JOURNAL OF MATERIALS SCIENCE **35** (2000) 2477–2480

Effects of addition of MnO on piezoelectric properties of lead zirconate titanate

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The effects of manganese addition on the piezoelectric properties, microstructure, sintering characteristic and Curie temperature have been studied for Pb(Zr,Ti)O_3 (PZT) ceramics. The valence states of manganese are measured by Electron Spin Resonance (ESR). Those studies show that manganese coexist mainly in the way of Mn^{2+} and Mn^{3+} in PZT ceramics. When the concentration of Mn ion is below 0.5 mole%, it is preferentially incorporated in the lattice Pb site in Mn^{2+} or Mn^{3+}, which gives rise to the increase of K_p and d_{33}. In the intermediate concentration region of 0.5–1.5 mole%, Mn ion will be incorporated in the lattice of (Ti, Zr) site in Mn^{3+} acted as acceptor, which increases Q_m without causing large changes of K_p and d_{33}. When the concentration of Mn ion is larger than 1.5 mole%, it will accumulate at the grain boundaries and give rise to the decrease of piezoelectric properties of PZT ceramics. Small amount of Fe may decrease the solubility limit of Mn ion in PZT ceramics and it may also prevent the oxidation of Mn^{2+} and Mn^{3+}. *© 2000 Kluwer Academic Publishers*

1. Introduction

Lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$, PZT) is a promising candidate material for resonators, actuators and transducers due to its excellent piezoelectric, ferroelectric and many other electrical properties [1, 2]. Various dopants were usually added into PZT in order to enhance the piezoelectric properties for some technologically demanding applications [3, 4]. Manganese oxide (MnO) is one of the most effective dopants to improve the piezoelectric properties of PZT. The effects of the addition of MnO on the piezoelectric properties of PZT have been studied by the earlier investigators [5–8]. It was found that both the mechanical quality factor (Q_m) and the electromechanical coupling factor (K_p) of PZT could be enhanced with increasing the amount of MnO. However, the intrinsic mechanism of the influence of MnO on PZT is not well understood. It is thus interesting to investigate how the addition of MnO influences the piezoelectric properties of PZT. In the present work, various quantities of MnO were added into two "hard" PZT compositions, respectively, and the resulting PZT ceramics were characterized for piezoelectric properties and microstructure characteristics.

2. Experimental procedure

The basic PZT compositions selected for the study are: $Pb_{0.95}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ (PZTS) and $Pb(Zr_{0.53}Ti_{0.47})_{0.98}(Sb_{2/3}Mn_{1/3})_{0.02}O_3$ (PZTM), and various quantities of $MnCO_3$ ($x = 0$–7.5 mol%) were added into the above two compositions as dopants, respectively. The starting materials were commercially available PbO (99.94%), ZrO_2 (99.68%), TiO_2, (98.61%), SrCO3 (97.22%), Sb_2O_3 (99.99%) and $MnCO_3$ (92.87%). Powders of appropriate weight ratios, as required by the stoichiometric composition of PZTS and PZTM, were mixed in a conventional ball mill using iron balls as the milling media in distilled water for 24 hours, respectively, followed by drying the slurries at 120°C. The two powder mixtures were then calcined at 850°C for a fixed duration of 2 hours, respectively. The calcined powders were mixed with various accurate weights of $MnCO_3$ using conventional mill, respectively, followed by drying the slurries at 120°C again. The dried powders were uniaxially pressed into pellets of 20 mm in diameter at 250 MPa. Sintering of the pellets was carried out in a covered alumina crucible at temperatures in the range of 1240 to 1270°C for a fixed duration of 2 hours.

Scanning electron microscope (SEM) (Model EPMA-8708QH2, Shimadzu, Japan) was employed to characterize PZTS ceramics sintered at different temperatures. Electron Spin Resonance (ESR) (Model ER-200D SRC, Germany) was used to determine the valence state of Mn ion in the PZT ceramics. The sintered ceramics were lapped into disks of $\Phi 17 \times 1$ mm, then were provided with fired-on silver electrodes. Poling was carried out in silicone oil bath at 100°C using a dc field of 3.5–4 KV/mm for 15 minutes. The electromechanical coupling factor (K_p) and mechanical

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quality factor (Q_m) were calculated by the resonance-antiresonance method, and the piezoelectric constant (d_{33}) was measured using d_{33} meter model Zj-2 (Acoustic Institute, China). The curie temperature (T_c) was determined by temperature dependence of the dielectric constant at 10 KHz.

3. Results and discussions

3.1. Variation of Curie temperature with MnO content

Fig. 1 shows the Curie temperatures (T_c) of PZTS and PZTM ceramics as a function of amount of MnO. For PZTS ceramics, the Curie temperature of PZTS decreases rapidly with increase in amount of MnO over the range from 0 to 0.5 mol%. Further increasing the amount of MnO above 0.5% results in a slight fall in Curie temperature. For PZTM ceramics, in contrast, the Curie temperature decreases a little when the amount of MnO is below 1 mol%. So, it is believed that manganese is mainly incorporated into the lattice when its concentration is below 1.5 mol%, and it will accumulate at the grain boundaries when the amount is above 1.5 mol%. In other words, it seems that the solubility limit of Mn ion in PZT ceramics is about 1.5 mole%, rather than 2.5 mole% obtained by Ng and Alexander [9]. The difference between our results and Ng and Alexander's may results from different processes, especially the grinding media used, the latter paragraph will discuss this problem in detail.

3.2. Variation of grain size with the amount of MnO

Fig. 2 shows SEM photographs of sintered surfaces of the sintered PZTS ceramics doped with various amount of MnO, together with that of the pure PZTS ceramic. The grain size of samples doped with 1.0 and 1.5 mol% MnO (Fig. 2b, c) are comparatively uniform, with size range from 1 μm to 3 μm, which is slightly larger than that of pure PZTS (0.5–1.5 μm) (Fig. 2a). This result is contradictory with the results of Wersing [10]. Further increasing the amount of MnO gives rise to an inhomogeneous grain size, and the average grain size is also reduced (Fig. 2d, e). The latter phenomenon was observed by a lot of research workers [9–11]. From these results one can expect that Mn ion is homogeneously dissolved in PZT ceramics when its concentration is below 1.5 mol%, further addition of MnO will inhibit the grain growth as some Mn may accumulate at the grain boundary [9–11]. These results are obviously consistent with the solubility limit indicated by Curie temperature measurements. In view of the fact that doping with a small quantity of MnO is beneficial for the grain growth, it is believed that Mn ion leads to the formation of the vacancies in the Pb position. The investigations of $PbTiO_3$ ceramics doped with Fe or Mn have shown that Fe^{3+} or Mn^{2+} can be incorporated partly in the lead sublattice [12], so it is reasonable to consider that Mn ion is incorporated partly into the Pb sites in PZT ceramics as well when the concentrations of MnO are very small.

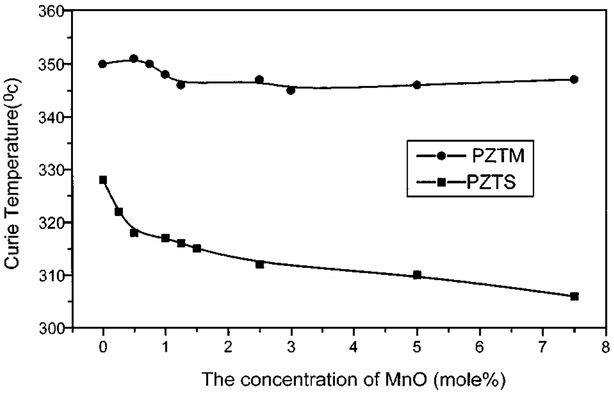

Figure 1 Effects of the concentration of MnO on Curie temperature of PZT ceramics.

3.3. The valence state of Mn ion in PZT

Fig. 3 shows the ESR spectrum of PZT added with 0.75 mole% MnO. A broad peak around 3400G was observed, which is attributed to Mn^{2+} [7–10], the g factor measured is about 2.00, nearly equal to g_e of free electron ($g_e = 2.0023$), which also indicates that the 3d-orbit of Mn is half-filled ($3d^5$), and Mn is present in the way of Mn^{2+}. But the wide peak of Mn^{4+} around 1500G reported by Bykov and Kamiya [11, 13] was not observed in our studies. The main difference may comes from the different processing conditions, especially the media of balling, the grinding media used in our study is iron-ball, so a small quantity of Fe (about 0.25 wt% measured by ICP method) is brought into the specimens through balling. As Fe is mutilvalence ion which can be oxided during the cooling process [11], so the partial pressure of O_2 is reduced and reaction (3) is difficult to take place. In other words, Fe ion may inhibit the oxidation of Mn_2O_3 (reaction (3)). That is probably one of the reasons that Mn^{+4} was not detected by ESR in our study.

$$2Mn_3O_4 + \frac{1}{2}O_2 \xrightarrow{900^\circ C} 3Mn_2O_3 \tag{1}$$

$$2Fe_3O_4 + \frac{1}{2}O_2 \xrightarrow{800^\circ C} 3Fe_2O_3 \tag{2}$$

$$Mn_2O_3 + \frac{1}{2}O_2 \xrightarrow{600^\circ C} 2MnO_2 \tag{3}$$

Furthermore, Fe is also incorporated into Ti or Zr sites as a acceptor, it may compete with Mn^{3+}, as Ti or Zr can only be replaced with Mn or Fe to a limited extent in order to keep the structure of octahedra, so the solubility limit in our study is lower than Ng's results.

According to the principle of electron spin resonance, Mn^{3+} is difficult to be detected by ESR as its 3d-electron is oven number [14]. But from the facts that Mn doping makes the increase of Q_m, one can deduces that Mn^{3+} will replace Ti^{+4} acted as acceptor. Furthermore, as the color of sintered specimens gets darker with the concentration of Mn, one can also expect that Mn^{3+} is present in PZT ceramics (the color of Mn^{2+} is pale).

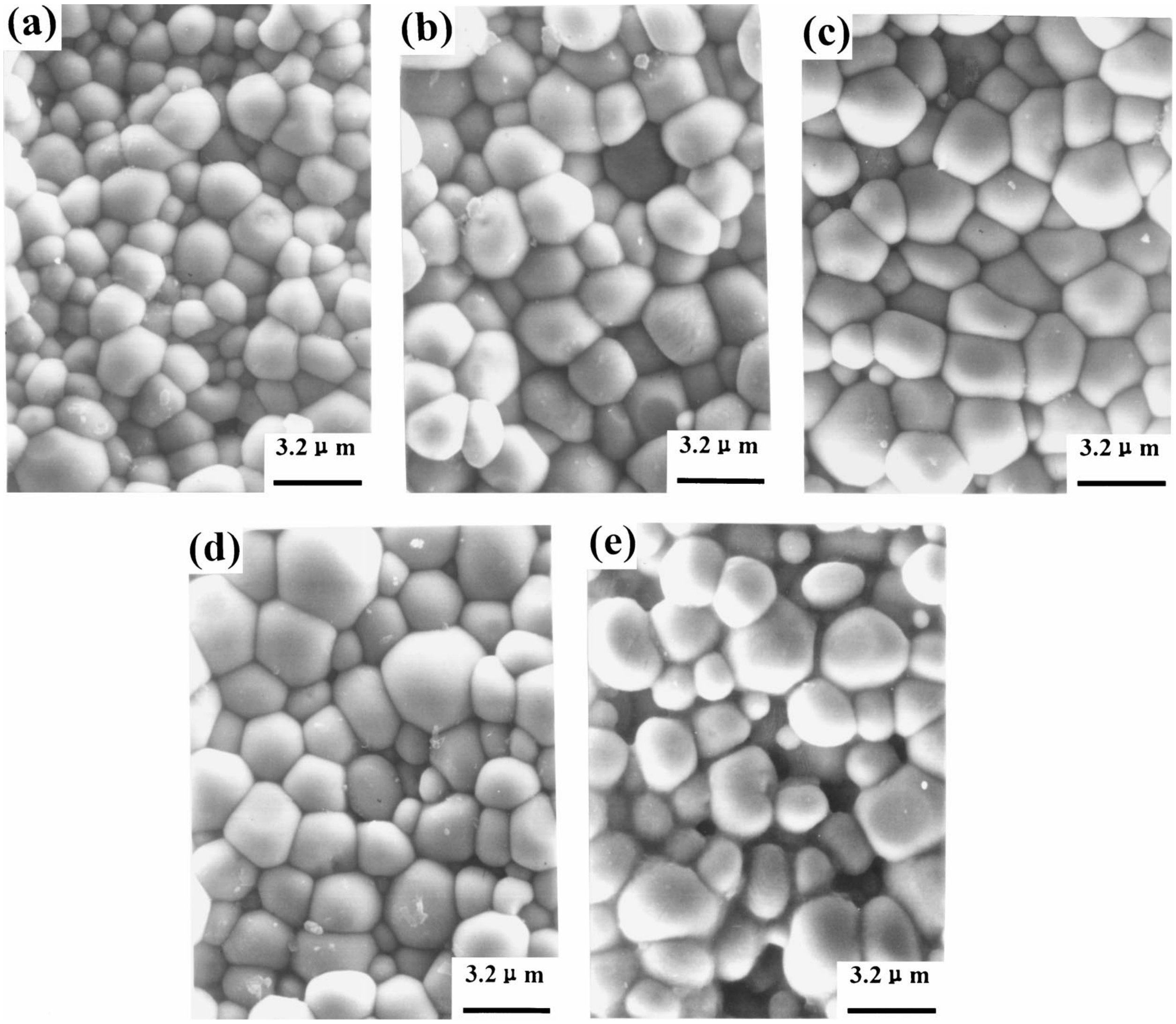

Figure 2 SEM photographs of the natural surfaces of the sintered PZTS specimens with various MnO content: (a) 0 mole%Mn; (b) 1 mole%Mn; (c) 1.5 mole%Mn; (d) 3 mole%Mn; (e)7.5 mole%Mn.

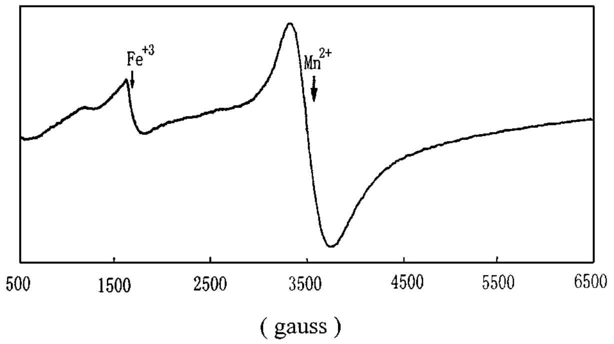

Figure 3 The ESR spectrum of Mn-doped PZT specimens.

3.4. Electromechanical properties

Figs 4 and 5 show piezoelectric properties (K_p, d_{33}, tan δ and Q_m) as functions of amount of MnO for PZTS and PZTM ceramics. From these figures it is seen that the effect of MnO addition on the piezoelectric properties of PZT ceramics can be divided into three regions i.e low, intermediate and high dopant regions.

For PZTS ceramics, when the amount of MnO is lower than 0.5 mol%, K_p and d_{33} are rapidly increased, respectively, but Q_m is slightly decreased. When the amount of MnO is increased to 1.5 mol%, Q_m increases with x without leading much change in K_p and d_{33}. In the high concentration of $x > 1.5$, there is an abrupt decrease in Q_m, K_p and d_{33} also decrease slowly with x. For PZTM, Q_m first increases with x and becomes maximum at $x = 0.75$, then decreases rapidly with x, but K_p and d_{33} decrease monotonically with MnO content in three concentration regions. However, tan δ increases monotonically with the amount of Mn in both PZTS and PZTM ceramics within the whole concentration scope, it clearly appears that there is no correlation between Q_m measured around 100 kHz (radial mode) and tan δ measured at 1 kHz. These results are contradictory with the conclusion of Gerthsen and Hardtl [15], but it is consistent with the results of Eyraud [11].

In view of the results of T_C, SEM and ESR described in Section 3.1, Section 3.2 and Section 3.3, it is quite probable that Mn ion is preferentially incorporated in the lattice Pb site in Mn^{2+} or Mn^{3+} when the amount of MnO is in the low concentration region of $0 < x < 0.5$, which give rise to the formation of vacancies in the Pb position making domain wall mobile, so Q_m is slightly decreased, but the piezoelectric properties are greatly improved. In the intermediate concentration of

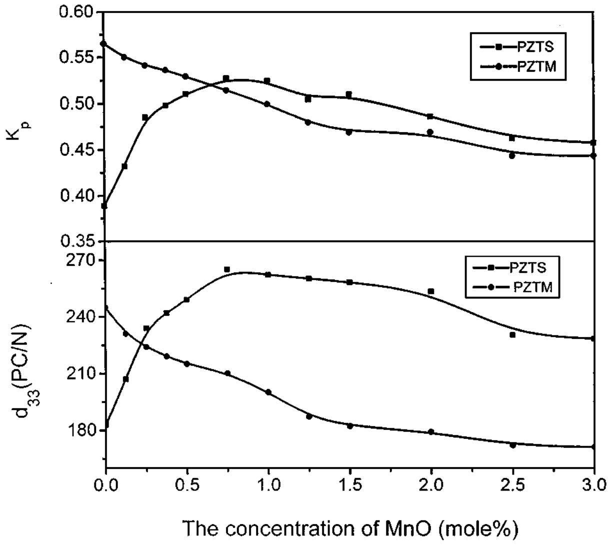

Figure 4 The relationship of K_p and d_{33} with the amount of MnO.

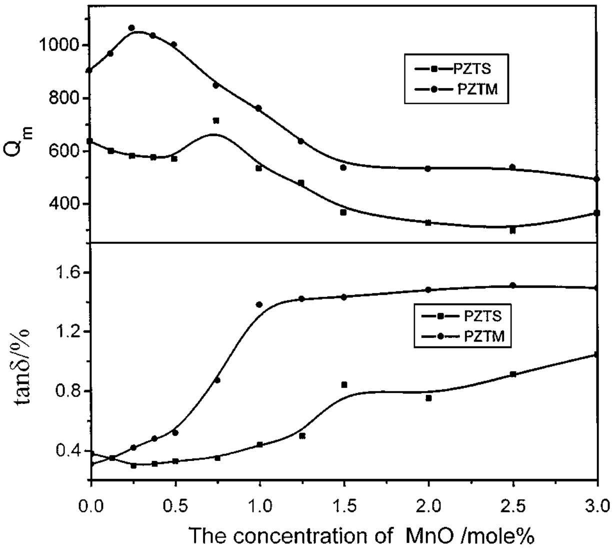

Figure 5 The relationship of Q_m and $\tan\delta$ with the amount of MnO.

$0.5 < x < 1.5$, Mn ion will be incorporated in the lattice of (Ti, Zr) site in Mn^{3+} and give rise to the formation of oxygen vacancies, in other words, Mn ion will act as acceptor and increase Q_m without causing large changes of K_p and d_{33}. In the high concentration region of $x > 1.5$, Mn ion will precipitate at the grain boundaries, which inhibit the growth of grain and the piezoelectric properties are weaken. Furthermore, according the results of Kamei [7], the c/a radio of PZT ceramic is decreased by the doping of manganese, so the spontaneous polarization (P_s^*) is also reduced, which may be another reason of leading to the decrease of piezoelectric properties.

4. Conclusions

Based on the results that have been obtained in the present work, the following conclusions can be drawn:

1. Mn ion coexists in Mn^{3+} and Mn^{2+} in as-studied PZT ceramics.
2. In the low concentration region of $0 < x < 0.5$, Mn ion is preferentially incorporated in the lattice Pb site in Mn^{2+} or Mn^{3+} acted as donor, and greatly improve the piezoelectric properties. In the intermediate concentration region of $0.5 < x < 1.5$, Mn ion will be incorporated in the lattice of (Ti, Zr) site in Mn^{3+} acted as acceptor, the Q_m is increased without causing large changes of K_p and d_{33}. In the high concentration region of $x > 1.5$, Mn ion will accumulate at the grain boundaries and give rise to the decrease of piezoelectric properties of PZT ceramics.
3. Small amount of Fe may decrease the solubility limit of Mn ion in PZT ceramics and it may also prevent the oxidation of Mn^{2+} and Mn^{3+}.

Acknowledgement

The authors would like to express their appreciation to Professor Cheng Shiming and Doctor Xue Junmin, who assisted in various aspects of this work.

References

1. S. TAKAHASHI, in "Proceeding of the six International Meeting on Ferroelectricity" (Kobe, 1985) p. 41.
2. S. FUJISHIMA, in "Proceeding of the six International Meeting on Ferroelectricity" (Kobe, 1985) p. 56.
3. K. H. HARDTL, *J. Amer. Ceram. Soc.* **64** (1981) 283.
4. J. S. KIM, *J. Korean Ceram. Soc.* **27** (1990) 187.
5. M. TAKAHASHI, *Jap. J. Appl. Phys.* **9** (1970) 1236.
6. S. TAKAHASHI and M. TAKAHASHI, *J. Appl. Phys.* **11** (1972) 31.
7. S. TAKAHASHI, *Ferroelectrics* **41** (1982) 143.
8. K. CARL and K. H. HARDTL, *ibid.* **17** (1978) 473.
9. Y. S. NG and S. M. ALEXANDER, *ibid.* **51** (1983) 83.
10. W. WERSING, *ibid.* **12** (1976) 143.
11. T. KAMIYA, T. SUZUKI and T. TSURAMI *et al.*, *Jpn. J. Phys.* **31** (1992) 3058.
12. D. HENNINGS and H. POMPLUN, *J. Amer. Ceram. Soc.* **57** (1974) 527.
13. I. P. BYKOV, M. D. M. GLINCHVK and B. B. CKOPOXOD, *Sov. Phys. Solid State* **341** (1992) 1343 (in Russian).
14. A. ABRAGAM and B. BLEANEY, in "Electron paramagnetic Resonance of transition ions" (Oxford University Press, London, 1970) p. 137.
15. P. GERTHSEN, K. H. HARDTL and N. A. SCHMIDT, *J. Appl. Phys.* **51** (1980) 1131.
16. I. P. BYKOV, M. D. M. GLINCHVK and V. V. SKOROKHOD, *Ferroelectrics* **127** (1992) 89.
17. L. EYRAUND, P. GONNARD and M. TROCCAZ, *ibid.* **93** (1989) 127.

Received 30 March
and accepted 22 November 1999