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Electrical properties of lanthanum and potassium doped barium titanate ceramics

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ABSTRACT

Phase pure perovskite $(Ba_{0.95}La_{0.025}K_{0.025})TiO_3$ (BLKT) ceramics were prepared by conventional ceramic processing. X-ray diffraction (XRD) measurement indicates that the sintered BLKT ceramics exist in pseudo-cubic structure. The relaxor behavior induced by ionic doping is confirmed by studying frequency and temperature dielectric behavior, polarization relaxation and P-E hysteresis loops upon heating. Remanent polarization (P_r) and coercive field of the BLKT ceramics are slight less than those of the pure BT ceramics. Piezoelectric constant d_{33} of the BLKT ceramics is 138-165pC/N within a pellet. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Lanthanum and potassium doping;
Crystal structure;
Relaxation;
Electrical properties.

INTRODUCTION

Lead zirconate-titanate, $Pb(Zr_xTi_{1-x})O_3$ (PZT), is conventional widely used piezoelectric ceramics in sensor, actuator and transducer applications[1-3]. However, due to crucial environmental problems arisen by lead-based electronic materials, it is necessary to search for lead-free piezoelectric materials with excellent properties.

Barium titanate, $BaTiO_3$ (BT), has been extensively used in capacitors, thermistors and piezoelectric devices due to its environmental harmony and good electrical properties[4,5]. Electrical properties of bulk materials can be manipulated by cations doping, varying the oxygen content or control of microstructure. Mixing cations of different charge at the A sites is the most straightforward experimental method for systematically tuning the properties of the perovskites[6,7].

In this paper, the influence of simultaneous La and K doping on structure, phase transition character and manipulation of electrical properties of the BT ferroelectric ceramics are studied systematically.

EXPERIMENTAL PROCEDURE

$(Ba_{0.95}La_{0.025}K_{0.025})TiO_3$ (BLKT) ceramics were prepared by conventional solid-state reaction method. High-purity carbonates and oxides, $BaCO_3$ (99.9%), La_2O_3 (99.9%), K_2CO_3 (99.9%) and TiO_2 (>99.9%), were used as raw materials. In order to obtain stoichiometric composition, the raw materials were dried separately before weighing.

Well-mixed stoichiometric raw materials were calcined at 950°C for 10h and at 1000°C for 10h separately with intermediate grinding. With the addition of 5wt% polyvinyl alcohol (PVA) binder the calcined powders were isostatically pressed into pellets and sintered at 1300°C for 2h.

Crystal structure of the sintered ceramics was measured by X-ray diffraction measurements (XRD, Rigaku RINT-2200VS diffractometer) using well-polished pellets. For electrical properties characterization, silver paste was fired on both surfaces of the well-polished ceramics as electrodes. Dielectric property was measured using a computer-interfaced impedance/gain-phase analyzer (NF Electronic Instruments 2340 LCZ Meter) from 20 to 475K. This temperature range encompasses all the structural transitions temperature of BT. P-E hysteresis loop was characterized by a Radiant Precision Premier LC ferroelectric material test system, where a Sigma Model M10 chamber was attached to measure the P-E loops upon heating. Piezoelectric property was measured by a ZJ-3AN Berlincourt-type quasistatic d_{33} meter. For piezoelectric measurement, the specimens were poled at 115-120°C in silicon oil with an electric field of 2kV/mm for 15min and then slowly cooled down to room temperature with maintaining half of the applied electric field.

RESULTS AND DISCUSSION

Figure 1 shows XRD pattern of the BLKT ceramics sintered at the optimized condition. The sintered BLKT ceramics exist in pure perovskite structure. However, due to the co-dopings of 2.5mol% lanthanum and 2.5mol% potassium, room-temperature crystal structure changes from tetragonal phase of the pure BT ceramics to pseudo-cubic phase of doped BLKT. The sintered BLKT ceramics exhibit large density, reaching 94.53% of the theoretical density, confirming such sintering condition is optimum.

Temperature dependence of dielectric constant of the BLKT ceramics is shown in Figure 2. Due to La and K co-dopings, the value of dielectric maximum (ε_m) is slightly smaller than that of the pure BT ceramics, and the temperatures of the well-known rhombohedral FE phase-orthorhombic FE phase, orthorhombic FE phase-tetragonal FE phase-cubic paraelectric (PE) phase transitions change from 183K, 278K and 393K to 100.0K, 275.8K and 353.2K, respectively. The dielectric response peaks appeared at 353.2K become broader accompanied by slight frequency dispersion as compared to pure BT ceramics. However, the dielectric constant above T_C can be fitted well by Curie law in the temperature range 354-430K. Such character indicates that the structural phase transition is a first-order FE phase transition, which is confirmed by dielectric thermal hysteresis since thermal hysteresis is apparent in the temperature range 350-390K with ΔT=3K. The change of the phase transition character can be attributed to compositional fluctuation and/or structural disorder introduced by chemical modification, which leads to mi-

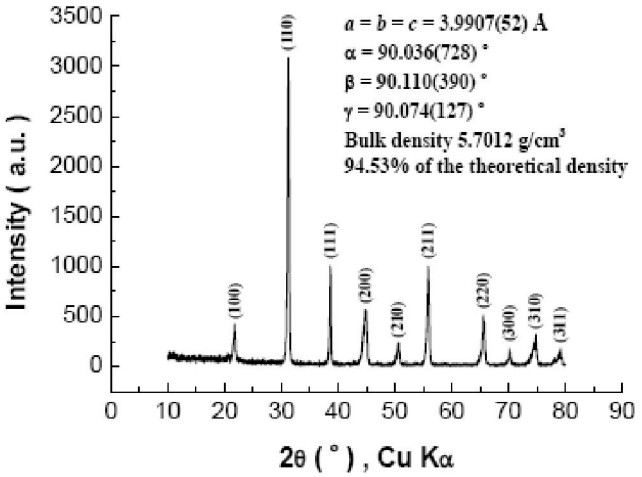

Figure 1 : XRD pattern of the BLKT ceramics sintered at 1300°C for 2h

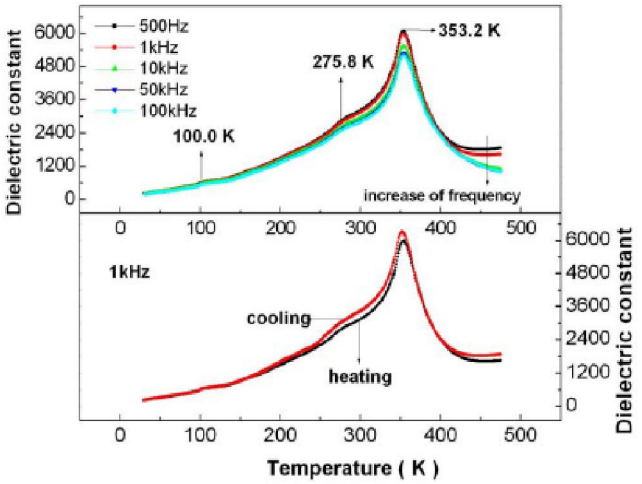

Figure 2 : Temperature dependence of dielectric constant of the BLKT ceramics measured at several frequencies upon heating

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croscopic chemical heterogeneity and defect creation[8].

Figure 3 shows P-E hysteresis behavior of the BLKT ceramics at various frequencies. Frequency relaxation in remanent polarization (P_r) is pronounced for an ac drive field level of 2kV/mm, where the P_r magnitude decreases from 5.74μC/cm^2 at 1Hz to 2.28μC/cm^2 at 10Hz. Combined with the phenomena of dielectric frequency dispersion around T_{max} and the slight diffused phase transition, the BLKT ceramics exhibit slight relaxor nature similar to that reported in perovskite-based relaxor solid solutions. The origin of relaxor behavior can be attributed to the development of a quenched random field associated with the compositional/structural disorder. In the BLKT ceramics, the ordering in the A-site position of the perovskite structure is related to the chemical heterogeneity introduced by ionic doping. With the decrease of temperature, correlated polar clusters nucleate but cannot induce long-range ferroelectric ordering. If the magnitude of random field is sufficient to overcome the long-range ferroelectric interactions, polar clusters will dominate the relaxor process. Accordingly, the relaxor behavior is a reflection of underlying cation ordering resulting in the formation of local random field[9,10].

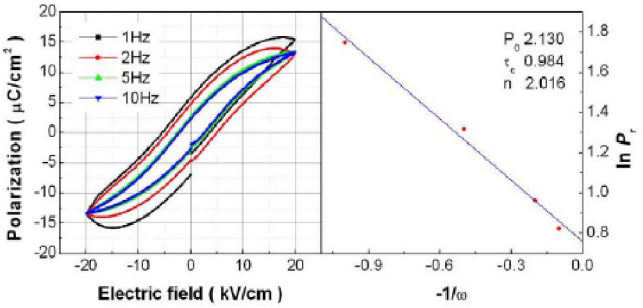

Figure 3 : P-E hysteresis loops of the BLKT ceramics taken at maximum a.c. electric drive field of 2kV/mm. The frequency dependence of remanent polarization determined from the hysteresis loops at 2kV/mm is shown in the right plot. The data are fitted using Eq. (1) and the fitting parameters are shown in the plot

The frequency dependence of P_r can be modeled by using the existing model of random field states:

$$P_r(\varpi) = P_0 \exp(-1/\tau_c)^{1-n} \quad (1)$$

where ϖ is frequency, τ_c is a characteristic relaxation time and n is an exponent. The data shown in Figure 3 are analyzed using Eq. (1) and the fit pattern is plotted and the fitting parameters are shown in the plot. A good correlation between the experimental data and the random field model can be seen in Figure 3. Accordingly, when electric drive is greater than coercive field (E_c), the elimination of irregularity occurs, which results in the complete switching of the remanent polarization.

Figure 4 shows polarization behavior of the BLKT ceramics. At room temperature, due to the La and K co-dopings, remanent polarization (P_r) and coercive field are slight less than those of the pure BT ceramics. With the increase of temperature, the hysteresis loops become narrower accompanied by the decrease of P_r and E_c since thermal oscillations increase as temperature increases, which results in the decrease of polarizability due to the sharpness of the anharmonic terms[11] and domain walls reorient easily at elevated temperatures. Polarization decreases sharply between 388K and 393K, which is larger than the pseudo-cubic FE-cubic PE phase transition determined by dielectric measurement. The existence of polarization above the Curie temperature indicates that FE phase clusters remain to some extent. At 398K no hysteresis remains and ε′ is single valued at a value characteristic of the PE phase.

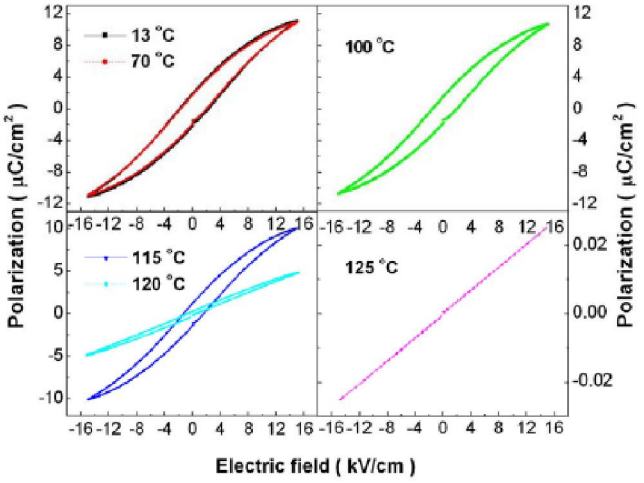

Figure 4 : P-E hysteresis loops of the BLKT ceramics measured at different temperatures

The value of piezoelectric constant d_{33} is 138-165pC/N within a disk sample, which is comparable to that of the pure BT ceramics. The variation of d_{33} value within a pellet is an ordinary phenomenon in ferroelectrics, which can be attributed to the inhomogeneity of composition and/or the existence of micropolar regions.

CONCLUSIONS

Pure perovskite BLKT ceramics were prepared by conventional mixed oxide method. Due to the La and K co-dopings, the BLKT ceramics exist in pseudo-cubic structure at room-temperature. Furthermore, the value of ε_m and the temperatures of ferroelectric phase transitions decrease accompanied by slight dielectric frequency dispersion of the BLKT ceramics as compared to the pure BT ceramics. The relaxor behavior was confirmed by studying dielectric and polarization relaxation, which can be scaled well with the random field states model. The relaxor behavior arises by the creation of chemical, compositional and structural heterogeneity induced by localized cationic ordering. Piezoelectric constant of the BLKT ceramics is comparable to that of the pure BT ceramics, which is promising lead-free piezoelectric material.

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