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The role of PbO content on the dielectric and piezoelectric properties of PZN-based ceramics

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Stoichiometric and nonstoichiometric (with less and excess PbO) PZN based ceramics with the ABO_3 perovskite structure were prepared by the columbite method. The results show that the content of PbO has a great influence on the structure and the electrical properties of PZN based ceramics. In the compositions with less PbO ($A/B < 1$), the dielectric constant and piezoelectric coefficients decrease due to the appearing of pyrochlore phase. While in the compositions with excess PbO ($A/B > 1$), the dielectric constants and the piezoelectric coefficients increase to a maximum at 1–2 mol % excess PbO, then decrease with increasing PbO content. This behavior can be attributed to the grain boundary layer caused by excess PbO. The grain boundary layer can be eliminated by thermal annealing and was examined by transmission electron microscopy. After annealing at 1123 K for 4–8 h, a very strong enhancement in the dielectric and piezoelectric properties was observed in the annealed PZN ceramics. In this work, $d_{33} = 680$ pC/N, $k_m \approx 27{,}000$, $k_p \approx 50$ % were achieved in annealed PZN ceramics. © *2001 Kluwer Academic Publishers*

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1. Introduction

Lead zinc niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) is a typical relaxor ferroelectric material with a broad diffusion phase transition and large dielectric constants. The crystal symmetry is rhombohedral at room temperature and cubic above 413 K. The solid solution between PZN, which has a rhombohedral symmetry, and $PbTiO_3$ (PT) has a morphotropic phase boundary (MPB) near 10 mole% PT. Single crystals with the composition near the MPB show extremely large dielectric constants ($\varepsilon > 22000$) and piezoelectric coefficients ($k_p \sim 92$ %, $d_{33} \sim 1500$ pC/N), much larger than those of PZT ceramics [1]. Because of their high dielectric constants and excellent electrostrictive properties in the single crystal form, and the relatively low sintering temperature (1323–1373 K), PZN and the compositions in the PZN-PT system are promising materials for capacitors and actuators.

However, It is very difficult to prepare PZN-PT ceramic specimens with the perovskite structure by conventional ceramic processing due to the formation of the pyrochlore phase. It has been reported that perovskite PZN or PZN-0.1PT crystals are thermodynamically unstable over a wide range of temperature (873–1673 K) [2]. To date, the most useful method to stabilize the perovskite structure is to add some dopants such as $BaTiO_3$ (BT) and $SrTiO_3$ (ST) [3]. The dielectric constant of the pyrochlore phase is only about 120 [4], so the existence of the pyrochlore phase will be detrimental to the dielectric properties of lead based ferroelectric ceramics.

Much work have been done to eliminate the pyrochlore phase in lead magnesium niobate (PMN) ceramics in the past years, and the results show that the loss of PbO during the processing is an important factor in controlling the microstructure and the electrical properties [4, 5]. Till now, there are two conflicting results about the effects of excess PbO on the structure and electrical properties of PMN ceramics. Lejune and Boilet [6] studied PMN compositions with excess PbO up to 6 wt%. Kang and Yoon [7] studied PMN with excess PbO at much higher PbO content, up to 40 mol%. Both studies showed that excess PbO reduced the pyrochlore and hence increased the yield of perovskite structure and a higher density was observed by increasing the amount of excess PbO. Both observations led to the conclusions that excess PbO could increase the dielectric constant, mainly because of the improvement of the concentration of the high dielectric constant perovskite phase. Also, a liquid phase would form around 1103–1113 K because of the excess PbO, which also aided the densification. But a conflicting observations reported by Swartz [8] and Guha [9] showed that the addition of PbO in excess of 2 wt% (2.8 mol%) decreased the dielectric constant, because of the presence of the excess PbO layer in the grain boundary.

The content of PbO is also an important factor in the preparation and properties of PZN based ceramics. In this paper, the PZN-BT-PT ceramics with less and with excess PbO were prepared. The effects of PbO on the structure and dielectric and piezoelectric properties were studied. Thermal annealing was used to eliminate

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the grain boundary layer, and its effects on the electrical properties were also discussed.

2. Experiment procedure

The stoichiometry of the basic composition in present studies is 0.86PZN-0.09PT-0.05BT. It has a complex ABO_3 perovskite structure in which A/B equals 1. In order to explore the effect of the PbO content, the compositions with less ($A/B < 1$) and excess PbO ($A/B > 1$) were prepared on the basis of the basic composition, shown in Table I. The PZN-BT-PT ceramics with different A/B ratios were prepared by the columbite method [10]. $ZnNb_2O_6$ (ZN) was precalcined at 1373 K for 4 h. Then ZN was mixed with PbO, TiO_2 and $BaCO_3$. After ball-milling, the mixed powders were calcined at 1123 K for 2 h. The calcined powders showed 99% perovskite phase when checked by X-ray diffraction. Then a binder was added to the powders, and pellets of 1.5 mm thickness and 12 mm diameter were formed. The pellets were sintered at 1373 K for 4 h. To limit PbO loss from the pellets, a PbO-rich atmosphere was maintained by placing $PbZrO_3$ powder inside the covered alumina crucible. To explore the effect of thermal annealing, some of the sintered specimens were thermally annealed at 1123 K for 4–8 h.

The bulk densities of the sintered specimens were determined by the Archimedes' method. The phase structure of the powders and the sintered ceramics were analyzed by using a Rigaku D/Max-2400 diffractometer using Cu K_α radiation. The relative amounts of the pyrochlore and perovskite phases were determined by measuring the major x-ray peak intensities of the perovskite and pyrochlore phases, that is (110) and (222) respectively. The percentage of the perovskite phase was estimated by the following equation:

$$\%_{\text{perovskite}} = \frac{I_{\text{perov}(110)}}{I_{\text{perov}(110)} + I_{\text{pyro}(222)}} \times 100 \qquad (1)$$

The fractured surfaces were examined by SEM analysis (HITACHI S-2700). The samples for transmission electron microscopy (TEM) were mechanically polished to 30 μm, and finally obtained by ion beam thinning. Microscopic examination was carried out by using TEM (JEOL JEM-200CX).

The specimens were polished and electroded for the dielectric and piezoelectric studies. Silver paste was fired on both sides of the samples at 823 K for 10 min as the electrodes for the dielectric and piezoelectric measurements. The dielectric constants were measured with a HP4274 LCR meter, at a heat rate of 2–3 K/min. The samples were poled by applying a DC field of 4 kV/mm at 353 K for 30 min. The piezoelectric planar coupling coefficient k_p was determined by a resonance-antiresonance method, using a HP4192A complex impedance analyzer. The values of the peizoelectric constant d_{33} were determined using a d_{33}-meter.

TABLE I Compositions studied in PZN-BT-PT system with various A/B ratios

	CP1	CP2	CP3	CP4	CP5	CP6	CP7
A/B	0.97	0.98	1.00	1.01	1.02	1.04	1.06

3. Results and discussions

3.1. XRD and SEM characterization

Fig. 1 is the XRD patterns of composition CP1-CP5. The following results can be obtained from this figure: (1) In composition CP1 and CP2 with less PbO ($A/B < 1$), there is some pyrochlore phase appearing. The content of the pyrochlore phase decreases with incresing PbO content. The pure perovskite structure can be obtained in the composition with 1 mol% excess PbO. (2) The excess PbO can move the morphotropic phase boundary (MPB) to the tetragonal-rich side. Since the composition 0.86PZN-0.09PT-0.05BT (CP3) lies near the MPB in the PZN-BT-PT phase diagram [11], the tetragonal and rhombohedral phase coexist in this composition. Fig. 2 shows the XRD peaks of $2\theta \approx 45^\circ$ versus the amount of excess PbO in the PZN ceramic system, the peaks of $2\theta \approx 45^\circ$ splits into two peaks with increasing PbO content. That is to say the content of the tetragonal phase increases with increasing PbO content.

Fig. 3 shows the SEM photos of the fractured surface of composition CP1 to CP7. In composition CP1 and

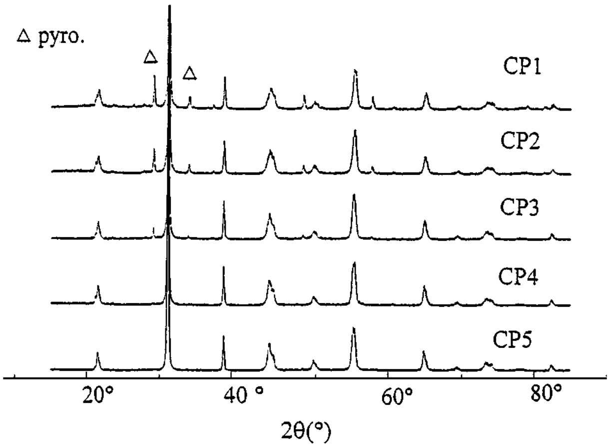


Figure 1 The XRD patterns of composition CP1 to CP5.

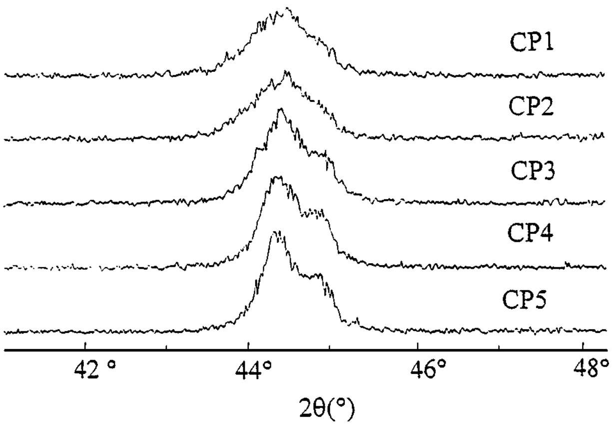


Figure 2 The XRD peaks of $2\theta \approx 45^\circ$ versus the amount of excess PbO in PZN ceramic system.

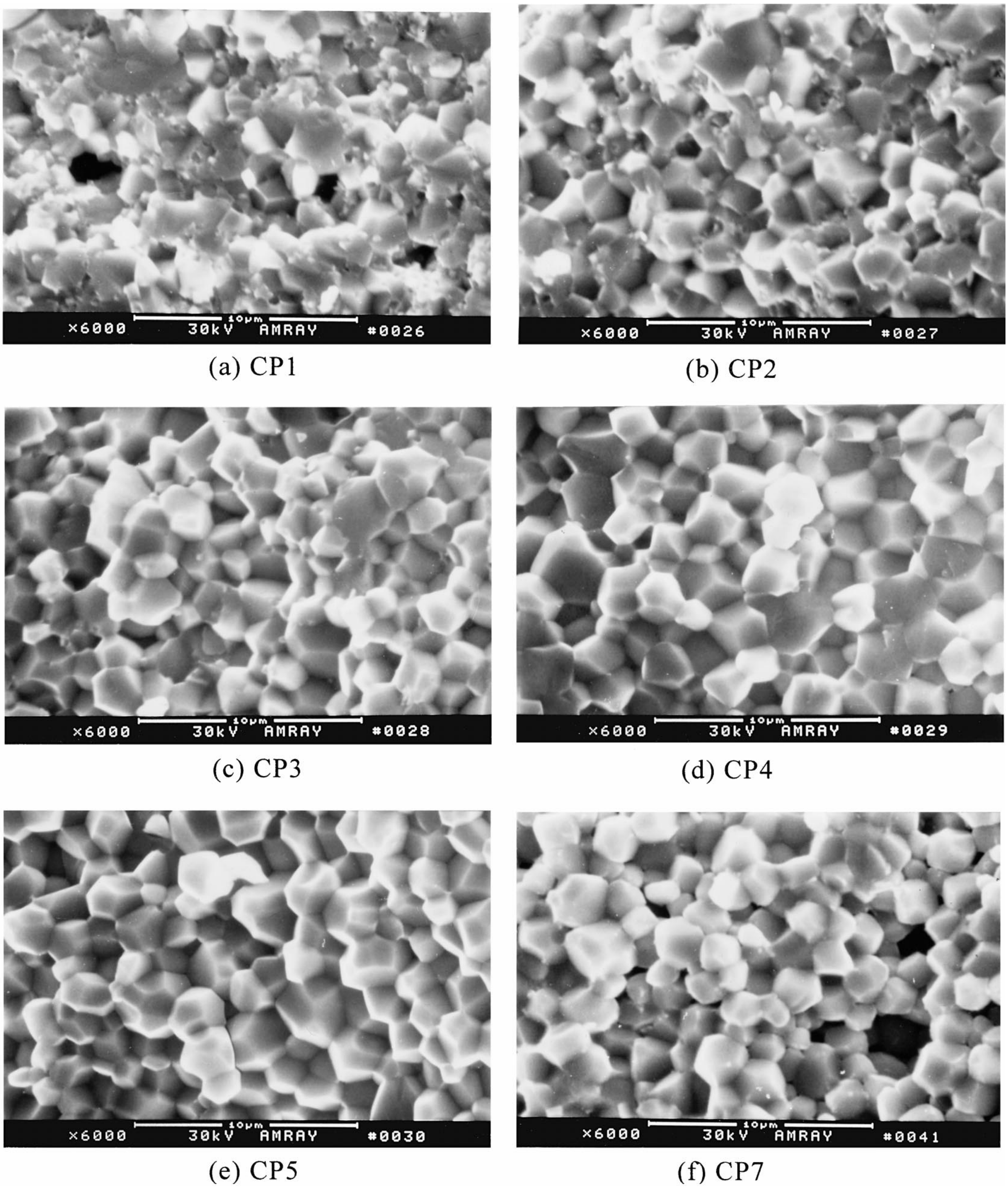


Figure 3 The SEM photos of the fractured surface of composition CP1 to CP7.

CP2 with less PbO, the fracture is mainly transgranular fracture, the grain boundary isn't clear and there are pores in it. In the composition with excess PbO, the main character of fracture is intergranular fracture and the ceramic is very dense. But in CP7, the grain size is smaller than that of CP4, and there are pores appearing again. That is to say, the composition with a small amount of excess PbO (such as CP4 or CP5) has a bigger grain size and denser microstructure, but too much excess PbO will not aid in the densification and the increasing of the grain size. Fig. 4 shows the relative densities of composition CP1-CP7. The density of CP4 is the biggest. These compositions with a denser structure and purer perovskite structure are believed to have better electrical properties.

3.2. Dielectric and piezoelectric properties

Figs 5–7 are the dielectric constant and dissipation factor versus temperature and frequency of compositions CP1, CP3 and CP5 respectively. From the composition with less PbO to the composition with excess PbO, the MPB moves to the tetragonal phase side, the relaxor character decreases, and the maximum dissipation factor also decreases. The composition CP3 has the highest dielectric constant. This is easy to understand: in the composition with less PbO, the pyrochlore phase will be detrimental to the dielectric constant, and in the compositions with excess PbO, the grain boundary layer will decrease the dielectric constant, thus the dielectric constant reaches a peak value in the stoichiometric composition CP3, although there is a little

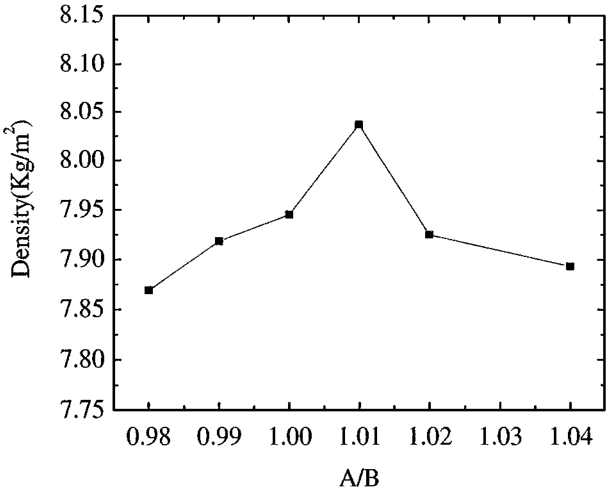


Figure 4 The relative densities of composition CP1 to CP7.

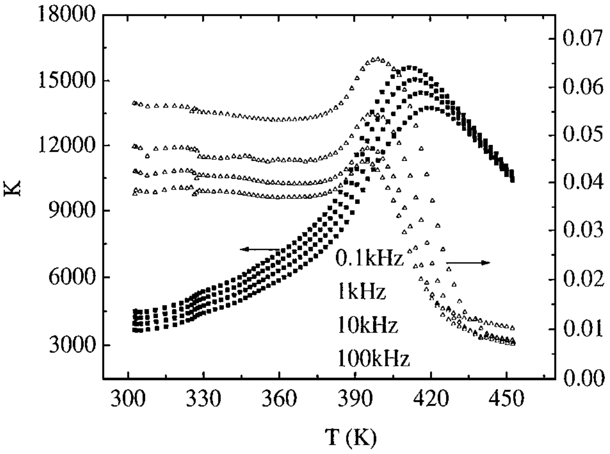


Figure 5 Dielectric constant and dissipation factor versus temperature and frequency of composition CP1.

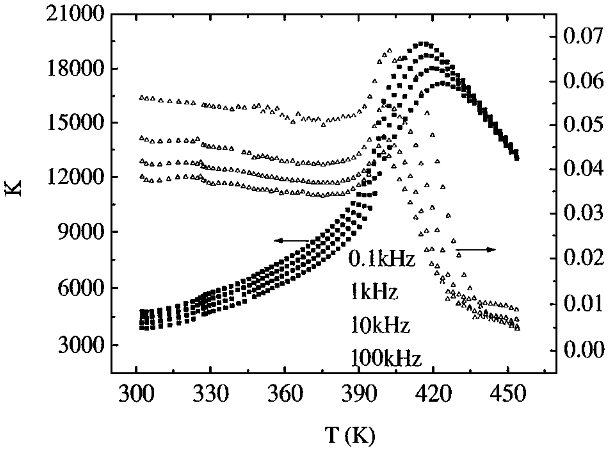


Figure 6 Dielectric constant and dissipation factor versus temperature and frequency of composition CP3.

pyrochlore phase in this composition. The results show that the grain boundary layer is much more detrimental to the dielectric constant than that of the pyrochlore phase.

The piezoelectric properties are shown in Table II. The d_{33} reaches its peak value in composition CP5 with 2 mol% excess PbO, and then decreases with the increase of excess PbO. This result reveals that the pyrochlore phase has a worse influence on the piezoelectric properties than that of a grain boundary layer. This is different from the results in the dielectric properties. The dielectric constant reaches a peak value in composition CP3.

TABLE II Piezoelectric parameters of as-sintered CP ceramics

	CP1	CP2	CP3	CP4	CP5	CP6	CP7
k_p	32	33	43	44	46	36	32
k_{31}	17	18	23	24	25	20	17
d_{33}	308	336	503	511	538	426	320
d_{31}	−127	−128	−190	−187	−207	−150	−124

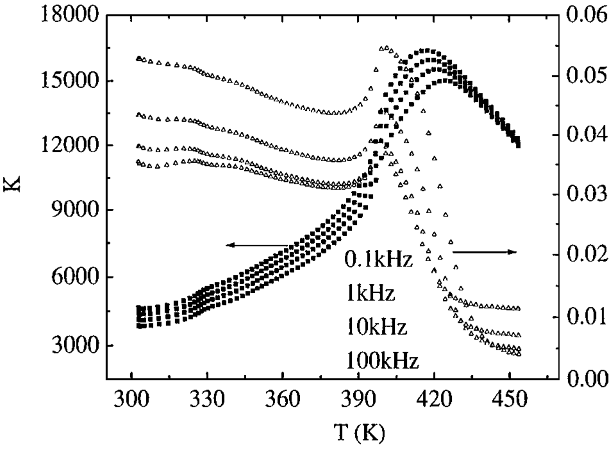
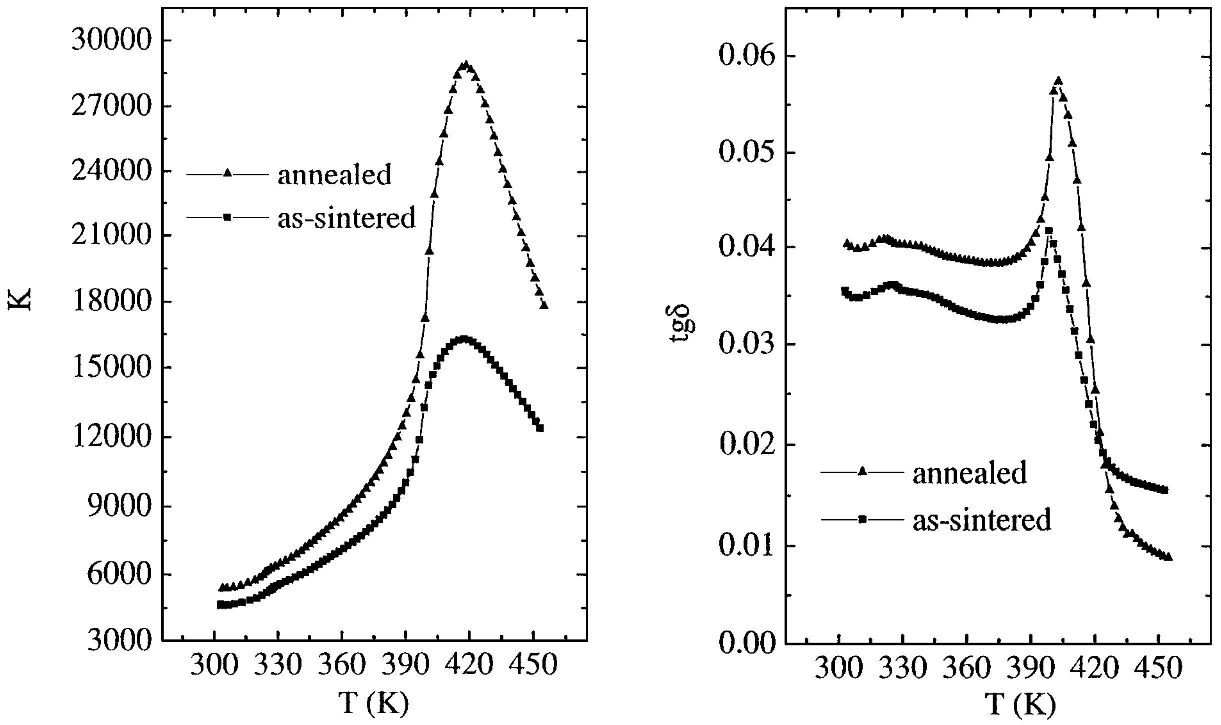


Figure 7 Dielectric constant and dissipation factor versus temperature and frequency of composition CP5.

It has been reported in our previous work [12] that thermal annealing is a good way to improve the dielectric and piezoelectric properties in lead-based relaxor ferroelectric ceramics. Fig. 8 shows the dielectric constant and dissipation factor versus temperature of CP4 with reference to annealing. Since a liquid phase will form at about 1103–1113 K due to excess PbO [9], so 1123 K is a proper annealing temperature [13]. After annealing at 1123 K for 8 h, an enhancement was observed in the dielectric constant and dissipation factor, especially in the maximum dielectric constant K_m, which increases from 16000 to about 29000 by about 80%. But at room temperature (RT), the dielectric constant only increases by about 15%, from 4670 to 5370. Other compositions have similar results. Fig. 9 is the K_m versus A/B ratios with reference to annealing in PZN based ceramics with the ABO_3 structure. The increase in the dielectric constant in the compositions with $A/B \geq 1$ is larger than that in the compositions with $A/B < 1$ after annealing. The piezoelectric coefficient d_{33} is also increased by annealing. Fig. 10 shows d_{33} vs. A/B with reference to annealing. After annealing at 1123 K for 8 h, d_{33} increases from 538 pC/N to 680 pC/N, k_p increases from 46% to 49%. Composition CP5 has the highest dielectric constant and piezoelectric constant. What is interesting is that for the composition with $A/B < 1$, d_{33} increases after annealing at 1123 K for 4 h, but decreases after annealing for 8 h. This decrease can be attributed to the increase of the pyrochlore phase. The XRD result shows that after annealing, there is more pyrochlore



(a)dielectric constant

(b)dissipation factor

Figure 8 Dielectric constant (a) and dissipation factor (b) versus temperature of composition CP4 with reference to annealing.

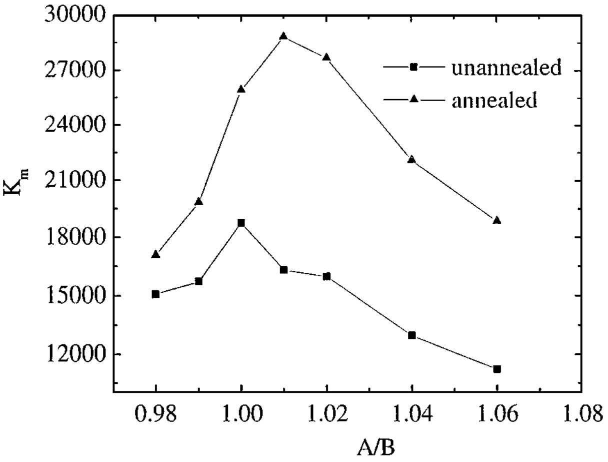


Figure 9 K_m versus A/B ratio with reference to annealing in PZN-based ceramics.

phase appearing in the compositions with less PbO. This result reveals that in order to obtain better dielectric and piezoelectric properties in lead based ferroelectric ceramics with the pure perovskite structure, a small amount of excess PbO should be added when preparing the ceramics, and then the excess PbO should be eliminated by thermal annealing at about 1123 K for 4–8 h.

3.3. Grain boundary layer

The measurements of the dielectric and piezoelectric properties in PZN ceramics with various A/B show that excess PbO has a great influence on the structure and properties. In lead based ferroelectric ceramics, the sintering is a liquid sintering because of the low melting point of PbO. A small amount of excess PbO will be available for the formation of the perovskite structure and the densification of the materials. But if there is too much excess PbO, the PbO will stay in the grain boundary and form a grain boundary layer. Since this layer has a low dielectric constant of about 20, the overall dielectric constant will be decreased due to the excess PbO. However, the grain boundary can be eliminated by after-sintering annealing as we mentioned above. Fig. 11 is the TEM observations of the grain boundary in CP3 before and after annealing. In the as-sintered specimen, a grain boundary layer and a triple point exist, and this intergranular layer is amorphous, since a halo diffraction pattern was observed (Fig. 11b). After annealing, the grain boundary layer disappears, and it is straight and

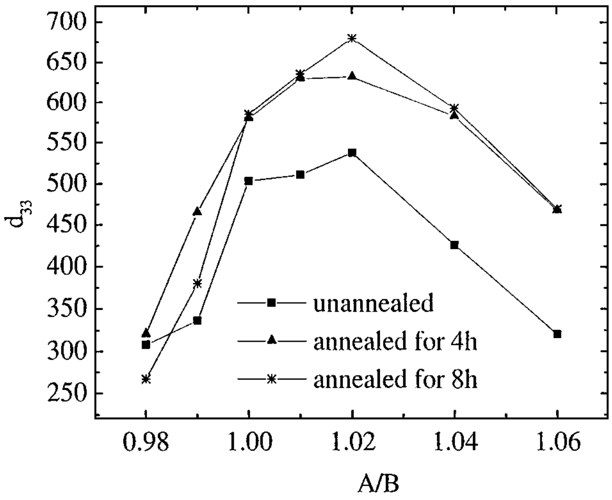
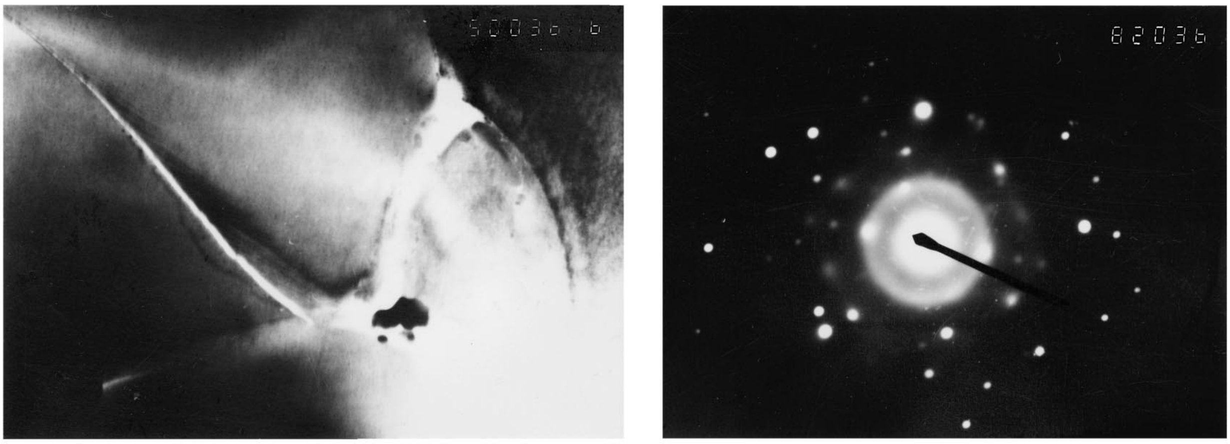


Figure 10 d_{33} versus A/B ratio with reference to annealing.



(a) as-sintered (50000 ×)   (b) halo diffraction pattern

(c) annealed (50000 ×)

Figure 11 The grain boundary layer of CP3 with reference to annealing observed by TEM. (a) as-sintered (b) halo diffraction pattern (c) annealed.

"clear". The grain size does not change after annealing. According to the series-mixing model for diphasic systems [14], the dielectric constant of polycrystalline ceramics can be written as

$$\frac{D}{K_s} = \frac{D_g}{K_g} + \frac{D_{gb}}{K_{gb}}$$

Where K_s is the relative dielectric constant of the specimen, K_g is the inherent dielectric constant of grain excluding the grain boundary layer. K_{gb} is the dielectric constant of the grain boundary layer. D_g and D_{gb} are the thickness of the grain core and grain boundary layer respectively; D is the total thickness of the grain. Since K_{gb} is about 20, the elimination of the grain boundary by thermal annealing can improve the dielectric properties. The above formula suggests that the dielectric constant will increase with the same ratio over a wide temperature range (from RT to over T_m) with almost the same ratio after elimination of the grain boundary layer, and this phenomena has been discussed in Jang's work [15]. What is different in the present work is that the increase ratio is not the same at different temperature ranges: the ratio is small at room temperature and at the temperature range far above T_m, but it is very large at the temperature range near T_m. So the grain boundary model can't explain the very large increase in dielectric constant near T_m after annealing.

Besides the elimination of the grain boundary, thermal annealing can also release the internal stress and eliminate the defects that pin the motion of the domain walls, especially in the microregions in a grain near the grain boundary. This will be available to the displacement of the domain walls and the poling of the ceramics. A number of lead vacancies will probably form after annealing for a long time, which also results in the easy motion of domain walls thereby enhancing K, d_{33} and k_p [16]. Near T_m, the macrodomains change to microdomains, and the motion of domain walls is very active, so a large increase in the dielectric constant was observed near T_m in annealed specimens. Since the domain motion is a loss process, the dissipation factor also decreased after annealing. Fig. 12 is the hysteresis loop of composition CP3 reference to annealing. After annealing, the remnant polarization (P_r) increases and the coercive field (E_c) decreases, which means that the annealed ceramic specimens are easily poled and should have better piezoelectric properties. The mechanism during thermal annealing is complex, including the grain boundary layer, defects and the displacements of domain walls. And the annealing conditions (time, atmosphere, etc.) will also affect the properties of the samples. Further study will be reported in the future.

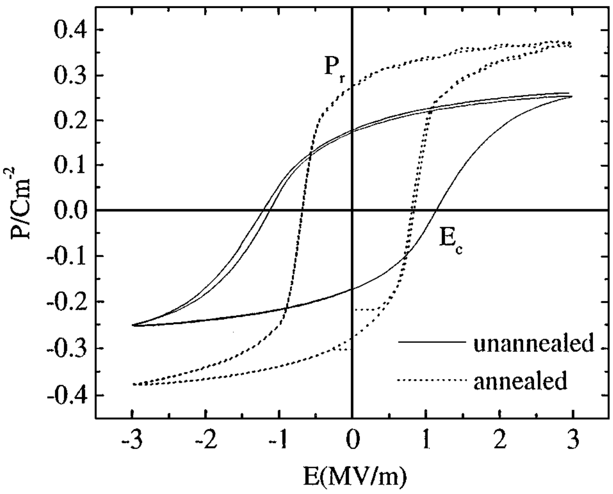


Figure 12 Hysteresis loop of composition CP3 with reference to annealing.

4. Conclusion

The content of PbO has a great influence on the microstructure and the electrical properties of the lead-based relaxor ferroelectric ceramics. When PbO is inefficient, the pyrochlore will decrease the dielectric and piezoelectric properties, especially the piezoelectric coefficients; when there is too much excess PbO, the grain boundary layer will dilute the dielectric and piezoelectric properties, especially the dielectric constants. A small amount of excess PbO can inhibit the appearance of the pyrochlore phase and yield a perovskite structure. After sintering, the excessive PbO can be eliminated by annealing. So the best dielectric properties and piezoelectric properties can be achieved in annealed lead-based ferroelectric ceramics with a small amount of excess PbO. For the PZN-BT-PT ceramic system, $d_{33} = 680$ pC/N, $K_m \approx 27000$, $k_p \approx 50$ % were achieved in the studied composition with 1–2 mo1% excess PbO. The observed enhancement of electrical properties in annealed specimens can be related to the elimination of the grain boundary layer and the easy motion of the domain walls after annealing.

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