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Effect of Ta substitution on microstructure and electrical properties of $0.80Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.20PbTiO_3$ ceramics

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Abstract

The influence on microstructure and electrical properties of Ta-substituted $0.80Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.20PbTiO_3$ (0.80PMN–0.20PT) ceramics has been investigated. The grain size decreases with Ta concentration increases. The sample with 10 at.% Ta substitution has dense structure and better dielectric and piezoelectric properties, with density ~7.7 g/cm^3, ε_m ~45,000, k_p ~34% and d_{33} ~158 pC/N. Less or more Ta doping in 0.80PMN–0.20PT ceramics is all harmful to dielectric and piezoelectric properties.
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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 [1,2]. The relation between processing and properties of PMN–PT materials has been intensively investigated in the past. The frequent problem in the preparation of PMN–PT ceramics is the formation of unwanted lead-deficient cubic pyrochlore $Pb_3Nb_4O_{13}(P_3N_2)$ via the conventional mixed-oxide method [3]. The two-stage columbite approach, however, has been found to be the most effective and reproducible method of preparation. Pure perovskite PMT–PT [4] and PMN–PT [1] could be easily prepared throughout the whole composition range via two-stage columbite method. For the tantalum (Ta) is an 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 Jin T. Wang [5].

In the present study, the two-stage columbite precursor method was adopted, 0.80PMN–0.20PT was selected as the starting composition. Due to the MgO decomposed from $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$ during calcination is more reactive and finer in grain size [6]. $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$ was used to introduce Mg and Nb was partially substituted by Ta. The effect of different amount of Ta substitution on microstructure and electrical properties of 0.80PMN–0.20PT ceramics was investigated.

2. Experimental procedure

The compositions of specimens were calculated according to the general formula $0.80Pb[Mg_{1/3}(Nb_{(1-x)}Ta_x)_{2/3}]O_3$–$0.20PbTiO_3$, with $x = 0, 0.05, 0.1, 0.2$. Starting chemicals were PbO, Nb_2O_5, Ta_2O_5, TiO_2, and $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$. In the first stage, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$, Nb_2O_5 and Ta_2O_5 were mixed in a stoichiometric ratio, and a precursor columbite phase $MgNb_{2(1-x)}Ta_{2x}O_6$ ($x = 0.0, 0.05, 0.1, 0.2$) (MNTa) was formed after ball milling for 5 h using alcohol, drying and calcining at 1100 °C for 6 h in an uncovered alumina

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crucible. In the second stage, the precursor powders were mixed with PbO (with 0.5 wt.% excess for compensating lead loss) and TiO_2. Then ball milled, dried and calcined in a covered alumina crucible at 850 °C for 2 h to form the perovskite powders. 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 1250 °C for 2 h in a multiple-enclosure crucible setup sealed with the perovskite powders of identical composition to minimize PbO volatilization.

The density was calculated by the geometrical method. The fracture surface of the sintered samples was examined by JSM-5800 scanning electron micrographs (SEM). 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 using a DC field of 3 kV/mm at 60 °C for 20 min. The piezoelectric planar coupling coefficient k_p and mechanical quality factor Q_m were determined by a resonance–anti-resonance method using a HP4192A complex impedance analyzer. The values of the piezoelectric constant d_{33} were determined using a d_{33}-meter. The *P–E* hysteresis loops were measured using a modified Swayer-Tower circuit. The 1 Hz sine wave voltage was supplied using a Trek 610 high voltage DC amplifier.

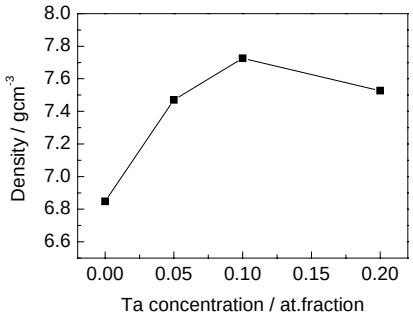

Fig. 1. Density vs. Ta concentration in 0.80PMN–0.20PT ceramics.

3. Results and discussions

3.1. Density

The density of the four compositions is shown in Fig. 1. All samples were sintered at 1250 °C for 2 h. When x increases from 0 to 0.1, density increases from 6.8 to

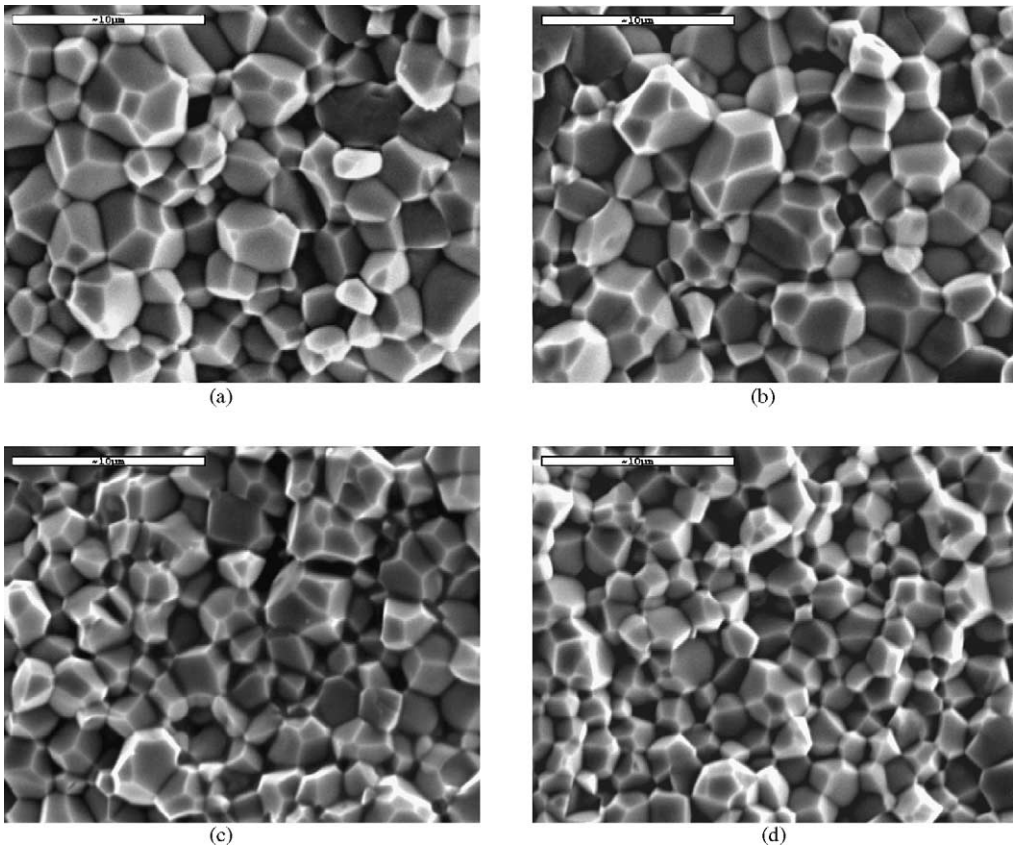

Fig. 2. SEM photographs of fracture surface for $Pb[Mg_{1/3}(Nb_{(1-x)}Ta_x)_{2/3}]_{0.80}Ti_{0.20}O_3$ ceramics sintered at 1250 °C for 2 h, where (a) $x = 0.0$, (b) $x = 0.05$, (c) $x = 0.1$, (d) $x = 0.2$.

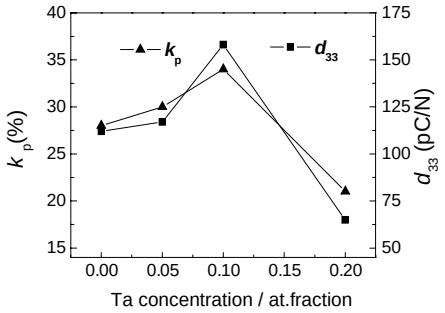

Fig. 3. k_p and d_{33} vs. Ta concentration in 0.80PMN–0.20PT ceramics.

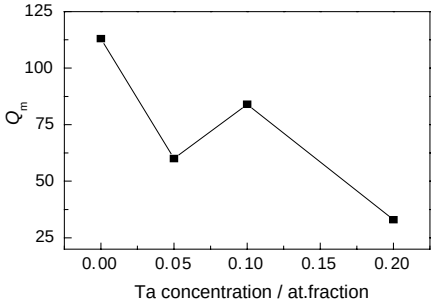

Fig. 4. Q_m vs. Ta concentration in 0.80PMN–0.20PT ceramics.

7.7 g/cm^3. This is undoubtedly attributed to the incorporation of Ta during the solid solution formation. Though the radii of Nb^{5+} and Ta^{5+} are similar, but the molecular mass of Ta is larger than that of Nb. However, when x increases to 0.2, the density decreases to 7.5 g/cm^3, this is probably due to poor densification of the sample.

3.2. Microstructure

Fig. 2 shows the scanning electron micrographs of the fracture surface of the samples. In all compositions, the fracture is mainly intergranular fracture, the grain boundary is clear; their microstructure is dense, while some pores exist. The grain size of all compositions is close to 2–6 μm. The grain size decreases with Ta concentration increase, and the grain uniformity becomes well with Ta addition increase.

3.3. Piezoelectric properties

Fig. 3 shows piezoelectric planar coupling coefficient k_p and piezoelectric constant d_{33} as function of Ta concentration in 0.80PMN–0.20PT ceramics. The value of k_p can be calculated from the measured values of resonance frequency f_r and anti-resonance frequency f_a using Eq. [7]:

$$k_p \approx 1.125\sqrt{\frac{f_a^2 - f_r^2}{f_r^2}}$$

The peak value of k_p is 34%, and that of d_{33} is158 pC/N, which all appear at $x = 0.1$. The value of k_p and d_{33} increases with Ta concentration increases from 0 to 10 at.%, but when $x = 0.2$, the value of k_p and d_{33} decreases to 21% and 65 pC/N, respectively.

Fig. 4 shows Q_m as a function of Ta concentration in 0.80PMN–0.20PT ceramics. Using the measured values of resonance frequency f_r and anti-resonance frequency f_a, and corresponding impedance Z_r and Z_a. The value of Q_m can be calculated by the following Eq. [7]:

$$Q_m = \frac{f_a}{2\,\Delta f}\sqrt{\frac{Z_a}{Z_r}}$$

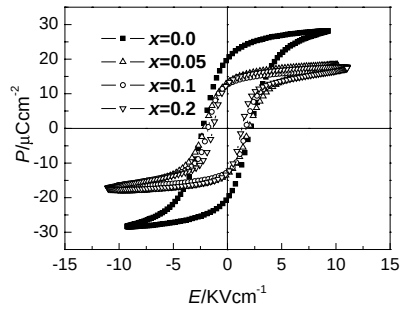

Fig. 5. P–E hysteresis loops of $Pb[Mg_{1/3}(Nb_{(1-x)}Ta_x)_{2/3}]_{0.80}Ti_{0.20}O_3$ ceramics.

The mechanical quality factor Q_m of the sample without Ta doping is larger than that of the compositions with Ta doping. When $x = 0.1$, the value of Q_m is the maximum in the samples with Ta substitution, which is 84.

Fig. 5 show P–E hysteresis loops of 0.80PMNTa–0.20PT ceramics. The coercive field E_c has little change with Ta concentration increase, whereas, the saturation polarization P_s and remnant polarization P_r of the composition without Ta doping is higher than that of the samples with Ta substitution. But the value of P_s and P_r has little change with Ta concentration increase.

3.4. Dielectric properties

Fig. 6 shows the maximum value of dielectric constant ε_m and diffusive factor δ as a function of Ta concentration in 0.80PMN–0.20PT ceramics at 1 kHz. The diffusive factor

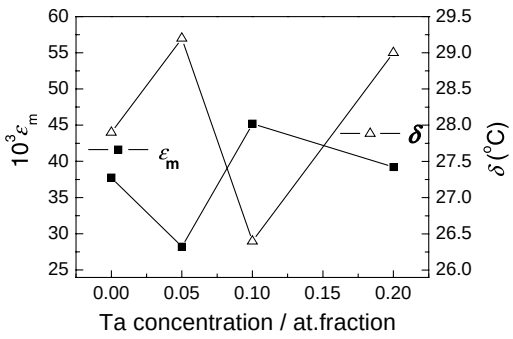

Fig. 6. ε_m and δ vs. Ta concentration in 0.80PMN–0.20PT ceramics.

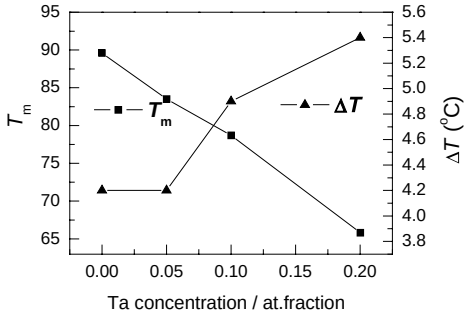

Fig. 7. T_m and ΔT vs. Ta concentration in 0.80PMN–0.20PT ceramics.

δ can be calculated from the quadratic formula [8]:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{1}{2\varepsilon_m \delta^2}(T - T_m)^2$$

where ε_m is the maximum dielectric constant, T_m is the temperature of maximum dielectric constant measured at 1 kHz. δ is a coefficient related to the peak broadening of the phase transition. δ is also called diffusive factor. The value of δ is contrary to the value of ε_m. The value of ε_m decreases with small amount of Ta doping. However, when the value of x continuously increases, the value of ε_m attains the maximum value (∼45,000) at 10 at.% Ta substitution, while the value of δ attains the minimum value (∼26 °C). It means the diffusion phase transition becomes very strong.

Fig. 7 shows T_m and δT as a function of Ta concentration in 0.80PMN–0.20PT ceramics. T_m is the temperature corresponding to the maximum value of dielectric constant. ΔT is described as $\Delta T = T_{m/100\,kHz} - T_{m/1\,kHz}$. With Ta concentration increase from 0 to 20 at.%, the value of T_m is continuously decreasing from 89.6 to 65.8 °C. The temperature shifts down about 35 °C. Since the value of T_m of PMT (about −88 to −85 °C) [4] is lower than that of PMN (about −10 to −5 °C) [1]. With Ta concentration increase, the PMT component increases. This leads to the value of T_m decrease. The dependence of $T_m(x)$, where x is Ta concentration (at.%), was fitted by the linear law: $T_m(x) = 89–118x$ (°C). When small amount of Ta is doped in 0.80PMN–0.20PT ceramics, the value of δT keeps the same. With Ta concentration increase, the value of δT increases. It means the frequency dispersion becomes strong.

4. Summary

Investigations of the effect of Ta doping on microstructure and electrical properties of 0.80PMN–0.20PT ceramics were performed. The results show that the sample with 10 at.% Ta substitution has dense structure. The grain size decreases with Ta concentration increase. When the sample has 10 at.% Ta concentration, the value of k_p and d_{33} is maximum, which is 34% and 158 pC/N, respectively, and the value of ε_m attains the maximum value, which is ∼45,000, as well as the value of δ attains the minimum value (∼26 °C), this means the diffusion phase transition becomes very strong. With Ta concentration increase, the value of ΔT increases. This shows the frequency dispersion becomes strong. The less or more Ta doping in 0.80PMN–0.20PT ceramics, however, is harmful to dielectric and piezoelectric properties. An appropriate amount (10 at.%) of Ta impurity in Nb_2O_5 is not a threat to microstructure, but a help to the dielectric and piezoelectric properties of 0.80PMN–0.20PT.

Acknowledgements

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