were prepared by the one-step calcination method using $Mg(NO_3)$ instead of MgO as starting chemical. XRD analysis shows that the Ta-doping has little effect on the perovskite formation. The dielectric properties as a function of temperature and $P$–$E$ and $\varepsilon$–$E$ loops were studied for 0.68PMNTa–0.32PT ceramics. The $T_m$ and $T_c$ is shift down for ~13 °C with Ta addition. The $\varepsilon_m$ with Ta-doping ($\varepsilon_m$ ~25,000) is higher than that without doping ($\varepsilon_m$ ~24,000). Both of the diffusion phase transition and frequency dispersion are weak. But the relaxor feature with Ta-doping is more apparent than that without doping. Both of the $P_r$ and $E_c$ decrease with Ta addition, and the remnant and maximum strain increase with Ta-doping. With these results we can think 10 mol.% Ta impurity in $Nb_2O_5$ is not a threat to perovskite formation but a help to the dielectric and piezoelectric properties of 0.68PMN–0.32PT.

## Acknowledgements

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## References

[1] K. Kusumoto, T. Sekiya, Processing and properties of $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ solid solutions from PbO- and MgO-excess compositions, Mater. Res. Bull. 33 (9) (1998) 1367–1375.

[2] S.W. Choi, T.R. Shrout, S.J. Jang, A.S. Bhalla, Morphotropic phase boundary in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ system, Mater. Lett. 8 (6/7) (1989) 253–255.

[3] S.L. Swartz, T.R. Shrout, Fabrication of perovskite lead magnesium niobate, J. Mater. Res. Bull. 17 (10) (1982) 1245–1250.

[4] P. Ravidranathan, S. Komarneni, A.S. Bhalla, Synthesis and dielectric properties of solution sol–gel-derived $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ ceramics, J. Am. Ceram. Soc. 74 (12) (1991) 2996–2999.

[5] L.B. Kong, J. Ma, W. Zhu, O.K. Tan, Rapid formation of lead magnesium niobate-based ferroelectric ceramics via a high-energy ball milling process, Mater. Res. Bull. 37 (2002) 459–465.

[6] K.R. Han, S. Kim, New preparation method of low-temperature sinterable $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder and its dielectric properties, J. Mater. Sci. 35 (2000) 2055–2059.

[7] J.T. Wang, F. Tang, Effect of Ta-doping on dielectric properties of $yPbMg_{1/3}(Nb_{(1-x)}Ta_x)_{2/3}O_3$–$(1 - y)PbTiO_3$, Mater. Chem. Phys. 75 (2002) 86–89.

[8] L. Mitoseriu, A. Stancu, C. Fedor, P.M. Vilarinho, Analysis of the composition-induced transition from relaxor to ferroelectric state in $PbFe_{2/3}W_{1/3}O_3$–$PbTiO_3$ solid solutions, J. Appl. Phys. 94 (3) (2003) 1918–1925.

[9] D. Viehland, J. Powers, Effect of uniaxial stress on the electromechanical properties of $0.7PbMg_{1/3}Nb_{2/3}O_3$–$0.3PbTiO_3$ crystals and ceramics, J. Appl. Phys. 89 (3) (2001) 1820–1825.