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High piezoelectric properties of $BaTiO_3$–xLiF ceramics sintered at low temperatures

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Abstract

$BaTiO_3$–xLiF ceramics were prepared by a conventional sintering method using $BaTiO_3$ powder about 100 nm in diameter. The effects of LiF content (x) and sintering temperature on density, crystalline structure and electrical properties were investigated. A phase transition from tetragonal to orthorhombic symmetry appeared as sintering temperatures were raised from 1100 °C to 1200 °C or as LiF was added from 0 mol% to 3 mol%. $BaTiO_3$–6 mol% LiF ceramic sintered at 1000 °C exhibited a high relative density of 95.5%, which was comparable to that for pure $BaTiO_3$ sintered at 1250 °C. $BaTiO_3$–4 mol% LiF ceramic sintered at 1100 °C exhibited excellent properties with a piezoelectric constant $d_{33} = 270$ pC/N and a planar electromechanical coupling coefficient $k_p = 45\%$, because it is close to the phase transition point in addition to high density.

Keywords: B. Grain size; C. Dielectric properties; C. Piezoelectric properties; D. $BaTiO_3$ and titanates; Low temperature sintering

1. Introduction

Lead-free piezoceramics are urgently needed to replace lead-based piezoceramics as a result of growing environmental concerns. Barium titanate ($BaTiO_3$) is the first practically applied piezoceramics. Although $BaTiO_3$ ceramics had been reported to have a moderate d_{33} of 190 pC/N for several decades, the surprising high d_{33} values (350 pC/N, 460 pC/N, 788 pC/N) have been obtained recently by microwave sintering, two-step sintering, and template grain growth.[1–3] Unfortunately, these preparation methods are not suitable for mass production due to high cost or complex processes. Therefore, obtaining high piezoelectric properties of $BaTiO_3$ ceramics by traditional processes has attracted much attention. However, the ideal densification temperature of $BaTiO_3$ ceramics is as high as 1300 °C,[4] which also impedes the application of $BaTiO_3$ ceramics. Meanwhile, its grains are apt to grow up at a high sintering temperature. It is well known that finer grain sizes are favorable to obtain high-performance $BaTiO_3$ ceramics because of smaller domain sizes. Therefore, reducing sintering temperature is necessary for the fabrication and practical application of high performance $BaTiO_3$ piezoelectric ceramics. Several promising approaches such as adding sintering aids, using chemical processing and reducing the particle size of the starting materials, have been explored.[5] Among them, adding sintering aids is a simple, effective and easily controllable method. Caballero et al.[6] reported that ZnO-doped $BaTiO_3$ ceramics sintered at 1250 °C showed a high relative density of 99% and a permittivity value close to 3000. LiF-containing additives are very effective in lowering the sintering temperature of $BaTiO_3$. Naghib-Zadeh et al.[7] found that the relative density of $BaTiO_3$ ceramic sintered at 900 °C is more than 98% by adding 2 wt% LiF–$SrCO_3$. However, little attention has been paid to the piezoelectric properties of $BaTiO_3$ ceramic other than its dielectric properties. The piezoelectric properties of $BaTiO_3$ ceramics are dependent not only on density but also grain size, impurities and structural defects.[8] To obtain high piezoelectric $BaTiO_3$ ceramics at a low sintering temperature, the LiF content and sintering temperature need to be optimized. In the present study, the density, phase structure and electrical properties of $BaTiO_3$–xLiF ceramics were investigated with a special emphasis on the effects of LiF content (x) and sintering temperature.

2. Experimental procedures

Barium titanate ($BaTiO_3$, 99%, 100 nm) and lithium fluoride (LiF, 99%) were used as raw materials. These powders

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were weighed according to the composition of $BaTiO_3$–xLiF (x = 0–6 mol%). The mixture was milled by ZrO_2 balls in an ethanol solution. After ball milling for 2 h, the slurry was dried at 80 °C. The dry powders were then compacted to disks of 10 mm in diameter and 1.5 mm in thickness at 80 MPa using 2 wt% polyvinyl alcohol (PVA) as a binder, following which the disks were heated to 600 °C at 5 °C/min and held at 600 °C for 1 h, thereby removing the binder. The samples were cooled to room temperature and then the temperature was raised directly to sintering temperature (1000–1250 °C) at 10 °C/min and held for 2 h. The specimens were coated with silver paint on their upper and bottom surfaces and fired at 550 °C for 30 min for electrical measurement. The coated samples were poled under a dc field of 1.5–3 kV/mm at room temperature for 30 min in a silicone oil bath. The density of the samples was determined by accurately measuring their mass, diameter and thickness. The crystal structure was studied using XRD with a Cu Kα radiation (λ = 1.5416 Å) filtered through a Ni foil (Rigaku; RAD-B system, Tokyo, Japan). The microstructure of the sintered samples was observed by scanning electron microscope (SEM, ZEISS-EVO18, Germany). The piezoelectric properties were measured using a quasi-static piezoelectric coefficient d_{33} testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The planar electromechanical coupling coefficient k_p was determined by resonance–antiresonance method using an Agilent 4294A precision impedance analyzer (Hewlett-Packard, Palo Alto, CA). The dielectric properties were measured using an Agilent 4294A precision impedance analyzer (Hewlett-Packard, Palo Alto, CA) from 100 Hz to 1 MHz. The temperature dependence of the dielectric properties was examined using a programmable furnace with an LCR analyzer (TH2828S) at 1 kHz in the temperature range of 13–150 °C. Ferroelectric hysteresis loops were measured at 100 Hz using a ferroelectric tester (RT6000HVA, Radiant Technologies, Inc., Albuquerque, NM).

3. Results and discussion

3.1. Densification sintering

Fig. 1 shows the temperature dependence of relative densities for the $BaTiO_3$–xLiF (x = 0–6 mol%) ceramics. Pure $BaTiO_3$ sintered at 1100 °C has a relative density of 83.4%, which reaches about 90% as the temperature is increased to 1200 °C and peaks at approximately 95% at a sintering temperature of 1250 °C. The relative density of $BaTiO_3$ ceramics is greatly improved by introducing LiF. Adding only 3 mol% LiF into $BaTiO_3$ sintered at 1125 °C yields a relative density of over 90%, which is comparable to that of pure $BaTiO_3$ sintered at 1200 °C. The enhancement of the relative density becomes more remarkable as the LiF is increased. A sample with the relative density of 95.5% can be obtained by doping 6 mol% LiF at a sintering temperature of 1000 °C, but the sintering temperature needs to be 1250 °C to obtain the same relative density in pure $BaTiO_3$ ceramics. The results suggest that introducing LiF into $BaTiO_3$ ceramics can significantly enhance the densification of the ceramics by liquid phase sintering since the melting point of LiF is as low as

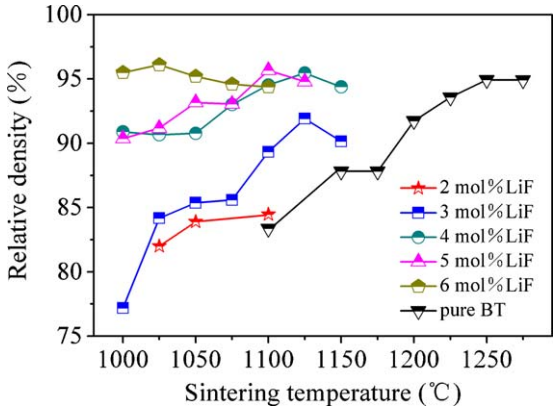

Fig. 1. Relationship of the relative density and sintering temperature for $BaTiO_3$–xLiF ceramics.

846 °C.[9] Nevertheless, further raising the sintering temperature prejudices the densification of all LiF-added compositions, as a result of the evaporation of the LiF.[9,10] Akishige et al.[10] found that F^- evaporates in the range of 740–1130 °C in 10% KF-doped $BaTiO_3$ ceramics, based on TGA results. Marder et al.[9] reported that 1 wt% LiF doped Y_2O_3 ceramics sintered at 700 °C obtained the highest density, while the density decreased as the sintering temperature was raised to 900 °C, as a result of the evaporation of LiF at high temperature.

Fig. 2 shows the optimal sintering temperature of the $BaTiO_3$–xLiF (x = 0–6 mol%) ceramics with maximum density. Because of the high sintering activity of 100 nm $BaTiO_3$ powder, the optimal sintering temperature for pure $BaTiO_3$ is 1250 °C, which is lower than the 1300 °C which is usually necessary for fabricating dense $BaTiO_3$ ceramics.[4] With the increase of x from 3 mol% to 6 mol%, the optimal sintering temperature is reduced from 1125 °C to 1025 °C. The optimal sintering temperature for $BaTiO_3$–6 mol% LiF ceramic is reduced by 225 °C as compared with that (1250 °C) for pure $BaTiO_3$.

3.2. Microstructure and phase structure

Fig. 3 shows the SEM images of the thermally etched surface of $BaTiO_3$–xLiF ceramics. All samples show clear grain boundaries. The grain sizes of pure $BaTiO_3$ sintered at 1100 °C

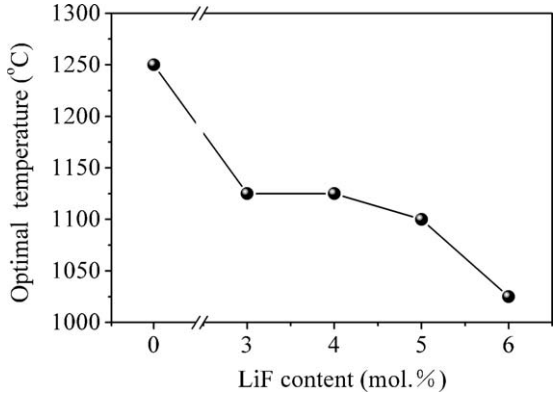

Fig. 2. Optimal sintering temperature of $BaTiO_3$–xLiF ceramics as a function of LiF content.

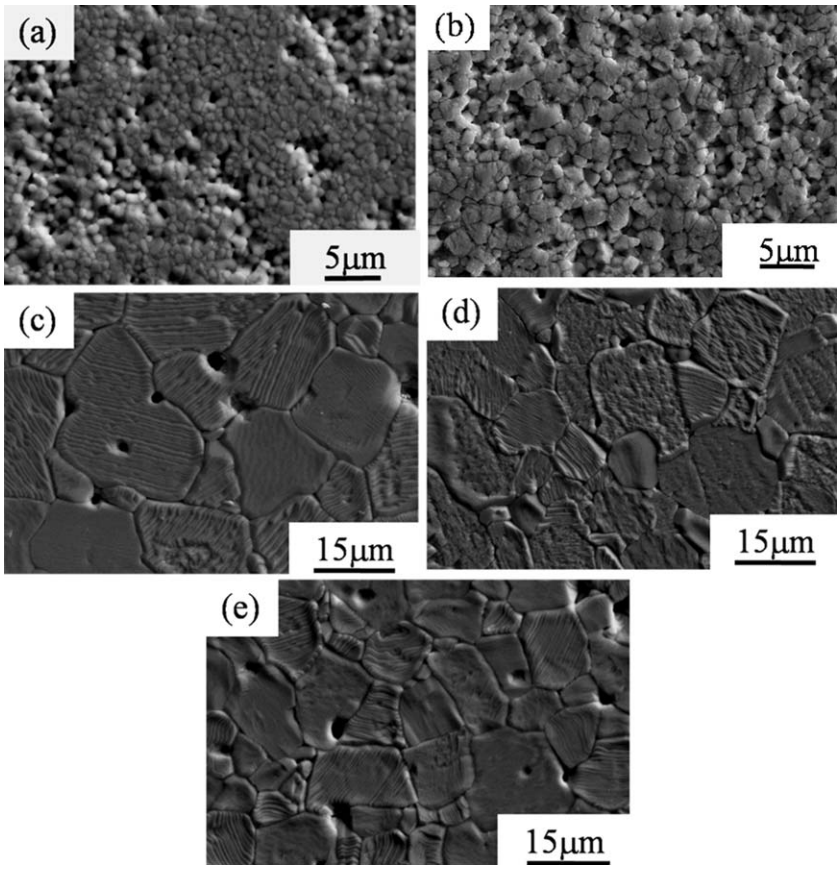

Fig. 3. SEM images of thermally etched surface of $BaTiO_3$–xLiF ceramics sintered at 1100 °C (a, c–e) and at 1200 °C (b). (a and b) $x = 0$ mol%; (c) $x = 4$ mol%; (d) $x = 5$ mol%; (e) $x = 6$ mol%.

and 1200 °C are about 0.85 μm and 2.5 μm, respectively, while the grains grow to 11–22 μm in the specimens to which LiF has been added. The reason is that liquid phase sintering greatly promotes grain growth.

Fig. 4(a) shows X-ray diffraction patterns of $BaTiO_3$–xLiF ceramics ($x = 0$–6 mol%) sintered at 1100 °C and pure $BaTiO_3$ ceramics sintered at 1200 °C. The standard diffraction peaks cited from the tetragonal $BaTiO_3$ (PDF#05-0626) and the orthorhombic one (PDF#81-2200) are indicated by vertical lines for comparison, whose ratios of two diffraction peaks around 45° are obviously different as shown in the enlarged XRD patterns of angles ranging from 44° to 46° in Fig. 4(b). The former ratio of (2 0 0) to (0 0 2) is greater than 1, while the later ratio of (2 0 0) to (0 2 2) is less than 1. All the samples exhibit a pure perovskite structure without any trace of impurity phase. The diffraction peaks for the pure $BaTiO_3$ sintered at 1100 °C correspond well with those of the PDF#05-0626, while those for the counterparts sintered at 1200 °C and the LiF-added samples sintered at 1100 °C correspond well with those of the PDF#81-2200, respectively. This result suggests that the crystallographic structure changes from tetragonal to orthorhombic symmetry by raising the sintering temperature from 1100 °C to 1200 °C or by adding LiF. On the other hand, when the LiF content varies from 0 mol% to 6 mol%, the (0 2 2) peak near 45° tends clearly toward lower diffraction angles, as a result of the enlargement of lattices, according to Bragg's equation ($2d \sin\theta = \lambda$), because of the substitutions of Li^+ ($r = 0.76$ Å) for Ti^{4+} ($r = 0.61$ Å) in B site.[11,12]

3.3. Electrical properties

Fig. 5 shows the piezoelectric constant d_{33}, the planar electromechanical coupling coefficient k_p (a) and the grain size (b)

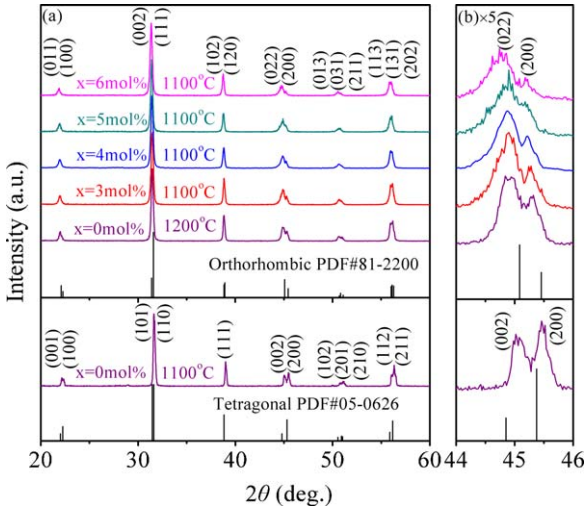

Fig. 4. X-ray diffraction patterns between the 2θ range of 20–60° (a) and 44–46° (b) for $BaTiO_3$–xLiF ceramics.

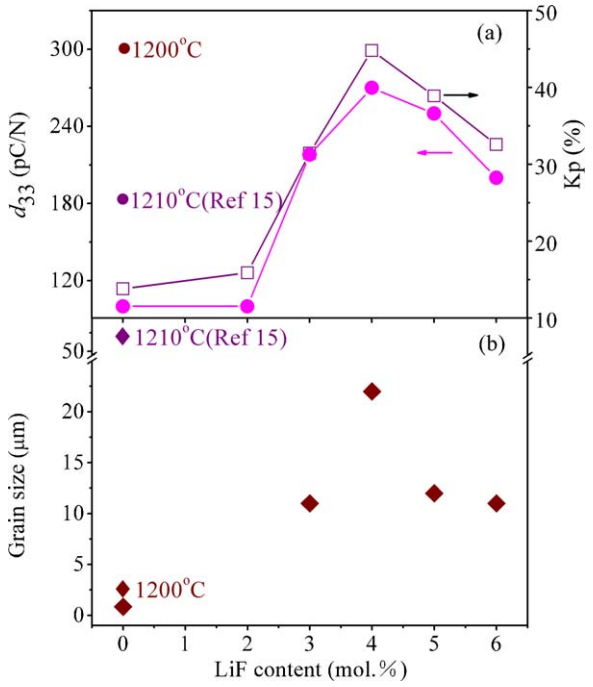

Fig. 5. The d_{33} and k_p (a) and grain size (b) for the $BaTiO_3$–xLiF ceramics as a function of LiF content.

for the $BaTiO_3$–xLiF ceramics sintered at 1100 °C as a function of LiF content. The d_{33} and grain size of pure $BaTiO_3$ sintered at 1200 °C are also shown for comparison. The pure $BaTiO_3$ sintered at 1200 °C with a grain size of 2.5 μm shows a high d_{33} value (300 pC/N), while the counterpart sintered at 1100 °C with a grain size of 0.85 μm exhibits a considerably low d_{33} value (100 pC/N) because of its low density (83.37%). The 4 mol% LiF added sample with a grain size of 22 μm exhibits a maximum d_{33} = 270 pC/N as the sintering was performed at 1100 °C. Fine grain size favors a high d_{33}, so the $BaTiO_3$ sample sintered at 1200 °C has a grain size of about 2.5 μm and shows a d_{33} = 300 pC/N which is much higher than 193 pC/N[13] for the sample with a grain size of >50 μm. Some previous reports[1,4] have also demonstrated that smaller grains tend to have smaller domain sizes and higher d_{33}, since the domain walls with small areas will respond more actively to external electrical or stress signals. The $BaTiO_3$–4 mol% LiF ceramics with the biggest grain size (22 μm) show d_{33} value (270 pC/N), which is higher than the d_{33} values (218 pC/N, 250 pC/N, 200 pC/N) for counterparts obtained with smaller grain sizes. As mentioned above, the higher d_{33} value corresponds to the finer grain size, but this cannot explain the fact that the d_{33} value for $BaTiO_3$–4 mol% LiF ceramics is higher than those for counterparts with smaller grain sizes. The lower d_{33} value (218 pC/N) in the 3 mol% LiF added sample is attributable to the relative density being less than 90%. The samples with 5–6 mol% LiF show smaller grain sizes (12, 11 μm) and similar densities as compared with that of the $BaTiO_3$–4 mol% LiF, but their d_{33} values (250, 200 pC/N, respectively) are lower than the 270 pC/N for the $BaTiO_3$–4 mol% LiF. Therefore, there must be something else contributing to the enhancement of their piezoelectric properties. Since the crystallographic structure of the $BaTiO_3$–4 mol% LiF

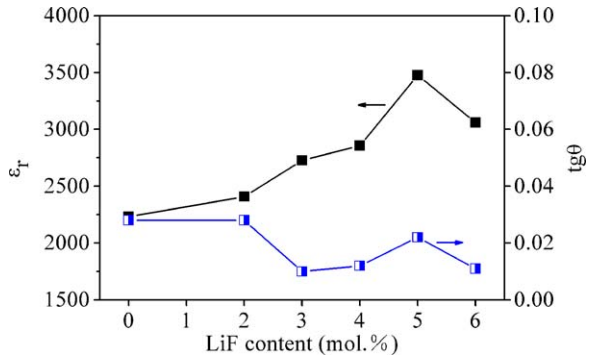

Fig. 6. Dielectric properties at 1 kHz of $BaTiO_3$–xLiF ceramics sintered at 1100 °C as a function of LiF content.

is closer to the transition between tetragonal and orthorhombic symmetry as compared with those of the 5–6 mol% LiF added samples (Fig. 4), the change of crystallographic structure may provide a favorable condition for easier motion of domains. In other words, the d_{33} value is principally determined by crystallographic structure rather than grain size if the sample has the same high density.

Fig. 6 shows the dielectric constant (ε_r) and dielectric loss ($tg\theta$) at 1 kHz for $BaTiO_3$–xLiF ceramics sintered at 1100 °C as a function of LiF content. Because of low relative density (<85%), the ε_r value of pure $BaTiO_3$ ceramic is 2231, and increases continually to a peak value of ε_r = 3500 as x = 5 mol%. The reason for this is that the increased density is favorable for enhancing dielectric property.[14,15] The pure $BaTiO_3$ ceramics show the highest $tg\theta$ = 0.028, which decreases to 0.01 as 3 mol% LiF is added. The variation in $tg\theta$ is similar to that in ε_r for the samples with 3–6 mol% LiF and is opposite to that in ε_r for the samples with 0–3 mol% LiF.

Fig. 7 shows the frequency dependence of the dielectric constant (ε_r) for $BaTiO_3$–xLiF ceramics sintered at 1100 °C. The ε_r for $BaTiO_3$–xLiF ceramics (x = 0–6 mol%) changes slightly with raising measuring frequencies from 100 Hz to 1 MHz, while the ε_r is unstable at high frequencies for the samples with x = 3–6 mol%. It has been reported that the ε_r of $(Ba_{0.95}Ca_{0.05})(Ti_{0.88}Zr_{0.12})O_3$ ceramics decreases as the frequency increases.[16] This is due to some relaxation polarization

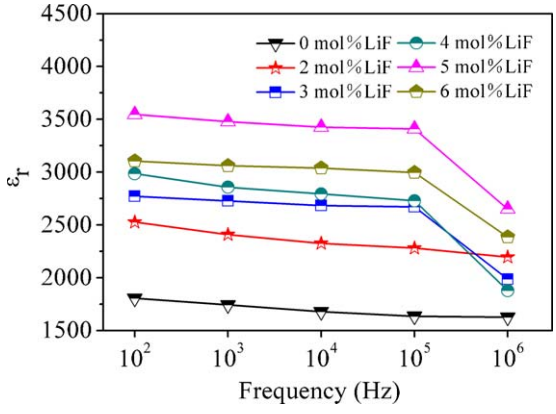

Fig. 7. Frequency dependence of ε_r for $BaTiO_3$–xLiF ceramics sintered at 1100 °C from 100 Hz to 1 MHz.

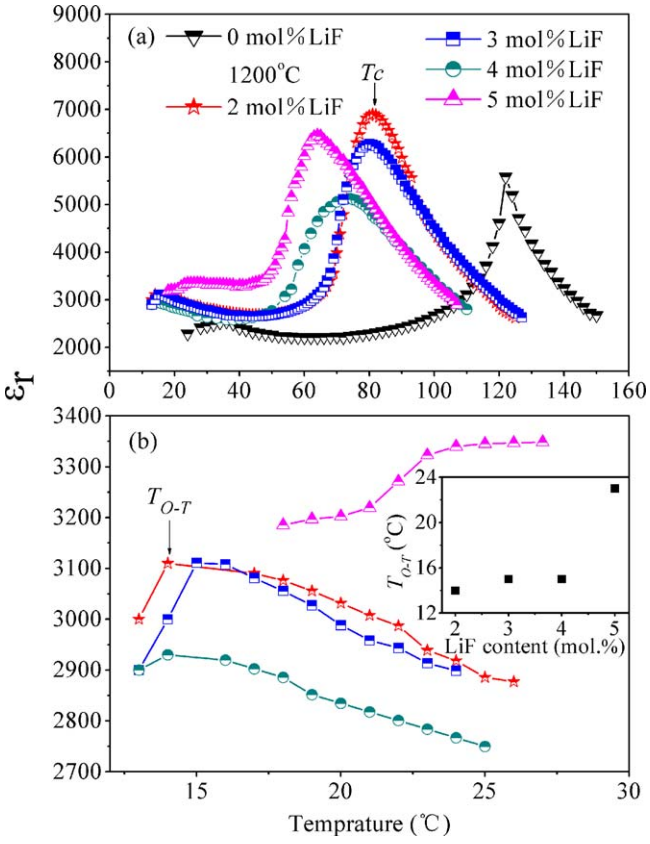

Fig. 8. Temperature dependence of ε_r for $BaTiO_3$–xLiF ceramics measured at 1 kHz between 13–150 °C (a) and 13–28 °C (b).

mechanisms at high frequencies, in which the electric charge carriers in the sample cannot respond to the rapid change in exterior electric fields when the applied electric fields exceed a certain frequency.[17]

Fig. 8 shows the temperature dependence of ε_r for $BaTiO_3$–xLiF ceramics measured at 1 kHz between 13 and 150 °C. As shown in Fig. 8(a), the Curie temperature (T_c) shifts to a lower temperature as x is increased. The structure distortion produced by the substitution of Li^+ for Ti^{4+} may be responsible for this kind of dielectric behavior.[18] On the other hand, both pure $BaTiO_3$ sintered at 1200 °C and LiF-added $BaTiO_3$ ceramics sintered at 1100 °C show an orthorhombic symmetry at room temperature (Fig. 4), so an orthorhombic–tetragonal phase transition temperature (T_{O-T}) can be observed in Fig. 8(b). The variation in the relationship between T_{O-T} and LiF content is shown in the inset of Fig. 8(b). The T_{O-T} of $BaTiO_3$–xLiF increases as x rises, suggesting that the crystallographic structure gradually approaches the orthorhombic symmetry. The measured T_{O-T} temperatures are lower than room temperature. However, this may be attributable to testing error.

Fig. 9 shows the polarization–electric field (P–E) hysteresis loops of $BaTiO_3$–xLiF ceramics measured at room temperature at 100 Hz. All samples possess a typical ferroelectric polarization hysteresis loop. The inset in Fig. 9 illustrates the variation of the remanent polarization P_r and coercive field E_c of $BaTiO_3$–xLiF ceramics as x is increased. The P_r for the LiF added ceramics reduces as compared to that for pure

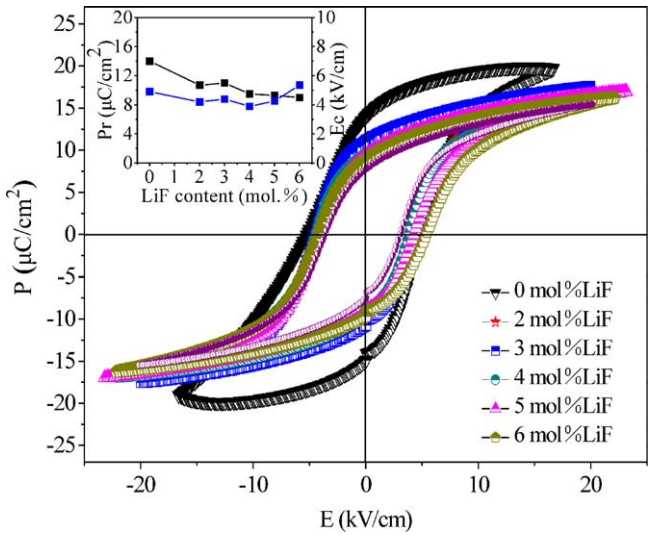

Fig. 9. Polarization–electric field (P–E) hysteresis loops of $BaTiO_3$–xLiF ceramics measured at room temperature at 100 Hz.

$BaTiO_3$, while E_c increases at $x = 6$ mol% in comparison with pure $BaTiO_3$. This may be attributed to the pinning effect of domain walls caused by the increase of oxygen vacancies generated by the substitution of Li^+ for Ti^{4+}.[19,20] Fig. 9 also shows that the leak current for the LiF added samples is lower than that for pure $BaTiO_3$ because of their better dielectric properties at room temperature.

4. Conclusions

The effects of LiF content (x) and sintering temperature on the density, phase structure and electrical properties of $BaTiO_3$–xLiF ceramics were investigated. The densification sintering temperature of $BaTiO_3$ ceramic was reduced by approximately 250 °C after adding 6 mol% LiF. $BaTiO_3$–4 mol% LiF ceramic sintered at 1100 °C exhibited excellent electrical properties: $d_{33} = 270$ pC/N, $\varepsilon_r = 2857$, $tg\theta = 0.012$, $E_c = 3.89$ kV/cm, $P_r = 9.5$ μC/cm^2, because it was near the phase transition boundary between tetragonal and orthorhombic symmetry in addition to its high density. $BaTiO_3$–xLiF ceramics sintered at low temperatures with excellent electrical properties should be considered as promising lead-free piezoceramics.

Acknowledgments

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