

Effect of Mn and Sb Doping on Electromechanical Coupling Coefficient and Mechanical Quality Factor of PZT Piezoelectric Ceramics

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ABSTRACT

Introduction: The study of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ceramics is growing due to their wide use as piezoelectric materials. PZT piezoelectric ceramics are a solid solution of ferroelectric PT(PbTiO_3) with Curie temperature 490 °C and antiferroelectric PZ(PbZrO_3) with Curie temperature 230 °C. To increase the electromechanical coupling coefficient (k_p) and mechanical quality factor (Q_m) of PZT piezoelectric ceramics, Mn and Sb dopants were added.

Materials and Methods: The composition of PZT piezoelectric ceramics was $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})$ to keep them near the phase boundary and manganese and antimony were added as dopants. The powders were synthesized at 650 °C by sol gel method and sintered at 1150 °C.

Results: The variation of k_p and the Q_m of piezoelectric ceramics were measured by varying the Mn and Sb doping ratios. The effect of manganese and antimony dopants on the relative permittivity (ϵ_r), piezoelectric strain coefficient (d_{33}) and density of piezoelectric ceramics was also analyzed.

Discussion: Mn^{2+} ion acts as acceptor ion and creates oxygen vacancies in the perovskite structure, resulting in shrinkage and deformation of the crystalline unit cell. K_p , Q_m , and d_{33} gradually increased with increasing doping amount and then decreased again. Then the doping amount was near $X = 0.03$, the characteristic values had a maximum.

Conclusion: Considering the variation of K_p and Q_m with Mn and Sb addition ratio, the electromechanical coupling coefficient and Q-factor simultaneously reached high values when the Mn content was 30-35% and the Sb content was 65-70%. Therefore, we set the ratio of manganese to antimony 3:7. The analysis of the relationship between doping and piezoelectric properties shows that the piezoelectric properties are maximized, and the optimum doping is $X = 0.03$. The electromechanical coupling coefficient and Q-factor were 0.67 and 2900, respectively. The addition of manganese and antimony simultaneously increased the electromechanical coupling coefficient and the quality factor. However, the addition of manganese can increase the electromechanical coupling coefficient, but it has not yet reached enough quality factor values due to its tendency to decrease the quality factor.

Keywords: Mn; Sb; Electromechanical coupling coefficient; Mechanical quality factor; PZT piezoelectric ceramics

INTRODUCTION

The study of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ceramics is growing due to their wide use as piezoelectric materials. PZT

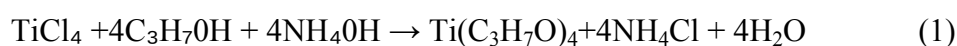
piezoelectric ceramics are a solid solution of ferroelectric $\text{PT}(\text{PbTiO}_3)$ with Curie temperature 490°C and antiferroelectric $\text{PZ}(\text{PbZrO}_3)$ with Curie temperature 230°C . The properties of PZT piezoceramics depend greatly on the ratio of titanium and zirconium, and the advantages of good control of the ratio of titanium and zirconium can be easily placed near the phase boundary even at room temperature [1-4]. With the increasing application of PZT piezoceramics, various methods have been investigated to control the properties of PZT piezoceramics. In particular, we focus our research on the control of the properties of PZT ceramics by the addition of various dopants. [11, 12] When PZT piezoelectric ceramics are used as underwater acoustic transducers, high value of K_p , Q_m , and hydrostatic voltage coefficient $g_h (=d_h/\epsilon_r)$ are required. The addition of manganese to PZT piezoelectric ceramics can reduce the ϵ_r and increase the d_h , thereby increasing the g_h . It also reduces the dielectric loss and increases the value of Q_m . [7-9]

However, the addition of manganese tends to increase the g_h and Q_m while decreasing the k_p . The research on simultaneous enhancement of the k_p and the Q_m of PZT piezoelectric ceramics by the addition of manganese and antimony is very scarce. In this work, we investigated the effect of the Mn and Sb dopants on the k_p , Q_m and g_h of PZT piezoelectric ceramics.

Experimental procedure

Synthesis of powders by sol-gel process

The metal salts containing Zr, Ti, Pb, Mn and Sb ions were dissolved in solvent to obtain a homogeneous sol and then the PMSZT powder was synthesized by sol-gel method. The raw materials are lead acetate, manganese acetate, antimony chloride, titanium chloride and zirconium chloride. The reaction was carried out by adding 18.4 ml of titanium chloride to a reactor with isopropyl alcohol $\text{C}_3\text{H}_7\text{OH}$. Ammonia hydroxide solution was slowly added, reacted at 20°C .



In this way, 24 g of ZrCl_4 and 0.97 g of SbCl_3 are dissolved in $\text{C}_3\text{H}_7\text{O}$ to synthesize $\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$ and $\text{Sb}(\text{C}_3\text{H}_7\text{O})_3$, respectively. Heat for 2 h at 75°C to make $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ anhydrous crystals, add 65 g of lead acetate and 0.32 g of manganese acetate to acetic acid and stir in a magnetic stirrer for 1 h at 50°C . Then lead acetate and manganese acetate dissolve in acetic acid and transform into a transparent liquid with a weak viscosity. Meanwhile, $\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$, $\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$ and $\text{Sb}(\text{C}_3\text{H}_7\text{O})_3$ were added to the $\text{CH}_3\text{CH}_2\text{OH}$ solution and stirred for 1 h at room temperature. The two solutions prepared above were mixed and stirred for another 1 h at 50°C . As a stabilizer, about 5% acetylacetone is added. oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$) is added as surfactant by 3 wt%. After evaporate the water, the yellow sol was obtained. It was dried at 50°C for 2 days to obtain the powder. The obtained powder was sintered at 650°C for 5 h to remove organic matter and obtain PMSZT ($\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.97}(\text{Mn}_{0.3}\text{Sb}_{0.7})_{0.03}\text{O}_3$) nanopowder.

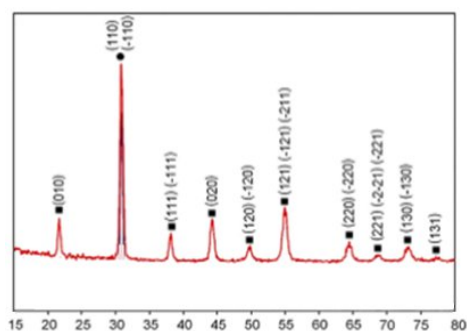


Fig. 1. XRD of PMSZT powder.

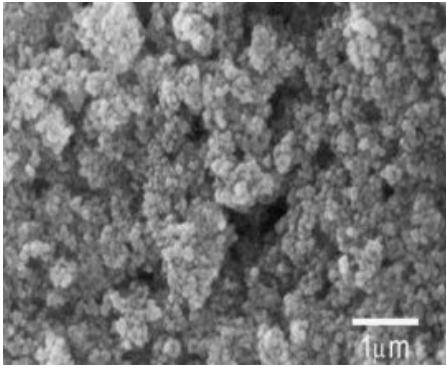


Fig. 2. SEM image of PMSZT nanopowder

Sintering process

The powder was added 3 wt% of PVA solution as a binder [5]. The mixture was made into a disk with a diameter of 25 mm and a thickness of 1.5 mm at a pressure of 100 MPa. As can be seen in Fig. 3, the sintering temperature was initially raised to 120 °C with a rate of temperature rise of 0.5 °C/min and kept for 1 h to release the moisture. Then, sintering was carried out at 500 °C for 3 h to remove organic matter [6]. After sintering at 1150 °C for 2 h, it was cooled to room temperature.

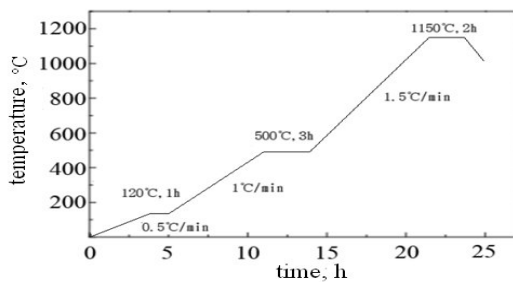


Fig. 3. Sintering process temperature curve

The sintered samples were coated with silver paste after surface grinding and heated at 550 °C for 20 min to coat the silver electrode. Then, the samples were polished in 120 °C silicone oil for 5 min with an 18 kV/cm DC electric field and aged for 24 h at room temperature. The piezoelectric strain coefficient d_{33} was measured by a piezoelectric coefficient measuring device. The resonant frequency f_r , antiresonant frequency f_a and permittivity were measured by an impedance bridge.

RESULTS AND DISCUSSION

Effect of mixing ratio of Mn and Sb

The variation of k_p and Q_m factor was measured by varying the ratio of Mn to Sb. The results are shown in Fig. 4.

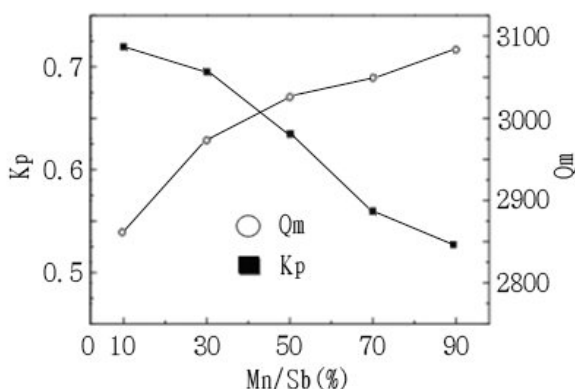


Fig. 4. Variation of Kp and Qm with Mn and Sb addition ratio.

Manganese has different valence states of divalent, tetravalent and seven valent, because it has valence variability. The crystal structure of PMSZT also varies with the molar percentage of Mn. Mn^{2+} ion is easily substituted for the sites where Ti^{4+} ions with ionic radius of 0.078 nm and Zr^{4+} ions with ionic radius of 0.082 nm are present because the ionic radius is 0.067 nm. Mn^{2+} ion acts as acceptor ion and creates oxygen vacancies in the perovskite structure, resulting in shrinkage and deformation of the crystalline unit cell. This leads to a decrease in the relative permittivity and an increase in the value of the Qm. Antimony is present in Sb^{3+} and Sb^{5+} forms, Sb^{3+} ions (0.09 nm) displace Pb^{2+} ions (0.126 nm) and Sb^{5+} ions (0.064 nm) displace Ti^{4+} ions (0.078 nm) and Zr^{4+} ions (0.082 nm). The valence state of Sb^{3+} ions is higher than that of Pb^{2+} ions, and the valence state of Sb^{5+} ions is higher than that of Ti^{4+} and Zr^{4+} ions, which leads to an excess positive charge in the crystal lattice. This leads to lead vacancies to maintain the electroneutral condition. On the one hand, the lattice distortion due to the difference in radius and the lattice distortion due to the vacancy of lead are introduced. This leads to a lowering of the potential barrier between the dipole moments and facilitates the movement of the dipoles. Then, the number of spontaneous polarizations aligned in the direction of the electric field increases and the piezoelectric properties improve. This is the softening effect that is obtained when antimony is added.

To observe the change in properties with doping amount, samples with doping amounts $X = 0.01, 0.02, 0.03, 0.04$, and 0.05 were prepared.

First, the change in density with X was measured by Archimedes method. The density change was measured to a maximum of 7.7 g/cm at $X = 0.01$, and the density decreased with increasing X , with a minimum of 7.54 g/cm at $X = 0.05$. Then, the changes of k_p , Q_m , d_{33} were measured. The k_p , ϵ_r and Q_m are expressed by Eqs. (2), (3), (4).

$$k_p^2 = 1.265 \times \frac{f_a^2 - f_r^2}{f_a^2} \quad (2)$$

Here, f_r is the resonant frequency, f_a is the antiresonant frequency.

$$\epsilon_r = \frac{C \times t}{S} \quad (3)$$

Here, C is the capacitance at 1 kHz, t is the thickness of the sample, and S is the electrode area.

$$\frac{1}{Q_m} = 2pZ_r C \times \frac{f_a^2 - f_r^2}{f_a^2} \gg 4pZ_r C (f_a - f_r) \quad (4)$$

where Z_r is the impedance of the sample.

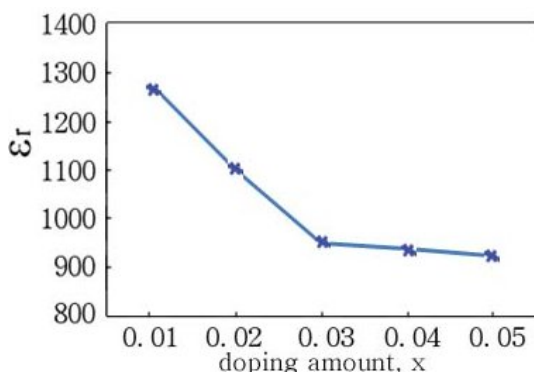


Fig. 5. Variation of relative permittivity with doping amount.

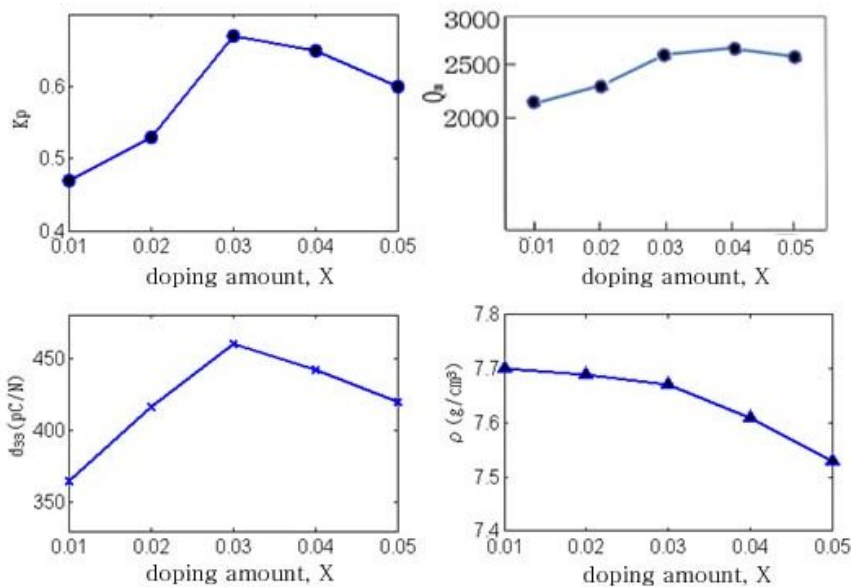


Fig. 6. Variation of characteristic parameters with doping amount.

Fig. 5 shows the variation curve of relative permittivity with doping amount. Fig. 6 shows the variation of K_p , Q_m and d_{33} with doping amount. As can be seen, K_p , Q_m , and d_{33} gradually increased with increasing doping amount and then decreased again. Then the doping amount was near $X = 0.03$, the characteristic values had a maximum. When the doping amount is too high, they will be overdoped, and they will aggregate at the grain boundaries, increasing the grain boundaries and decreasing the grain size. This increases the energy consumption when an external electric field is applied, resulting in an increase in dielectric loss. Also, K_p decreases with decreasing d_{33} due to the buffering action caused by the geometric deformation and stress.

CONCLUSIONS

Considering the variation of K_p and Q_m with Mn and Sb addition ratio, the electromechanical coupling coefficient and Q-factor simultaneously reached high values when the Mn content was 30-35% and the Sb content was 65-70%. Therefore, we set the ratio of manganese to antimony 3:7. The analysis of the relationship between doping and piezoelectric properties shows that the piezoelectric properties are maximized, and the optimum doping is $X = 0.03$. The electromechanical coupling coefficient and Q-factor were 0.67 and 2900, respectively. The addition of manganese and antimony simultaneously increased the electromechanical coupling coefficient and the quality factor. However, the addition of manganese can increase the electromechanical coupling coefficient, but it has not yet reached enough quality factor values due to its tendency to decrease the quality factor. Future work is expected to focus on finding impurities that do not interconnect the electromechanical coupling coefficient and the Q-factor.

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