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Effects of MnO_2 and Fe_2O_3 Additives on the Piezoelectric Properties of 0.05PMN-0.451PT-0.499PZ Ceramics

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The effects of MnO_2 and Fe_2O_3 on the piezoelectric properties of 0.05PMN-0.451PT-0.499PZ ceramics were investigated. The addition of MnO_2 increased mechanical quality factor (Q_m) but decreased the dielectric constant ($K_{33}{}^T$) and compliance ($S^E{}_{11}$) of the specimens. These results indicated that MnO_2 behaves as an acceptor in 0.05PMN-0.451PT-0.499PZ ceramics. The electromechanical coupling coefficient (K_p) of 0.05PMN-0.451PT-0.499PZ ceramics slightly increased with the addition of MnO_2 however, the enhancement of K_p was insignificant. A small amount of Fe_2O_3 was added to enhance the K_p of the 0.05PMN-0.451PT-0.499PZ + 0.5 wt% MnO_2 ceramics. The addition of Fe_2O_3 largely increased K_p through the increase of the $K_{33}{}^T$ and the polarization. The mechanical quality factor of the specimens decreased with the addition of Fe_2O_3 however, the reduction was negligible.

Key words: PMN, PZT, Piezoelectricity

I. Introduction

Since Ouchi *et al.* reported the piezoelectric properties of the $xPb(Mg_{1/3}Nb_{2/3})O_3$-$yPbTiO_3$-$zPbZrO_3$ (PMN-PZT) ceramics, a number of compositional modifications of PMN-PZT ceramics have been studied.[1-4] The effects of various dopants on the piezoelectric properties of PMN-PZT ceramics were also extensively investigated.[2,5] It has been reported that MnO_2 increases the Q_m and NiO increases the K_p and dielectric constant of 0.375PMN-0.375PT-0.25PZ ceramics.[5] Moreover, the addition of both MnO_2 and NiO additives is known to improve the Q_m.[5] Although there were a large number of works on PMN-PZT ceramics, most of the works were concentrated on the 0.375PMN-0.625PZT and the 0.125PMN-0.875PZT compositions because they have been known to have the good piezoelectric properties. According to the previous work, however, the 0.05PMN-0.95PZT ceramics exhibited a better impact strength durability compared with that of the 0.125PMN-0.875PZT ceramics.[6] The Q_m and K_p of the 0.05PMN-0.95PZT ceramics were similar to those of the 0.125PMN-0.875PZT ceramics which are relatively low for the application. Therefore, it is necessary to improve the Q_m and K_p of 0.05PMN-0.95PZT ceramics. In this work, MnO_2 and Fe_2O_3 additives were added to enhance the Q_m and K_p of 0.05PMN-0.95PZT ceramics. Moreover, the effect of MnO_2 and Fe_2O_3 on the microstructure of 0.05PMN-0.95PZT ceramics was also studied.

II. Experimental Details

Reagent-grade of PbO, ZrO_2, TiO_2, MgO, Nb_2O_5, MnO_2 and Fe_2O_3 were used as the starting materials. The materials were weighed in the appropriate molar ratio and mixed with ZrO_2 balls in an ethanol media for 24 h. The powders were dried, calcined at 850°C for 1 h in air, and pressed into a disk. These pellets were covered with two alumina crucibles and fired at 1200°C for 1 h. In order to minimize the vaporization of PbO, $PbZrO_3$ was used as the packing powder. The sintered pellets were ground to the thickness of 1 mm. electroded with silver paste and heat treated at 700°C for 10 min. The electroded specimens were poled in silicon oil at 120°C by applying DC field of 3.5 kV/mm for 30 min. Dielectric constant was measured using HP 4194A impedance/gain analyzer. Twenty-four hours after poling, K_p and elastic compliance constant ($S^E{}_{11}$) were obtained from the ratio of the resonance -antiresonance method in radial mode vibration.[7] The mechanical quality factor, Q_m, was calculated from the following equation.

$$Q_m = 1/[4\pi(f_a - f_r)RC]$$

f_a=antiresonant frequency
f_r=resonant frequency
R=resonant resistance
C=capacitance

Polarizations induced by a 0.1 Hz bipolar/ unipolar elec-

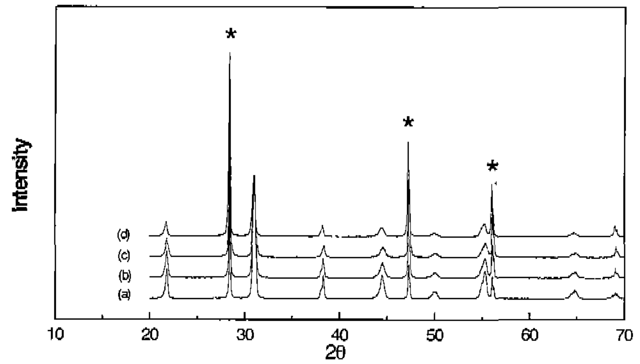

Fig. 1. X-ray diffraction patterns of 0.05PMN-0.451PT-0.499PZ ceramics doped with MnO_2 sintered at 1200°C: (a) none; (b) 0.1 wt%; (c) 0.5 wt%; (d) 0.6 wt%(*Si).

tric field were measured simultaneously using modified Sawyer-Tower method. Conventional strain gauge method was used to detect the change of transverse strains using a strain gauge (B-FAE, Minebea, Tokyo, Japan) attached to one side of the electrodes.[8]

III. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of the MnO_2 doped 0.05PMN-0.95PZT ceramics. All the specimens have the perovskite structure without second phases. The tetragonality of 0.05PMN-0.95PZT ceramics was small and slightly increased with the addition of MnO_2 as shown in Fig. 2.

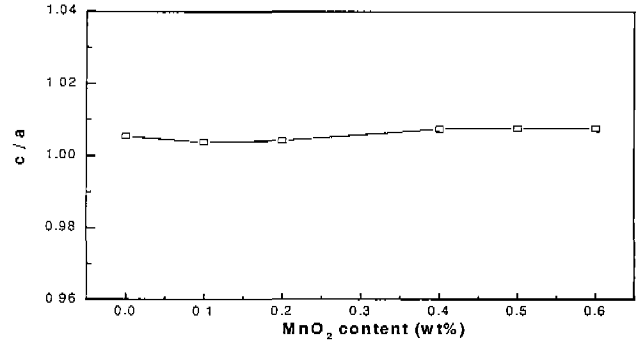

Fig. 2. Variation of c/a ratio of 0.05PMN-0.451PT-0.499PZ ceramics with MnO_2 content.

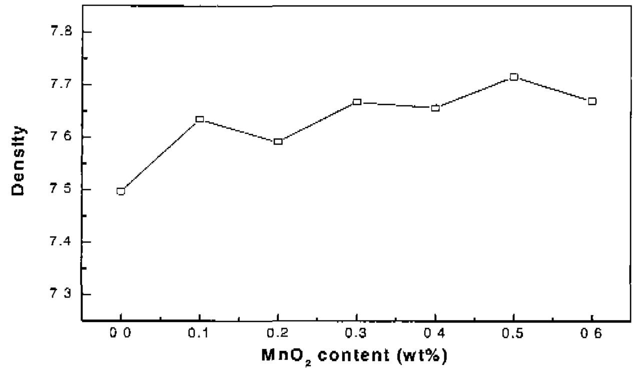

Fig. 3. Variation of Density of 0.05PMN-0.451PT-0.499PZ ceramics with MnO_2

The variation of the densities of 0.05PMN-0.95PZT + x wt% MnO_2 ceramics with MnO_2 content is illustrated in Fig. 3. The density of 0.05PMN-0.95PZT was about 7.50 and increased with the addition of the MnO_2. The maximum

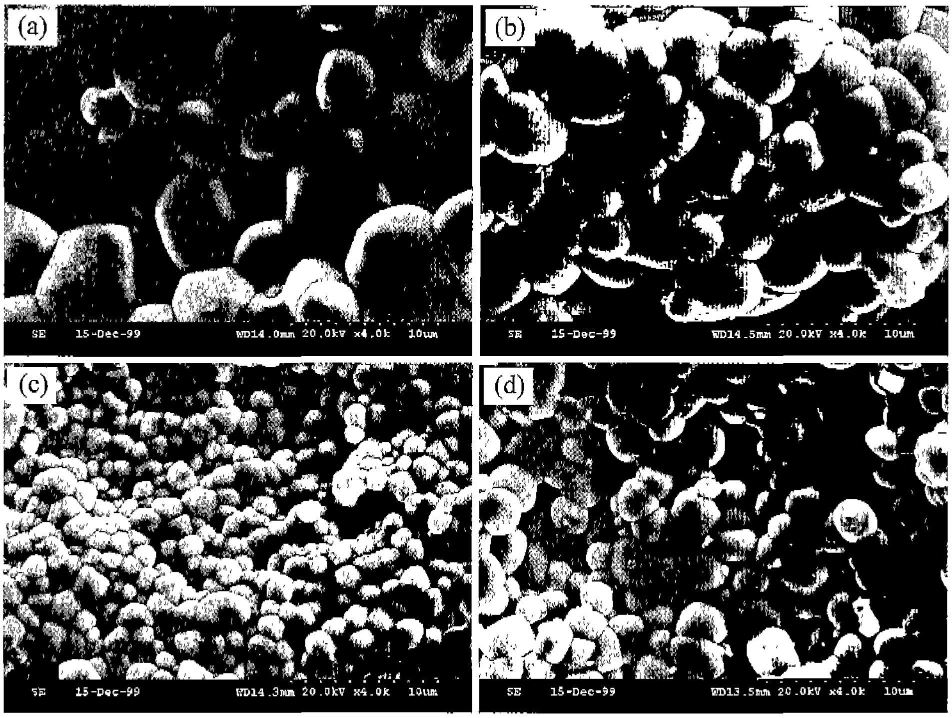

Fig. 4. SEM images of the fracture surface for MnO_2 doped 0.05PMN-0.451PT-0.499PZ ceramics: (a) none; (b) 0.2 wt%; (c) 0.5 wt%; (d) 0.6 wt%.

value of the density was obtained when x=0.5. The effect of MnO_2 on the microstructure of the specimen was investigated by SEM. Figs 4(a)~(d) show the SEM images of the fracture surface of the specimens. Large well developed grains with average grain size of 6.4 μm were observed for 0.05PMN-0.95PZT ceramics. The grain size of the speimens greatly reduced with the addition of the MnO_2 When x is less than 0.4 wt%, the average grain size of the specimens was 2.5-3.5 μm and it was about 1.0-1.5 μm as x exceeded 0.4 wt%. Therefore, it is considered that Mn ions inhibited the grain growth in 0.05PMN-0.95PZT ceramics. According to the previous work, the grain size of PZT decreased with increasing MnO_2 and the effects of MnO_2 on the piezoelectric properties of PZT was very similar to our results.[9] For 0.375PMN-0.375PT-0.25PZ ceramics, however, even though the effects of MnO_2 on the piezoelectric properties of the specimens were very similar to our results, the grain size of the specimens increased with MnO_2.[5] Therefore, it is difficult to explain the variation of the piezoelectric properties described below in term of the change of the grain size.

Fig. 5 exhibits the variations of Q_m, $K_{33}{}^T$ and $1/S^E{}_{11}$ of the specimens as a function of MnO_2. Mechanical quality factor of the specimens significantly increased with the addition of MnO_2 and exhibited a maximum value for the specimen with 0.5 wt% MnO_2. Previously, the increase of Q_m of Mn doped PZT was explained by the existence of the Mn^{2+} and Mn^{3+} ions which restricted the movement of the domain walls.[9] Even though, the valency states of Mn ions in our specimen has not been identified, they are not expected to be quite different from those in PZT. Therefore, it is likely that MnO_2 behaves as an acceptor in 0.05PMN-0.95PZT ceramics resulting in the increase of Q_m.

The dielectric constant of 0.05PMN-0.95PZT was about 600 and decreased with the increase of the Mn contents as shown in Fig. 5. The elastic stiffness constant, however, slightly increased with the addition of MnO_2. It is generally known that the reductions in dielectric constant and compliance ($S^E{}_{11}$) are due to the domain stabilization which is expected in hard materials. Therefore, the behaviors of $K_{33}{}^T$ and $1/S^E{}_{11}$ confirm that Mn ions behave as the acceptor ions in our specimens.

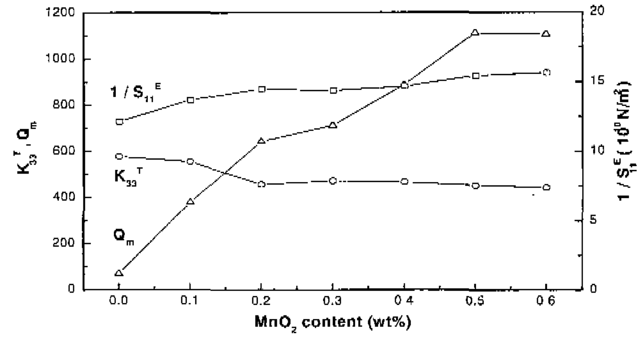

Fig. 5. Variations of Q_m, $K^T{}_{33}$ and $1/S^E{}_{11}$ as a function of MnO_2 for 0.05PMN-0.451PT-0.499PZ ceramics.

Figs 6(a) and (b) illustrate the polarization vs electric field hysteresis loops and the variations of remnant polarization (P_r) and the coercive field (E_c). As shown in these figures, the coercive field E_c increased with MnO_2 and has the maximum value when x=0.5 however, the remnant polarization decreased with the increase of MnO_2. The increase of E_c also indicates that the specimen becomes hard materials with the addition of MnO_2.

Fig. 7 shows the variation of K_p as a function of Mn content. Since the MnO_2 behaves as an acceptor in 0.05PMN-0.95PZT, K_p is expected to be decreased with the addition of MnO_2. However, K_p of the specimen slightly increased when $0.3 \leq x \leq 0.5$ and decreased as $x \geq 0.6$. In order to understand the anomalous variation of the K_p and to enhance the K_p of the Mn doped 0.05PMN-0.95PZT ceramics, the detailed studies were carried out on the factors which influence the value of K_p. Theoretically, K_p is expressed by the following equation[10]

$$K_p=[2/(1-\sigma^E)]^{1/2}\times[\varepsilon^T{}_{33}/S^E{}_{11}]^{1/2}g_{31}$$

and g_{31} is given by

$$g_{31}=2\times Q_{31}\times P_r$$

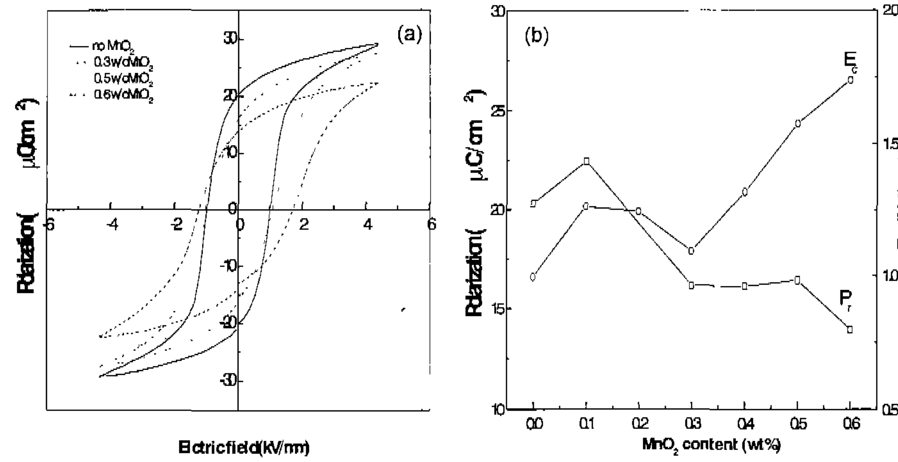

Fig. 6. Variations of (a) P-E curve and (b) E_c and P_r with MnO_2 content for 0.05PMN-0.451PT-0.499PZ ceramics.

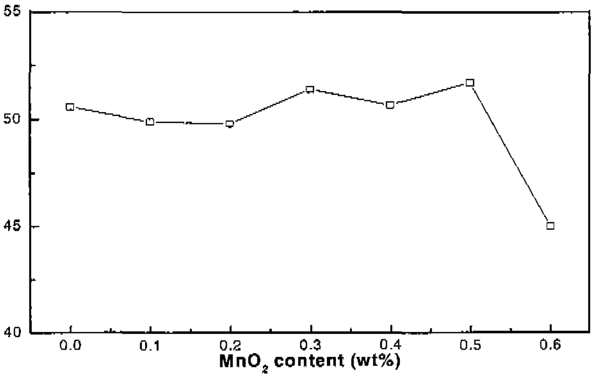

Fig. 7. Variation of electromechanical coupling coefficient as a function of MnO_2 for 0.05PMN-0.451PT-0.499PZ ceramics.

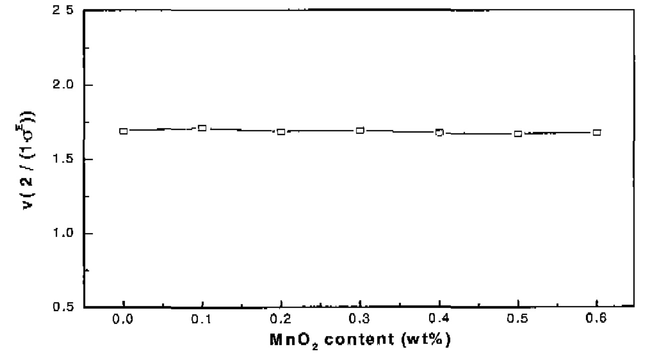

Fig. 8. Variation of $\sqrt{(2/(1-\sigma^E))}$ as a function of MnO_2 for 0.05PMN-0.451PT-0.499PZ ceramics.

where σ^E is Poission's ratio, g_{31} is piezoelectric constant, Q_{31} is electrostrictive constant. Therefore, K_p is given by

$$K_p=2[2/(1-\sigma^E)]^{1/2}\times[K^T_{33}/S^E_{11}]^{1/2}Q_{31}\times P_r.$$

According to the above equation, K_p depends on the five parameters. Variations of K^T_{33}, $1/S^E_{11}$ and P_r with MnO_2 were already discussed. The change of $[2/(1-\sigma^E)]^{1/2}$ as a function of MnO_2 is exhibited in Fig. 8. Poission's ratio was obtained from the ratio of the resonance frequency of the second mode to that of the fundamental mode. As shown in this figure, the variation of $[2/(1-\sigma^E)]^{1/2}$ is insignificient with the increase of MnO_2.

Since the electrostrictive constant (Q_{31}) is expressed by $S_{31} = Q_{31}\times P^2$ where S_{31} is strain, Q_{31} can be obtained using the strain vs electric field curves (see Fig. 9(a)) and the polarization vs electric field hysteresis loops shown in Fig. 6(a). The electrostrictive constant slightly increased with the Mn content as shown in Fig. 9(b).

According to the above results, K^T_{33} and P_r decreased with the increase of MnO_2 and the variation of $[2/(1-\sigma^E)]^{1/2}$ is not noticible therefore, they cannot contribute to the increase of the K_p. On the contrary the elastic stiffness constant ($1/S^E_{11}$) and Q_{31} increased with the increase of MnO_2. Therefore, it is considered that MnO_2 slightly increased the K_p of the specimen through the increase of the elastic stiffness constant and the electrostrictive constant.

The addition of MnO_2 significantly increased Q_m of 0.05PMN-0.95PZT ceramics, however the value of K_p is quite low. Therefore, it is necessary to add a new dopant which can enhance K_p without deterioration of the Q_m. According to our work, the addition of 0.5 wt% Fe_2O_3 in 0.05PMN-0.95PZT ceramics enhanced the K^T_{33} from 578 to 1,000 without the reduction in Q_m and the similar results were found in Fe_2O_3 doped 0.375PMN-0.375PT-0.25PZ ceramics.[5] Since K_p is proportional to $(K^T_{33})^{1/2}$, the addition of Fe_2O_3 is considered to increase K_p of the Mn doped 0.05PMN-0.95PZT ceramics. Moreover, the Fe_2O_3 additives are expected to increase the K_p through the increase of P_r because in general, the variation of P_r is similar to that of K^T_{33}. According to the previous work, NiO increased the K^T_{33} of 0.375PMN-0.375PT -0.25PZ ceramics but the addition of both MnO_2 and NiO did not improve the K_p.[5]

Based on the above analysis, the 0.05PMN-0.95PZT + 0.5 wt% MnO_2 + y wt% Fe_2O_3 ceramics were prepared and the piezoelectric properties of the specimens were measured. Fig. 10 shows the changes of K_p and Q_m as a function of the Fe_2O_3. The variation of K_p is insignificant with the addition of small amount of Fe_2O_3. However, as y exceeded the 0.4 wt%, it drastically increased and exhibited the maximum value, 0.63, at y=0.5. Q_m of the specimens slightly decreased with the addition of Fe_2O_3 however, the reduction can be negligible.

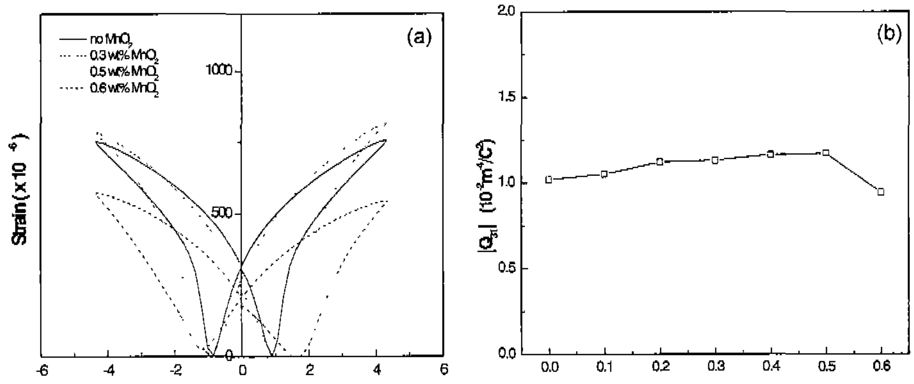

Fig. 9. Variations of (a) S-E curve and (b) $|Q_{31}|$ as a function of MnO_2 for 0.05PMN-0.451PT-0.499PZ ceramics.

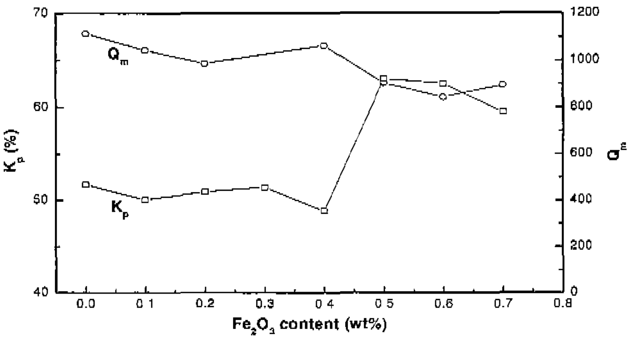

Fig. 10. Variations of K_p and Q_m as a function of Fe_2O_3 for 0.05PMN-0.451PT-0.499PZ+0.5MnO$_2$ ceramics.

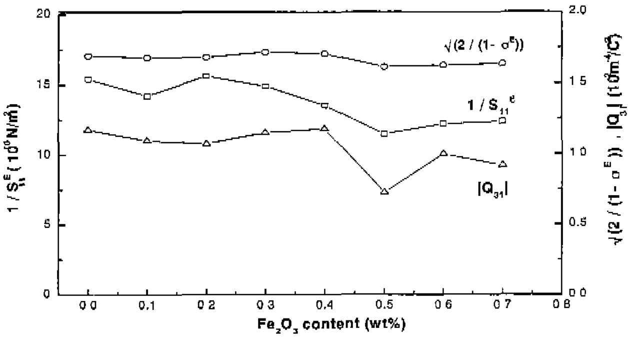

Fig. 11. Variations of $1/S^E_{11}$, $\sqrt{(2/(1-\sigma^E))}$ and $|Q_{31}|$ as a function of Fe_2O_3 for 0.05PMN-0.451PT-0.499PZ+0.5 wt% MnO_2 ceramics.

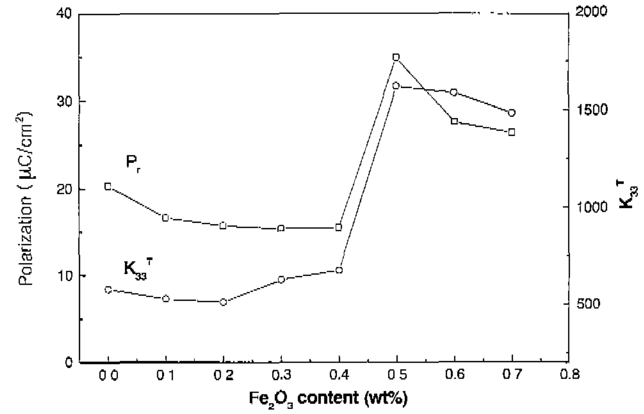

Fig. 12. Variations of P_r and K^T_{33} as a function of Fe_2O_3 for 0.05PMN-0.451PT-0.499PZ+0.5 wt% MnO_2 ceramics.

Fig. 11 shows the variations of $1/S^E_{11}$, $[2/(1-\sigma^E)]^{1/2}$ and Q_{31} as a function of Fe_2O_3 contents. The variations of $1/S^E_{11}$ and Q_{31} are insignificant when $y \leq 0.4$ wt% however, it decreased when Fe_2O_3 contents exceeded 0.5 wt%. On the contrary, the change of $[2/(1-\sigma^E)]^{1/2}$ was negiligible. Thus, they cannot contribute the enhancement of the K_p.

The variations of P_r and K^T_{33} are illustrated in Fig. 12. They are very similar to that of K_p. Therefore, it is considered that K_p of the specimen is enhaned by Fe_2O_3 through the increase of the P_r and K^T_{33} Even though the role of Fe ions in the MnO_2 doped 0.05PMN-0.95PZT ceramics is not clearly understood at this moment, the increase of K^T_{33} and the decrease of both $1/S^E_{11}$ and Q_m with the addition of Fe_2O_3 imply that Fe ions behave as the donor ions in Mn doped 0.05PMN-0.95PZT.

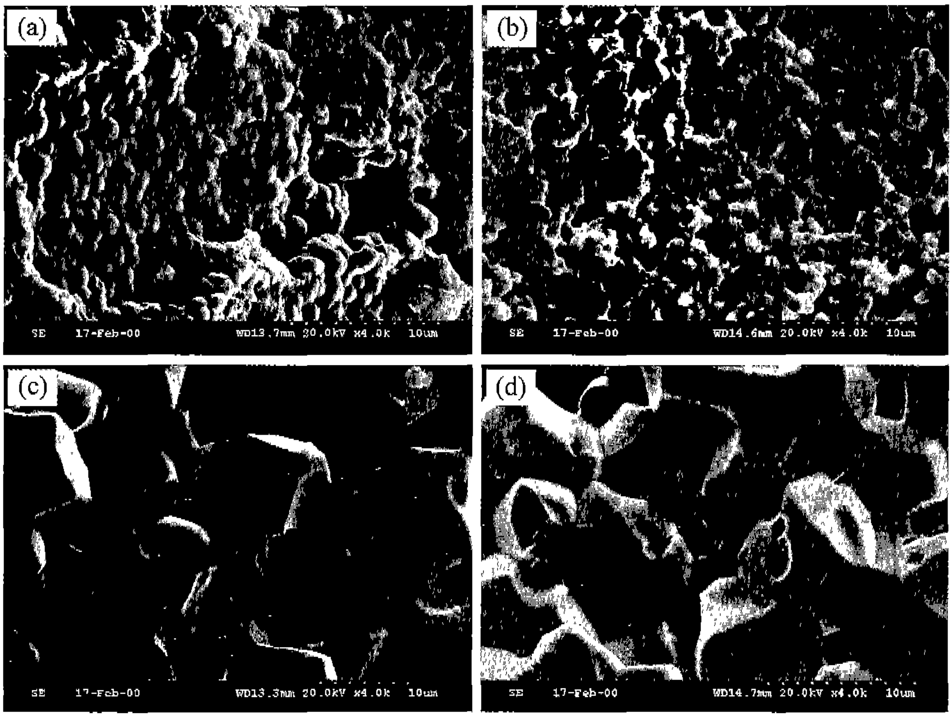

Fig. 13. SEM images of the fracture surface for the Fe_2O_3 doped 0.05PMN-0.95PZT+0.5 wt% MnO_2 ceramics: (a) 0.2 wt%; (b) 0.4 wt%; (c) 0.5 wt%; (d) 0.7 wt%.

The microstructure of the 0.05PMN-0.95PZT+0.5 wt% MnO_2+y wt% Fe_2O_3 with $0 \leq y \leq 0.7$ ceramics was investigated using SEM. Figs 13(a)-(e) show the SEM images of the fracture surface of the specimens. For the specimens with $y<0.5$, the average grain size was approximately 1.0 μm. However, it greatly increased as y exceeded 0.4. The average grain size of the specimens with $y \leq 0.5$ was about 8.0 μm. SEM result implies that the enhancement of the K_p is due to the increase of the grain size. However, for the 0.05PMN-0.95PZT doped with MnO_2, the average grain size significantly decreased with the addition of MnO_2 but the K_p of the specimens slightly increased. Moreover, for the 0.375PMN-0.625PZT, the average grain size greatly increased with the addition of MnO_2 but the variation of K_p was insignificant.[5] Therefore, even though the relation between the grain size and K_p can not be completely denied, it is difficult to explain the variation of K_p in terms of the average grain size.

IV. Conclusions

The dielectric and piezoelectric properties of MnO_2 and Fe_2O_3 doped 0.05PMN-0.451PT-0.499PZ ceramics were studied. The average grain size of the specimens decreased with the addition of MnO_2. Doping of MnO_2 additive in 0.05PMN-0.451PT-0.499PZ ceramics decreased the dielectric constant and remnant polarization but increased Q_m and E_c. K_p of 0.05PMN-0.451PT-0.499PZ ceramics slightly increased with the addition of MnO_2 but it was low. In order to improve the K_p, the additive Fe_2O_3 was added in the 0.05PMN-0.95PZT+0.5 wt% MnO_2 ceramics. When Fe_2O_3 content was less than 0.4 wt%; the variation of K_p is negligible, however as it exceeded 0.4 wt%, K_p increased drastically. K_p of the specimen is enhaned by Fe_2O_3 through the increase of the P_r and K^T_{33} Q_m of the specimens decreased with the addition of Fe_2O_3 however, the reduction was insignificant.

Acknowledgement

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