Phase transitions and electrical properties in La^{3+}-substituted $Bi_{0.5}(Na_{0.75}K_{0.15}Li_{0.10})_{0.5}TiO_3$ ceramics

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$Bi_{0.5}Na_{0.5}TiO_3$ (BNT), discovered by Smolenskii in 1960 [1], is considered to be a promising candidate as lead-free piezoelectric ceramics. It exhibits strong ferroelectricity at room temperature (RT) with a relatively large remanent polarization (P_r=38 μC/cm^2). However, pure BNT is difficult to be practically used due to its large coercive field (E_c=73 kV/cm) and high conductivity. To improve its properties, solid solutions of BNT with $BaTiO_3$ [2, 3], $SrTiO_3$ [4], $NaNbO_3$ [5], $Bi_{0.5}K_{0.5}TiO_3$ and $Bi_{0.5}Li_{0.5}TiO_3$ [6–8] have been investigated. Among them, $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ ceramics are regarded as a new group of BNT-based lead-free piezoelectric ceramics, which exhibit relatively high piezoelectric constant d_{33} (up to 180 pC/N) and planar electromechanical coupling factor k_p (up to 35.0%) [8]. On the other hand, lanthanum (La) has been introduced to modify BNT-based piezoelectric ceramics [9, 10]. It was reported that the piezoelectric properties could be improved by doping with an appropriate amount of La in both $(Bi_{0.5}Na_{0.5})_{(1-1.5x)}La_xTiO_3$ and $(1-x)(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$-$xLa_2O_3$ system ceramics. In this paper, La was added to $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ ceramics with fixed values of x and y (x=0.15, y=0.10) and a new kind of lead-free piezoelectric ceramics with excellent piezoelectric properties were obtained. The influences of La^{3+} on the crystal structure, phase transitions and electrical properties were investigated.

The starting materials were reagent grade oxide or carbonate powders of Bi_2O_3, TiO_2, La_2O_3, Na_2CO_3, K_2CO_3 and Li_2CO_3. All compositions were prepared by the conventional mixed oxide method. The formulas $[(Bi_{1-z}La_z)(Na_{0.75}K_{0.15}Li_{0.10})]_{0.5}TiO_3$ were prepared by varying z from 0 to 0.05. The mixed powders were calcined at 850–900 °C for 2 hr, and then the calcined powders were ground again by ball milling for 6 hr and pressed into disks of 10 mm diameter and 1 mm thickness. Then the disks were sintered at 1100–1150 °C for 2 hrs in air. X-ray diffraction (XRD) analyses were carried out to check the crystal structure of sintered samples using a Rigaku diffractmeter. Fired-on silver paste was used as electrodes for the electrical measurements. The specimens for measurement of piezoelectric properties were poled in silicon oil at 60 °C under a DC field of 40 to 60 kV/cm for 10 min. After poling, piezoelectric properties were measured by means of the resonance anti-resonance method using an impedance analyzer (Agilent 4294A). The planar electromechanical coupling factor (k_p) was calculated from the resonance and the anti-resonance frequencies according to Onoe's formula [11]. A piezo-d_{33} meter was used to measure the piezoelectric constant (d_{33}) at a frequency of 50 Hz. Temperature dependence of dielectric constant (ε_r) of the unpoled samples were measured at 100, 1 k and 10 kHz using a programmable furnace with a LCR meter (HP 4192A). The free permittivity and dissipation factor of poled samples at RT were obtained using the LCR meter at 1 kHz. The coercive field (E_c) and remanent polarization (P_r) were determined from P–E hysteresis loops obtained by a Radiant Precision LC2000 materials analyzer.

XRD patterns shown in Fig. 1 indicated that the samples with 0–2 at.% La formed a single perovskite phase after being sintered at 1130 °C for 2 hr. All diffraction patterns can be indexed as pseudocubic structures. However, some weak peaks at 2θ of 30° and 50° appeared in 3 at.% La-doped samples, which suggested the existence of a secondary phase identified to be $Bi_2Ti_2O_7$.

Fig. 2 shows the temperature dependence of dielectric constant at different frequencies for $[(Bi_{1-z}La_z)(Na_{0.75}K_{0.15}Li_{0.10})]_{0.5}TiO_3$ ceramics (z=0, 0.03, 0.04 and 0.05). It was obvious that diffusive phase transition (DPT) took place in all these materials within the measuring temperatures. For the non-doped sample, only a broad permittivity peak appeared and a maximum permittivity was found at 290 °C, which corresponded to the transition between antiferroelectric (AFE) and paraelectric phases. As La^{3+} concentration increased, the phase transition between ferroelectric (FE) and AFE became more pronounced and a permittivity platform was found at a lower temperature on dielectric constant vs.

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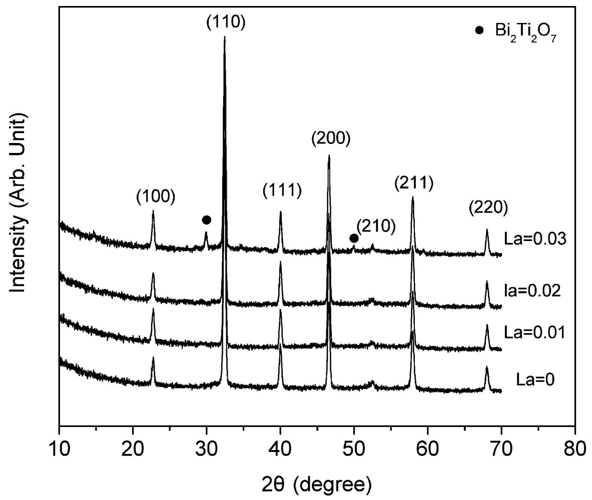

Figure 1 X-ray diffraction patterns of $[(Bi_{1-z}La_z)(Na_{0.75}K_{0.15}Li_{0.10})]_{0.5}TiO_3$ ceramics with 0–3 at. % La after being sintered at 1130 °C for 2 hr.

temperature curve. Moreover, the maximum permittivity was observed at 360 °C in all La-doped samples. Here, the temperature at which the transition between FE and AFE took place was called as depolarization temperature (T_d), and the temperature corresponding to maximum value of dielectric constant was named as maximum temperature (T_m). The decrease of T_d and increase of T_m with increasing La content was probably due to the stability enhancement of AFE phase by La addition.

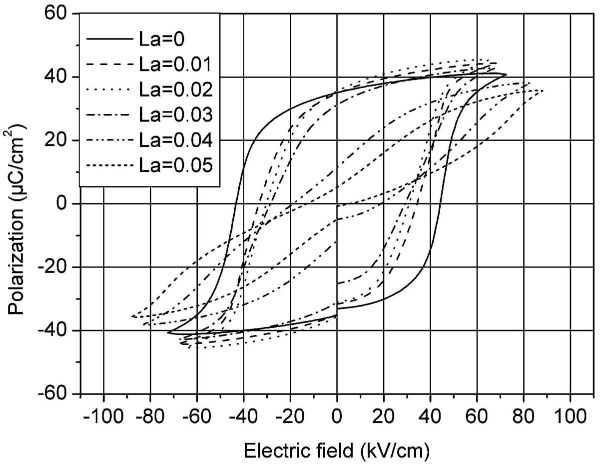

Figure 3 *P–E* hysteresis loops of $[(Bi_{1-z}La_z)(Na_{0.75}K_{0.15}Li_{0.10})]_{0.5}TiO_3$ ceramics with 0–5 at.% La at room temperature.

The *P–E* hysteresis loops of ceramics at RT are shown in Fig. 3. It is seen that the ceramics doped with 0–2 at.% La^{3+} are excellent ferroelectrics at RT with relatively large remanent polarization. When La addition increased to 3 at.%, deformed *P–E* hysteresis loop was observed, which indicated the coexistence of some AFE micropolar regions with FE matrix at RT With further increases in La content, the AFE characteristics of ceramics became increasingly distinct. Moreover, P_r increased in the beginning and then decreased, and E_c decreased continuously. The replacement of Bi^{3+} by La^{3+} led to lattice distortion,

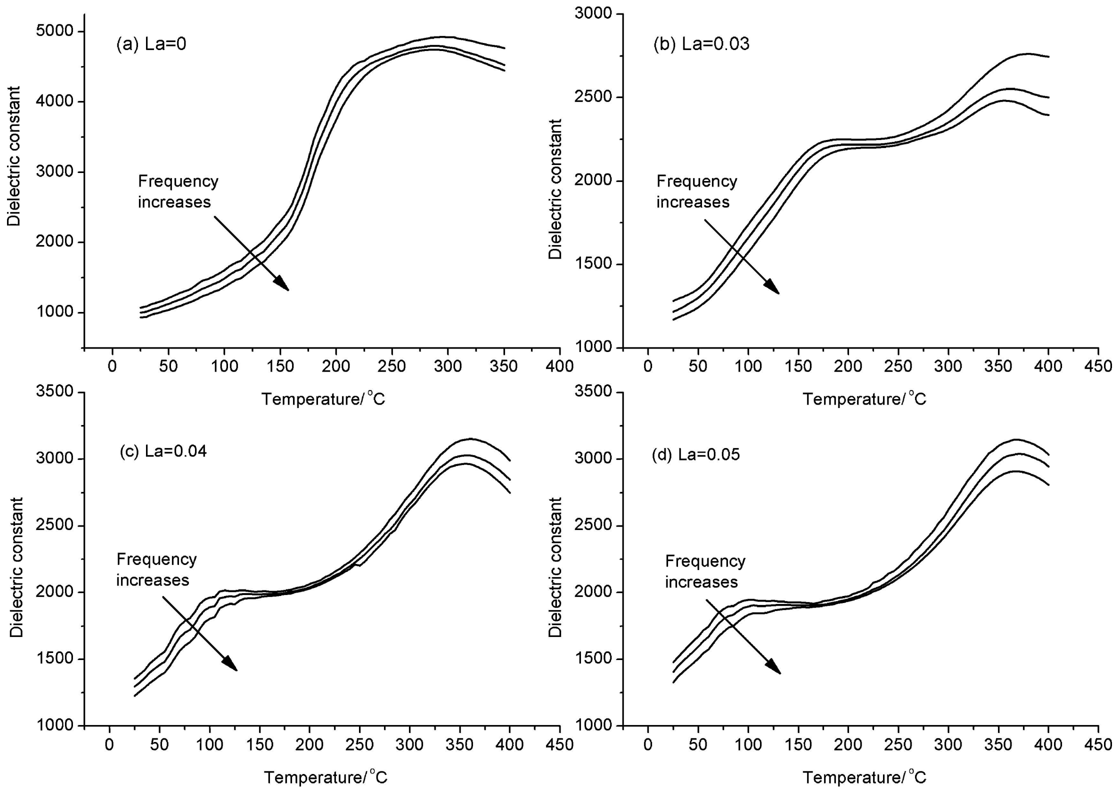

Figure 2 Temperature dependence of dielectric constant at different frequencies for $[(Bi_{1-z}La_z)(Na_{0.75}K_{0.15}Li_{0.10})]_{0.5}TiO_3$ ceramics with 0–5 at. % La.

TABLE I Effects of the amount of La on the electrical properties of $[(Bi_{1-z}La_z)(Na_{0.75}K_{0.15}Li_{0.10})]_{0.5}TiO_3$ ceramics with 0–5 at.% La

	La content (at.%)					
	0	0.01	0.02	0.03	0.04	0.05
ε	735	1235	1326	1342	1158	1392
$tg\delta$	0.030	0.040	0.036	0.034	0.033	0.038
d_{33} (pC/N)	146	170	125	99	34	–
k_p (%)	32.5	35.0	27.0	18.3	14.6	–
T_d (°C)	–	200	180	150	115	95
T_m (°C)	290	360	360	360	360	360
P_r ($\mu C/cm^2$)	35.0	35.7	36.6	30.6	11.4	5.2
E_c (kV/cm)	44.0	37.4	30.7	26.4	18.4	4.8

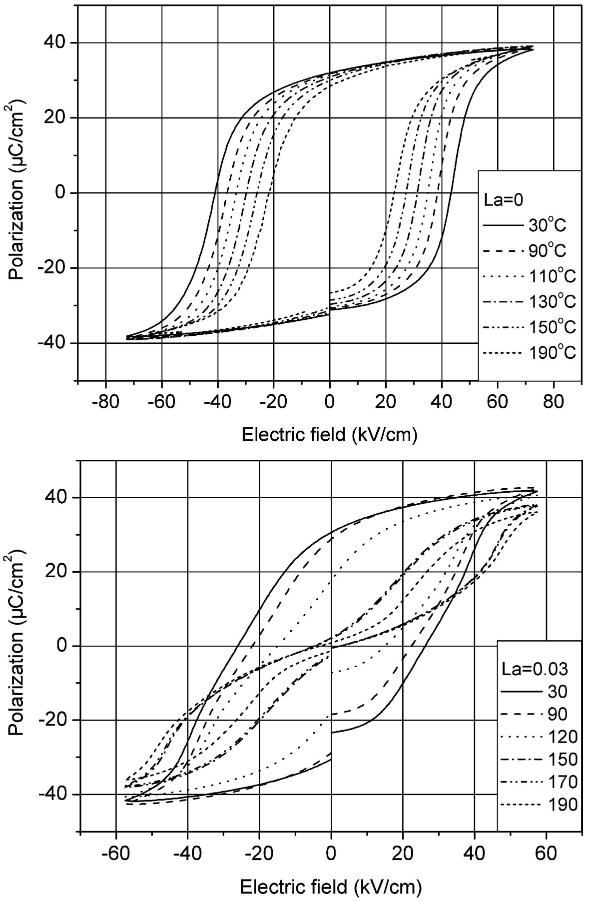

Figure 4 *P–E* hysteresis loops of (a) $Bi_{0.5}(Na_{0.75}K_{0.15}Li_{0.10})_{0.5}TiO_3$ (b) $[(Bi_{0.97}La_{0.03})(Na_{0.75}K_{0.15}Li_{0.10})]_{0.5}TiO_3$ ceramics at different temperatures.

which facilitated the movement of domain wall so that P_r increased in the beginning and E_c decreased. However, further increases in La content would decrease the contribution of Bi^{3+} to polarization, due to lower polarizability of La^{3+}. Therefore, P_r began to decrease as La exceeded 2 at.%. Table I gives the piezoelectric properties of samples. The values of d_{33} and k_p increased in the beginning and then decreased. Compared with non-doped sample, the piezoelectric properties were improved greatly by doping with 1 at.% La. The maximum values of d_{33} and k_p were 170 pc/N and 35.0%, respectively. The piezoelectric properties were diminished once the doping level was beyond 4 at.% La.

Fig. 4 shows the temperature dependence of the *P–E* hysteresis loops for non-doped and 3 at.% La-doped ceramics. With increasing temperatures, P_r and E_c decreased continuously in both samples. For non-doped sample, it was still a normal ferroelectric at 190 °C. However, for 3 at.% La-doped sample, deformed *P–E* curves were observed above 150 °C, which indicated the presence of AFE phases.

La-doped $Bi_{0.5}(Na_{0.75}K_{0.15}Li_{0.10})_{0.5}TiO_3$ ceramics were prepared by the conventional mixed oxide method. The structures, phase transitions and electrical properties were investigated. XRD proved that all the samples formed a perovskite structure with pseudocubic symmetry. The dielectric measurements revealed that the FE–AFE phase transition became distinct by La addition. A small amount of La (less than 2 at.%) led to an improvement in the ferroelectric and piezoelectric properties. The piezoelectric properties were diminished once the doping level was beyond 4 at.% La.

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