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Structure and Electrical Properties of Fe_2O_3-Doped PZT-PZN-PMnN Ceramics

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Abstract

The $0.8Pb(Zr_{0.48}Ti_{0.52})O_3 – 0.125Pb(Zn_{1/3}Nb_{2/3})O_3 – 0.075Pb(Mn_{1/3}Nb_{2/3})O_3 + x$ wt% Fe_2O_3 ceramics (PZT-PZN-PMnN), where x = 0 ÷ 0.35, has been prepared by two-stage calcination method. The effect of Fe_2O_3 content on the crystal structure and electrical properties of ceramics has been investigated. The results of X-ray diffraction (XRD) show that all samples have pure perovskite phase with tetragonal structure, the c/a ratio increases with increasing Fe_2O_3 content. At x = 0.25, electrical properties of ceramics are best: the density (ρ) of 7.86 g/cm³, the electromechanical coupling factor (k_p) of 0.64, the dielectric constant (ε_r) of 1400, the dielectric loss ($\tan\delta$) of 0.003, the mechanical quality factor (Q_m) of 1450, the piezoelectric constant (d_{31}) of 155 pC/N, and the remanent polarization (P_r) of 37 μC/cm², which makes it as a promising material for high power piezoelectric devices.

1. Introduction

Relaxor ferroelectric materials have the high dielectric constant, broad ferroelectric-paraelectric transition (the diffuse phase transition) and strong frequency dependence of dielectric properties [1] [2]. So far, researchers have been interesting on the Pb-based relaxors $Pb(B'_{1/3}B''_{2/3})O_3$ because they are promising materials for multi-layer capacitors, transducer and actuators [2]-[4].

The addition of small amounts of such relaxor materials was found to be beneficial for the electrical properties of PZT-based ceramics due to the formation of fine and uniform rhombohedral domains along tetragonal

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ones [4] [5]. Recently, it was observed that both the dielectric and piezoelectric properties of these PZT-relaxor materials are strongly influenced by the addition of other additives such as La, ZnO, CuO, MnO_2 and Fe_2O_3 [2] [4] [6]-[8]. The Fe_2O_3 addition is probably one of the most frequently used acceptors in ferroelectrics. The effects of Fe_2O_3 on PZT and PZT-based ternary ceramics have been studied [7]-[10]. However, the effect of Fe_2O_3 addition on the quaternary PZT-PZN-PMnN was scarcely reported.

Recently, we studied the effect of Zr/Ti ratio content on some physical properties of $0.8Pb(Zr_xTi_{1-x})]O_3 - 0.125Pb(Zn_{1/3}Nb_{2/3})O_3 - 0.075Pb(Mn_{1/3}Nb_{2/3})O_3$ [11]. We found that the electromechanical coupling factor (k_p), the piezoelectric constant (d_{31}) and the mechanical quality factor (Q_m) of the ceramics are enhanced with the increase of Zr/Ti ratio. At Zr/Ti ratio of 48/52, the ceramics has the optimal electromechanical properties, $k_p = 0.62$, $d_{31} = 140$ pC/N, $Q_m = 1112$. According to our results [12] showed that 0.7 wt% Li_2CO_3 was quite effective in lowering the sintering temperature of 0.8PZT-0.125PZN-0.075PMnN ceramics from 1150°C down to 930°C, with the retention of good piezoelectric properties.

In this study, we investigated the effect of Fe_2O_3 doping on structure and electrical properties of Fe_2O_3-doped $0.8Pb(Zr_{0.48}Ti_{0.52})O_3 - 0.125Pb(Zn_{1/3}Nb_{2/3})O_3 - 0.075Pb(Mn_{1/3}Nb_{2/3})O_3 + 0.7$ wt% Li_2CO_3 ceramics.

2. Experimental Procedure

The general formula of the studied material was $0.8Pb(Zr_{0.48}Ti_{0.52})O_3 - 0.125Pb(Zn_{1/3}Nb_{2/3})O_3 - 0.075Pb(Mn_{1/3}Nb_{2/3})O_3 + 0.7$ wt% $Li_2CO_3 + x$ wt% Fe_2O_3 (PZT-PZN-PMnN), where x is 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35 and are denoted by M_0, M_1, M_2, M_3, M_4, M_5, M_6, respectively. Reagent grade oxide powders (purity $\geq$ 99%) of PbO, ZnO, MnO_2, Nb_2O_5, ZrO_2, TiO_2, Li_2CO_3 and Fe_2O_3 were used as starting materials. Firstly, the powders of $(Zn,Mn,Fe)Nb_2(Zr,Ti)O_6$ were prepared by reactions of ZnO, MnO_2, Nb_2O_5, ZrO_2, TiO_2 and Fe_2O_3 at temperature 1100°C for 2 h. Then $(Zn,Mn,Fe)Nb_2(Zr,Ti)O_6$ and PbO were weighed and milled for 8 h. The powders were calcined at temperature 850°C for 2 h, producing the PZT-PZN-PMnN compound. Thereafter, predetermined amounts of Li_2CO_3 were mixed with the calcined PZT-PZN-PMnN powder, and then, powders milled for 16 h. The ground materials were pressed into disk 12 mm in diameter and 1.5 mm in thick under 100 MPa. The samples were sintered at 950°C for 2 h.

The crystal structure of the sintered samples was examined by X-ray diffraction (XRD, D8 ADVANCE). The density of samples was measured by Archimedes method. The synthesized pellets were poled in a silicone oil bath at 120°C by applying the DC electric field of 30 kV·cm^{-1} for 20 min then cooling down to room temperature (RT). They were aged for 24 h prior to testing.

The piezoelectric properties were determined with the resonance and antiresonance frequency using an impedance analyzer (HP 4193A and RLC HIOKI 3532). Dielectric measurements (capacitance and loss factor) were measured in the temperature range of 30 to 350°C at frequencies 1 kHz by using a programmable temperature controller and an impedance analyzer (RLC HIOKI 3532).

3. Results and Discussion

3.1. Effect of Fe_2O_3 Addition on the Structure and Microstructure of PZT-PZN-PMnN Ceramics

Figure 1 shows X-ray diffraction patterns (XRD) of the PZT-PZN-PMnN ceramics at the different contents of Fe_2O_3. All samples have pure perovskite phase with tetragonal structure. When increasing of Fe_2O_3 content, the tetragonality c/a ratio increases as shown in Figure 2.

Figure 3 shows the SEM micrographs of the fracture surface of the samples as Fe_2O_3 addition. It is seen from the micrographs that the grain size grows with the increase of Fe_2O_3 addition (Figure 5). Below the Fe_2O_3 solubility of 0.25 wt%, the grain sizes increase and the grain boundaries present regular shapes. However, when the addition of Fe_2O_3 is higher than 0.25 wt%, a few cavities appeared between the grains.

Figure 4 shows the variation of density of PZT-PZN-PMnN samples at the different Fe_2O_3 contents. It can be seen that the density of the PZT-PZN-PMnN samples as a function of the Fe_2O_3 content. With Fe_2O_3 content increased, the density of PZT-PZN-PMnN samples increased. It achieves a maximum value ($\rho = 7.86$ g/cm^3) at Fe_2O_3 content of 0.25 wt%, and then decreases. The variation in density of the ceramic samples is in good accordance with the microstructure. When the addition is less than 0.25 wt%, Fe^{3+} ions can incorporated into the perovskite and cause the increase of the density; however, the excess addition causes the aggregation at the grain
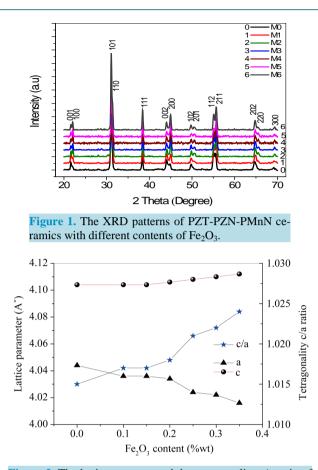
Figure 1. The XRD patterns of PZT-PZN-PMnN ceramics with different contents of Fe_2O_3.

Figure 2. The lattice constant and the tetragonality c/a ratio of PZT-PZN-PMnN ceramics with different contents of Fe_2O_3.
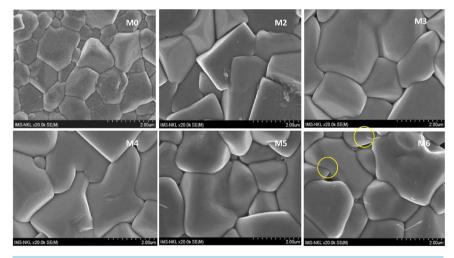

Figure 3. Microstructures of samples with the different Fe_2O_3 contents.

boundaries, thus leading to the decrease of the density of the samples [7] [8]. The variation in density may affirm the solubility limit of Fe_2O_3 in PZT-PZN-PMnN lattice.

The grain size, the density of ceramic have a strong effect on dielectric, piezoelectric and ferroelectric properties of ceramic materials. The relationships between the grain size and the density of ceramic and electrical properties are discussed in the next section.
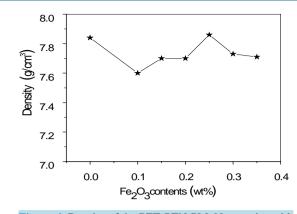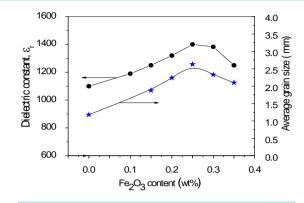
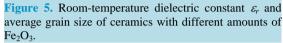**Figure 4.** Density of the PZT-PZN-PMnN ceramics with different amounts of Fe_2O_3.

3.2. Effect of Fe_2O_3 Content on the Electrical Properties of PZT-PZN-PMnN Ceramics
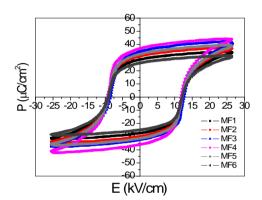
Figure 5 shows the room temperature dielectric constant ε_r at 1kHz of PZT-PZN-PMnN ceramics as function of the Fe_2O_3 contents. The ε_r increases with the Fe_2O_3 content increases and reaches highest value (1400) at x = 0.25. With contents x > 0.25, the dielectric constant ε_r decreased. This is related to grain size of ceramics. When the addition of Fe_2O_3 is lower than the solution limit, the drastic increase in grain size appears, which compensates for the effect of oxygen vacancy on pinning the motion of domains, thus leading to the increase of ε_r [2] [6]-[8]. When the addition is above 0.25 wt%, the occurrence of the cavities between the grains becomes obvious, which causes the decrease of the ε_r [7] [8].

Figure 6 shows the forms of feroelectric hysteresis loops of the samples measured at room temperature. From the changes of the shape of these loops with Fe_2O_3 contents, the remanent polarization P_r and the coercive field E_c were determined, as shown in **Figure 7**. A sharp increase in P_r was observed for M_0-M_4 samples, reaches the highest value (37 $\mu C/cm^2$) with M4 sample, and then decreases. This result is in good agreement with the studied dielectric and piezoelectric properties of the samples. While, the coercive field E_c increases with increasing of Fe_2O_3 content. This results (increased Ec) clearly indicate the "hard" characteristics with addition of Fe_2O_3, mainly caused by Fe ions substitution in B site leads to the creation of oxygen vacancies, which pin the movement of the ferroelectric domain walls [2] [7] [8].
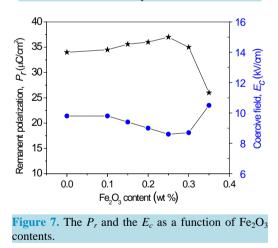
To determine piezoelectric properties of ceramics, resonant vibration spectra of samples were measured at room temperature. From these resonant spectra, piezoelectric parameters of samples were determined. **Figure 8** shows the electromechanical coupling factor (k_p, k_t), the piezoelectric constant (d_{31}), the mechanical quality factor Q_m and dielectric loss $\tan\delta$ change as a function of the amount of Fe_2O_3. The mechanical quality factor (Q_m) and the dielectric loss ($\tan\delta$) of the Fe_2O_3-doped PZT-PZN-PMnN ceramics markedly improved, as shown in **Figure 8**. As the Fe_2O_3 content in the PZT-PZN-PMnN ceramics was increased up to 0.25 wt%, the Q_m value increased steadily up to 1450 while dielectric loss $\tan\delta$ decreased steadily down to the lowest value (0.25 %) because the Fe ions at the (Ti, Zr, Nb) sites in the lattice acted as acceptors. More specifically, the substitution of Fe ions in the B-sites of the perovskite structure increases the number of oxygen vacancies. As mentioned above, these oxygen vacancies induce a space charge and internal field inside the PZT-PZN-PMnN grains, which inhibits the motion of the domain walls, thereby increasing the Q_m value and decreasing the $\tan\delta$ value [2] [7] [8] [10]. However, when the Fe_2O_3 content exceeded a certain threshold value (>0.25 wt%), the Q_m value decreased and the $\tan\delta$ value increased, apparently due to the solubility limit of Fe. When the amount of Fe_2O_3 added to PZT-PZN-PMnN ceramics exceeded the solubility limit, the excessive Fe ions could not incorporate into the lattice of perovskite structure, which accumulated at the grain boundaries and reduced the physical properties of ceramic materials [2] [7] [8]. As can be seen in **Figure 8**, the k_p, k_t and the d_{31} show a similar variation with increasing Fe_2O_3 content. When the content of Fe_2O_3 is lower than 0.25 wt%, the k_p, k_t and the d_{31} are increased with increasing Fe_2O_3 content. The optimized values for k_p of 0.64, k_t of 0.51 and d_{31} of 155 pC/N were obtained at x = 0.25. This is probably related to characteristics of the increasing grain size. As is well known, the increased grain size makes domain reorientation easier and severely promotes domain wall motion, which could increase the piezoelectric properties [2] [7] [8] [11] [12].

Figure 5. Room-temperature dielectric constant ε_r and average grain size of ceramics with different amounts of Fe_2O_3.

Figure 6. Hysteresis loops of Fe_2O_3-doped PZT-PZN-PMnN ceramic samples.

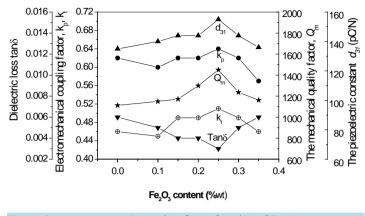**Figure 7.** The P_r and the E_c as a function of Fe_2O_3 contents.

4. Conclusions

We have investigated the effect of Fe_2O_3 addition on structure and electrical properties of $0.8Pb(Zr_{0.48}Ti_{0.52})$ – $0.125Pb(Zn_{1/3}Nb_{2/3})$ – $0.075Pb(Mn_{1/3}Nb_{2/3})O_3$ ceramics. The results of this study are summarized as follow:

All samples have pure perovskite phase with tetragonal structure; the c/a ratio increases with increasing Fe_2O_3 contents.

The dielectric, piezoelectric and feroelectric properties of ceramics were markedly improved by Fe_2O_3 addition. At the Fe_2O_3 content of 0.25% wt, electrical properties of ceramics are best: the density of 7.86 g/cm³, the

Figure 8. The k_p, k_t, d_{31}, Q_m, and $\tan\delta$ as a function of Fe_2O_3 contents.

electromechanical coupling factor (k_p) of 0.64 and (k_t) of 0.51, the dielectric constant, ε_r of 1400, the dielectric loss ($\tan\delta$) of 0.003, the mechanical quality factor (Q_m) of 1450, the piezoelectric constant (d_{31}) of 155 pC/N, and the remanent polarization (P_r) of 37 $\mu C/cm^2$, which makes it as a promising material for high power piezoelectric devices.

References

[1] Fan, H. and Kim, H. (2002) *Journal of Applied Physics*, **91**, 317-322. http://dx.doi.org/10.1063/1.1421036

[2] Xu, Y. (1991) Ferroelctric Materials and Their Applications (North-Holland, Amsterdam-London-Newyork-Tokyo).

[3] Seo, S.B., Lee, S.H., Yoon, C.B., Park, G.T. and Kim, H.E. (2004) *Journal of the American Ceramic Society*, **87**, 1238-1243. http://dx.doi.org/10.1111/j.1551-2916.2004.tb20095.x

[4] Yan, Y.K., Kumar, A., Correa, M., Cho, K.-H., Katiyar, R.S. and Priya, S. (2012) *Applied Physics Letters*, **100**, Article ID: 152902. http://dx.doi.org/10.1063/1.3703124

[5] Gao, F., Cheng, L., Hong, R., Liu, J., Wang, C. and Tian, C. (2009) *Ceramics International*, **35**, 1719-1723.

[6] Kim, Y.H., Ryu, H., Cho, Y.-K., Lee, H.-J. and Nahm, S. (2013) *Journal of the American Ceramic Society*, **96**, 31-317. http://dx.doi.org/10.1111/j.1551-2916.2012.05461.x

[7] Zhu, M.K., Lu, P.X., Hou, Y.D., Wang, H. and Yan, H. (2005) *Journal of Materials Research*, **20**, 2670-2675. http://dx.doi.org/10.1557/JMR.2005.0339

[8] Zhu, M.K., Lu, P.X., Hou, Y.D., Song, X.M., Wang, H. and Yan, H. (2006) *Journal of the American Ceramic Society*, **89**, 3739-3744. http://dx.doi.org/10.1111/j.1551-2916.2006.01281.x

[9] Li, J., He, Z.B. and Damjanovic, D. (2009) *Applied Physics Letters*, **95**, Article ID: 012905. http://dx.doi.org/10.1063/1.3173198

[10] Du, J., Qiu, J., Zhu, K., *et al.* (2012) *Journal of Materials Letters*, **66**, 507-510.

[11] L.D. Vuong, Gio, P.D., Chuong, T.G.V., Trang, D.T.H., Hung, D.V. and Duong, N.T. (2013) *International Journal of Materials and Chemistry*, **3**, 39-43.

[12] Vuong, L.D. and Gio, P.D. (2013) *International Journal of Materials Science and Applications*, **2**, 89-93.

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