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Effects of Cr_2O_3 addition on the piezoelectric properties and microstructure of $PbZr_xTi_y(Mg_{1/3}Nb_{2/3})_{1-x-y}O_3$ ceramics

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Abstract

The effects of the addition of Cr_2O_3 on the piezoelectric properties and microstructure were investigated for the $PbZr_xTi_y(Mg_{1/3}Nb_{2/3})_{1-x-y}O_3$ (PZTMN) system. The results showed that the Cr_2O_3 addition was effective in increasing the K_p and Q_m, which indicated that Cr-doped PZTMN ceramics possessed, simultaneously, the properties of 'soft' and 'hard' piezoelectrics. Furthermore, the properties were found to become 'hard' with an increase of sintering temperature even for the same compositions. Electron spin resonance (ESR) analysis showed that the Cr ion coexisted in both Cr^{3+} and Cr^{5+}, and that the valence change from Cr^{5+} or Cr^{6+} to Cr^{3+} happened when the sintering temperature was increased. Transmission electron microscopy (TEM) results showed that, with increasing Cr content, the normal stripe-like domain changed to a wavy domain structure due to domain wall pinning by the defect complexes of acceptor impurities and oxygen vacancies. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cr_2O_3; Domains; Perovskite; $Pb(Zr,Ti,Mg,Nb)O_3$; Piezoelectric properties

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1. Introduction

Compared with the binary solid–solution ceramic system $PbZrO_3$–$PbTiO_3$ (PZT), the ternary system $PbZrO_3$–$PbTiO_3$–$PbMg_{1/3}Nb_{2/3}O_3$ shows desirable features. It has higher piezoelectric activity, lower sintering temperature, higher density, and finer and more uniform grain structure.[1] In addition, the properties can be changed over a wider range by changing the composition or dopants. Due to these advantages, $PbZr_xTi_y(Mg_{1/3}Nb_{2/3})_{1-x-y}O_3$ ceramics have been widely applied as electroacoustic components.[1] In order to meet the stringent requirements for specific applications, various metal ions are added to improve the piezoelectric properties. Cr and Mn are known as stabilizers which are effective in decreasing the aging effect and increasing the mechanical quality factor (Q_m). Uchida and Ikeda[2] have studied the solubility limit of Cr_2O_3 in PZT and its temperature, bias, and aging characteristics. Vasileva, Nadoliisky and Toshev[3,4] have studied the effects of Cr on the coercive field, spontaneous polarization, electric conductivity, piezoelectric strain constant d_{31}, and planar coupling coefficient K_p. Recently, Cheon and Park[5] have reported the temperature stability of the resonant frequency in Cr_2O_3-doped PZT ceramics. However, not much information is available regarding the effects of Cr_2O_3 addition on the properties of the ternary system $PbZrO_3$–$PbTiO_3$–$PbMg_{1/3}Nb_{2/3}O_3$. In the present study, the piezoelectric properties were measured for Cr_2O_3-doped $PbZr_xTi_y(Mg_{1/3}Nb_{2/3})_{1-x-y}O_3$ (PZTMN) ceramics; the microstructure and valence states of the Cr ion were investigated in order to clarify the mechanism by which Cr addition influences the piezoelectric properties.

2. Experimental procedures

Commercial Pb_3O_4, ZrO_2, TiO_2, Nb_2O_5 and $MgCO_3$ with purities greater than 99% were mixed to form the compositions of $PbZr_xTi_y(Mg_{1/3}Nb_{2/3})_{1-x-y}O_3$ ($x=0.35$–0.4, $y=0.35$–0.4). The mixture was wet ball milled for 8 h using distilled water and iron balls as the grinding medium. The oven-dried powder was crushed and calcined at 850°C for 2 h. Different amounts of Cr_2O_3 (0–0.7 wt.%) were added to the calcined powder, which was

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once again ball milled for 16 h. After drying, the powders were pressed into pellets and sintered at different temperatures from 1200 to 1320°C. The sintered ceramics were lapped into disks of Φ17×1 mm, then were provided with fired-on silver electrodes. Poling was carried out in a silicone oil bath at 100°C using a dc field of 3.5–4 KV/mm for 10 min. The piezoelectric parameters were measured after 24 h after poling following the IRE standard. To avoid the broadening of the ESR (electron spin resonance) signal by the spin–spin interaction, the sample with the low concentration of 0.15 wt.% Cr_2O_3 was used. The electron spin resonance (ESR) measurements were performed at room temperature with a spectrometer (Model ER-200D SRC, Germany) operating at about 9.4 GHz. The microstructure analyses were undertaken by electron probe microanalysis (EPMA, 8705QH$_2$) and transmission electron microscopy (TEM, 2010) with energy dispersive spectroscopy (EDS, Link-ISIS, Oxford).

3. Results and discussion

3.1. Electromechanical properties

Fig. 1 shows the piezoelectric properties of d_{33} and K_p as functions of the amount of Cr_2O_3 for PZTMN ceramics sintered at temperature from 1200 to 1320°C. As the Cr-doped piezoelectric ceramics reveal higher mechanical quality factor Q_m, higher coercive field E_c, lower electrical loss tanδ, slightly lower piezoelectric constant d_{33} and mechanical coupling coefficient K_p, Cr doping is usually considered as hard doping. However, as a dopant, Cr is different from other hard ions such as Na^+, K^+, Fe^{2+} and Fe^{3+}. From Fig. 1, one can see that d_{33} and K_p increase with the amount of Cr_2O_3 when its concentration is lower than 0.06 wt.%. The K_p becomes maximum with the addition of 0.06 wt.% Cr_2O_3 and decreases rapidly with further addition of Cr_2O_3. However, the amount of Cr_2O_3 which brings about the maximum of d_{33} shows a slight difference with difference of sintering temperatures. It increased from 0.03 to 0.08 wt.% when the firing temperature was increased from 1200 to 1280°C. These characteristics in PZTMN ceramics modified by Cr_2O_3 in its low concentration region are similar to what was observed by Ng and Alexander[6] and the present authors[7] in MnO-modified PZT ceramics. This suggests that the anomalous properties may universally exist in PZT-based ceramics doped with stabilizers such as Mn and Cr in their low concentration regions. The detailed mechanism needs to be investigated further and will be reported separately.

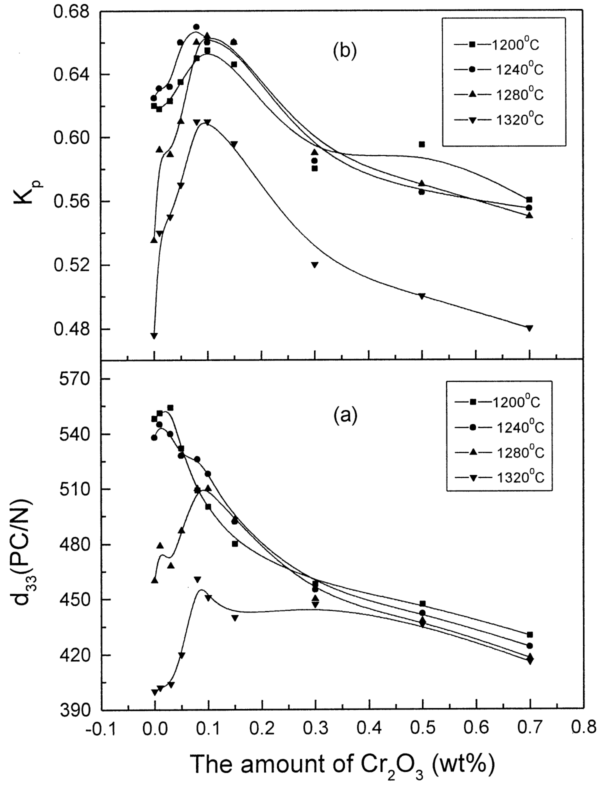

Fig. 1. Dependence of the piezoelectric coefficient d_{33} and the electromechanical coupling coefficient K_p on the amount of Cr_2O_3 for PZTMN ceramics sintered at different temperatures.

The other obvious feature is that K_p and d_{33} decrease with increasing of the sintering temperature for ceramics with the same composition, and the discrepancy decreases gradually with increasing the amount of Cr_2O_3. One of the reasons for ‘hard’ piezoelectrics may be the existence of intragrain pores. In general, grain size and porosity influence the piezoelectric properties, since the grain boundary and pore surface generate a depolarization field and inhibit domain-wall motion.[8,9] As shown in Fig. 2, the sample sintered at 1200°C has a relatively uniform grain structure with grain size of ~3 μm (Fig. 2a), the samples sintered at 1320°C, on the other hand, have large grains with size of ~15 μm; some intragrain pores are present also (Fig. 2b). Another important reason, which makes the piezoelectric properties ‘hard’, may derive from the valence change of the Cr ion with different sintering temperature. The mechanism will be discussed in Section 2 in detail.

Fig. 3 shows the electrical loss tanδ and the mechanical quality factor Q_m (the reciprocal of mechanical loss) as functions of the amount of Cr_2O_3 for PZTMN ceramics sintered at different temperature. In a large range of concentration, Q_m increases monotonically with the amount of Cr_2O_3. But a ‘U’-shaped region, with lowest electrical loss appearing at about 0.03–0.1 wt.%, was found in the electrical loss tanδ curves. It clearly appears that there is no correlation between the electrical loss tanδ measured at 1 kHz and the mechanical quality factor Q_m measured at 100 kHz (radial mode). These results are contradictory with the conclusion of Gerthsen

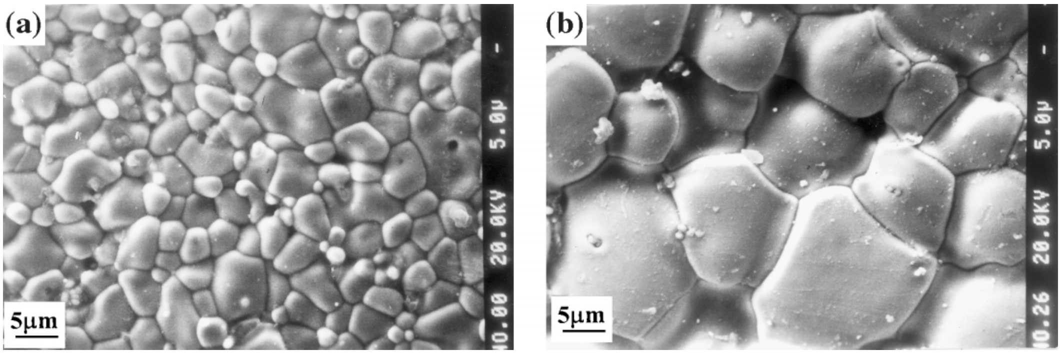

Fig. 2. SEM micrograph of the samples sintered at (a) 1200°C/2 h and (b) 1320°C/2 h.

et al.,[10] but they are consistent with the results of Eyraud et al.[11] It is well known that PZT-based ceramics possess *p*-type conductivity because of the PbO vapor evaporation during the sintering process.[12] At low concentration, Cr ion mainly exists as Cr^{6+} and it will be incorporated in the lattice at a (Ti, Zr) site acting as a donor;[3] which leads to the decrease of the charge carrier concentration due to the recombination of the electron and hole [Eqs. (1) and (2)]. As a result, the electrical conductivity of PZTMN is decreased, so the electrical loss is also decreased.

$$V_{Pb}^{\times} \rightarrow V_{Pb}'' + 2h^{\cdot} \quad (1)$$

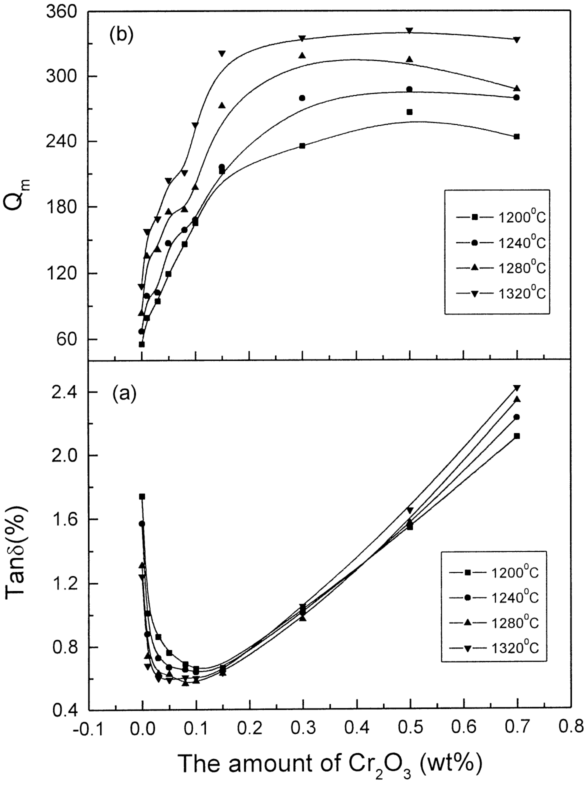

Fig. 3. Dependence of Cr_2O_3 of the electric loss tanδ and the mechanical quality factor Q_m on the amount of Cr_2O_3 for ceramics sintered at different temperatures.

$$Cr_{(Zr,Ti)}^{\times} \rightarrow Cr_{(Zr,Ti)}^{\cdot\cdot} + 2e' \quad (2)$$

However, with a further increase in the concentration of the Cr ion, the electric loss is increased rapidly. This may be due to the formation of a chromium oxide layer at this high concentration of chromium,[4,13] which would cause the increase of electrical conductivity of PZTMN ceramics, and the electrical loss is correspondingly decreased.

3.2. ESR investigation

In order to elucidate the role of the Cr ion, it is necessary to know its valence state. The observed ESR spectra were rather helpful in this respect. Fig. 4 shows the spectra of polycrystalline PZTMN samples doped with 0.15 wt.% Cr_2O_3 sintered at 1200 and 1320°C, respectively. Three sets of fine spectra with four hyperfine lines each were observed in the samples sintered at 1200°C for 2 h (Fig. 4a), which revealed the existence of Cr^{3+}. As stated earlier, the Cr ion is incorporated into the center of an octahedron replacing Ti^{4+} or Zr^{4+}. For the Cr^{3+} (*F*-state ion) with the structure of 3 d^3, the splitting of state energies under the crystal field environment of an octahedron with tetragonal distortion is schematically shown in Fig. 5. The ground state A_{2g} is orbitally nondegenerate, being split into two doublet states under zero-magnetic field to meet the demands of Kramer degeneracy[14] for an ion with an odd electron, and the external magnetic field causes a further removal of the spin degeneracy. As for ^{53}Cr, the nucleus spin, $I=3/2$, so each energy level is divided into $(2\times3/2)+1=4$ levels due to the hyperfine splitting. According to the selected rule of $\Delta M_s=\pm1$, $\Delta M_I=0$, this should produce 12 lines. Besides these 12 lines, further four hyperfine lines were also observed at about 3460 Gauss (Fig. 4a), which were thought to be caused by Cr^{5+}. The splitting of state energies for 3 d^1 (Cr^{5+}, *D*-state ion) is also schematically shown in Fig. 6. The lowest state in an octahedral field is a triply degenerate state, where the degeneracy can be partially removed by the tetragonal distortion; the doublet state is further

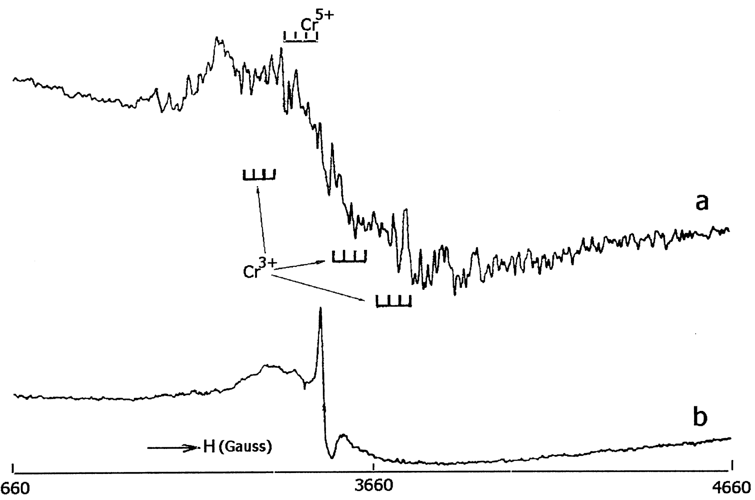

Fig. 4. ESR spectrum of Cr_2O_3-doped (0.15 wt.%) PZTMN ceramics sintered at (a) 1200°C/2 h and (b) 1320°C/2 h.

removed by the magnetic field. Four hyperfine spectra are then produced due to the hyperfine interaction between the electron and the nucleus, but for the samples sintered at 1320°C, only some broadened peaks, which showed some traces of hyperfine lines, were observed. This difference may arise from secular broadening effects[14] due to the increase of the concentration of Cr^{3+}. With increments in Cr^{3+} content, the distances between the ions are shorter, and the spin–spin interaction becomes stronger, which leads to the broadening and smearing of the spectra. These ESR results show that a change of Cr^{5+} to Cr^{3+} happens with the increase of sintering temperature.

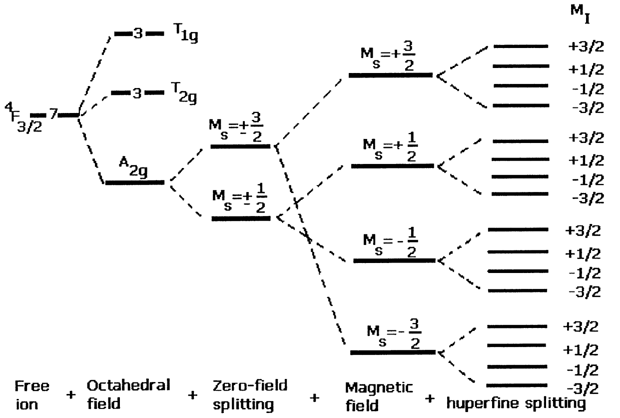

Fig. 5. Splitting of the states of $3d^3$ ion in an octahedral field with an added tetragonal distortion large compared with the spin–orbit coupling.

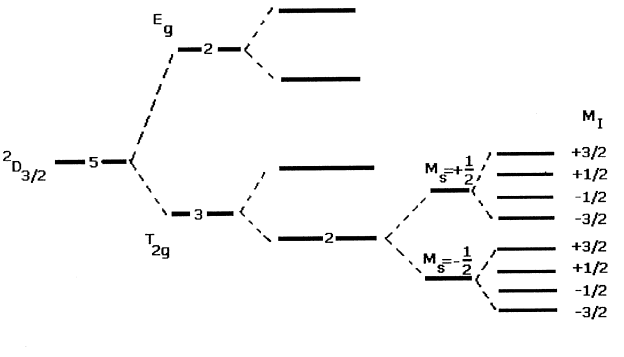

Fig. 6. Splitting of the states of 3 d^1 in an octahedral field with an added tetragonal distortion.

Although Cr^{6+} cannot be detected by ESR owing to its antimagnetic character, one cannot rule out the possibility of its existence in samples sintered at 1200°C. If Cr^{5+} or Cr^{6+} substituting for Ti^{4+} or act as a donor, the piezoelectric properties K_p will be improved and, d_{33} will be increased. On the contrary, if Cr^{3+} substitutes for Ti^{4+} or Zr^{4+} acting as an acceptor, the piezoelectric properties will get 'hard'. The above ESR results show that, with the increase of sintering temperature, the change of the valence of Cr ion may be one of the reasons that the piezoelectric properties get 'hard'.

3.3. Transmission electron microscopy studies

Room temperature bright field images of pure PZTMN and Cr-doped PZTMN samples are shown in Fig. 7a–c. Distinct changes in the domain size and morphology are evident with increasing the amount of Cr. For pure PZTMN, the domain structure has a lath-like morphology with laths several microns in length and ~150 nm in width (Fig. 7a). For PZTMN samples doped with 0.15 wt.% Cr_2O_3, the width of the domain was decreased to about 100 nm, and fine-scale subdomain structure with a striation-like morphology also can be seen to coexist with the micro-sized domain patterns. These normal micro-sized 90° domain are typical of a long-range order ferroelectric state. A further increment in Cr concentration to 0.7 wt.% resulted in dramatic changes in domain size and morphology, with significant wavy domains being developed. However, it should also be noticed that these wavy domains maintained a significant degree of preferred orientation along a particular family of crystallographically equivalent polar directions.

The Cr ion is known to be present mainly as Cr^{3+} in the high concentration condition,[3] it will be incorporated into sites of $(Zr, Ti)^{4+}$ as an acceptor, so oxygen vacancies are created correspondingly in order to meet the requirements of electroneutrality. Because the defect complexes of acceptor impurities and oxygen vacancies remain relatively mobile at temperature below the ferroelectric transformation,[15,16] they could readily diffuse to the domain boundaries, pinning the boundaries. As a consequence of domain pinning by the defect complexes, large domain structures do not evolve, and small wavy domains are developed instead. Recently, the similar wavy domains have also been observed by Tan and Viehland[15,16] in potassium-modified PZT ceramics.

The microstructures of the samples doped with 0.7 wt.% Cr_2O_3 observed by TEM also exhibited the existence of two kinds of non-ferroelectric phases besides the main PZTMN perovskite phase. As shown from Fig. 8a, pure ZrO_2 monoclinic grains were found to be surrounded by the PZTMN phase. This precipitation of free zirconia is believed to occur because of the loss of PbO by volatilization during the sintering process.[17,18]

Besides the pure ZrO_2 monoclinic grains, up to about 300–500 nm white grains were detected inside the grains or at the grain boundaries (Fig. 8b). EDS analysis

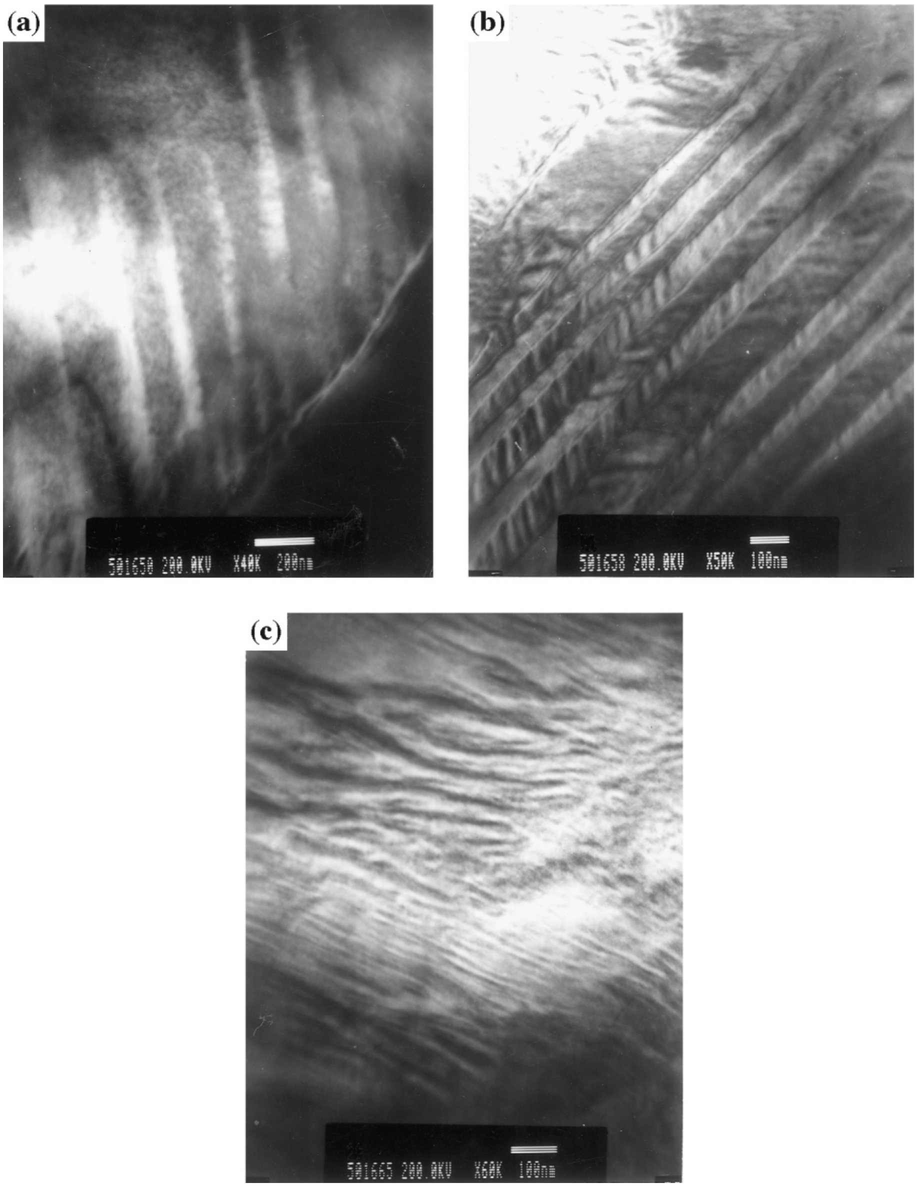

Fig. 7. Room temperature bright-field TEM images for PZTMN specimens with different amount of Cr_2O_3: 0 wt%, (b) 0.15 wt% and (c) 0.70 wt%.

showed that they were mainly composed of Cr, Ti, Mg, O and contained a little Fe as impurity (Fig. 8d). The difference in the Cr amount between the white grain and the main grain phase was obvious, which showed that the solubility limit of Cr_2O_3 is less than 0.7 wt.%. This result is consistent with that of Uchida's work,[2] which showed that the solubility limit of Cr_2O_3 in PZT is about 1.1 mol% (≈0.5 wt.%). The extra Cr has the tendency to segregate to the nonferroelectric phase inside the PZTMN grains or at the grain boundaries.

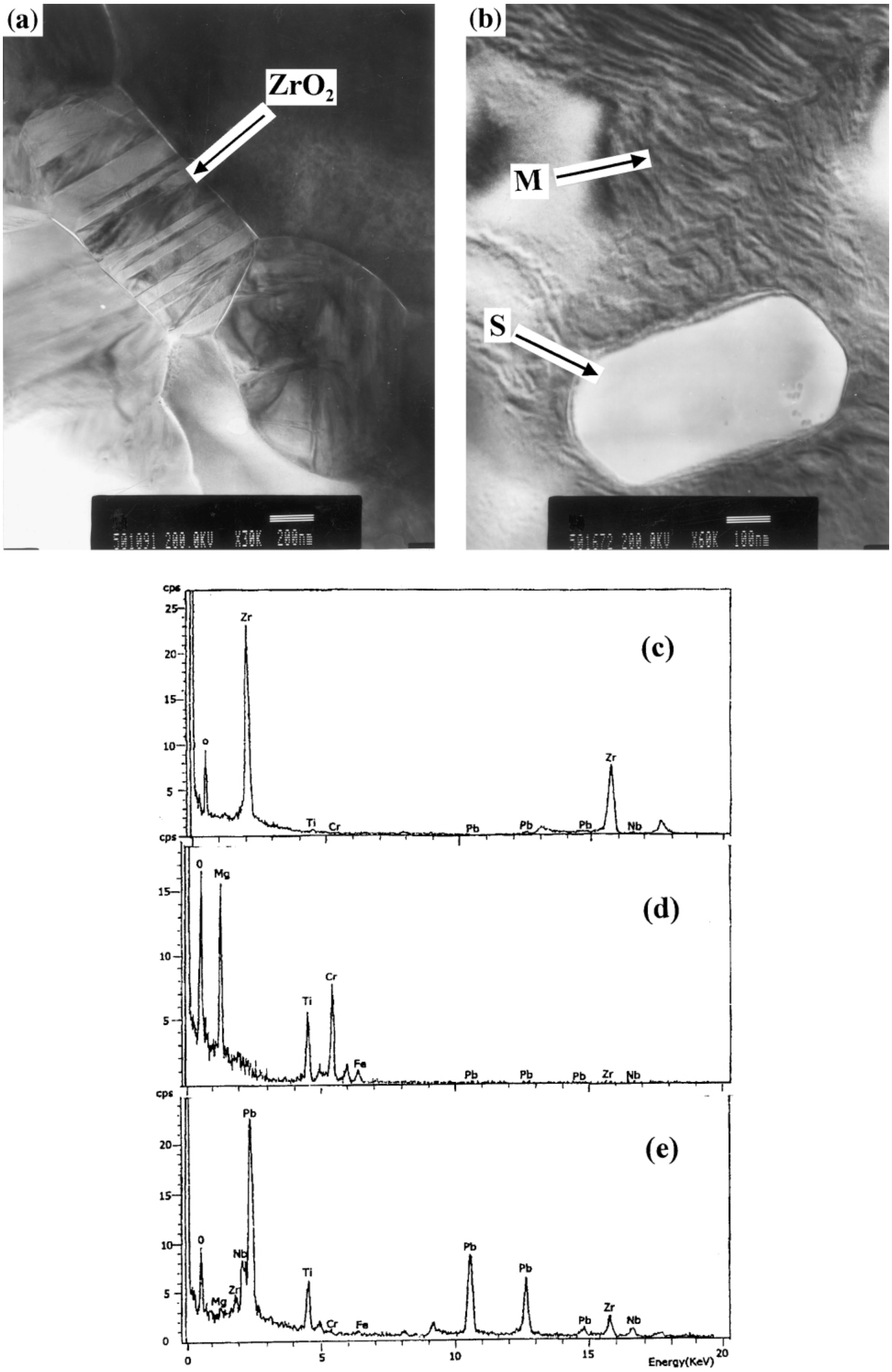

Fig. 8. (a) TEM micrograph of the twinned ZrO_2 in PZTMN ceramics doped with 0.7 wt.% Cr_2O_3. (b) TEM micrograph shows the Cr-rich secondary phase (white grain). (c) EDS spectra of the twinned ZrO_2 grain. (d) EDS spectra of the secondary phase quoted at "S" in the micrograph. (e) EDS spectra of the main ferroelectric phase quoted at "M" in the micrograph.

4. Conclusions

Based on the above-obtained results, the following conclusions can be drawn:

1. The piezoelectric properties of the ternary system $PbZrO_3$–$PbTiO_3$–$PbMg_{1/3}Nb_{2/3}O_3$ can be effectively modified by Cr_2O_3 addition. K_p, d_{33} arid Q_m were increased by the Cr_2O_3 addition when its concentration was below 0.08 wt.%, and the electrical loss $\tan\delta$ was decreased at the same time. A further increase in the Cr_2O_3 content may decrease the value of K_p and d_{33}, but Q_m and $\tan\delta$ will increase correspondingly.
2. The properties of Cr-doped PZTMN ceramics were sensitive to the sintering temperature, and it was found that the properties became 'hard' when the sintering temperature was increased. So the piezoelectric properties of PZTMN can be conveniently modified by controlling the sintering temperature.
3. The ESR results showed that the Cr ion coexisted in Cr^{3+} and Cr^{5+} in PZTMN ceramics, and a valence change from Cr^{5+} or Cr^{6+} to Cr^{3+} took place when the sintering temperature was increased, which was believed to be one of the reasons for the 'hardness' of piezoelectric properties.
4. With increment in the Cr content, the size and morphology of the domain underwent a change. The domain size was decreased, and the normal lath-like form changed to wavy domain due to domain pinning by defect complexes of acceptor impurities and oxygen vacancies.

Acknowledgements

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