J Electroceram (2007) 18:9–12
DOI 10.1007/s10832-007-9002-0

Dielectric and piezoelectric properties of La_2O_3 doped $(Bi_{0.5}Na_{0.5})_{0.92}(Ba_{0.8}Sr_{0.2})_{0.08}$ TiO_3 lead-free piezoelectric ceramics

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Received: 26 July 2006 / Accepted: 16 January 2007 / Published online: 8 February 2007

Abstract Lead-free piezoelectric ceramics $(Bi_{0.5}Na_{0.5})_{0.92}$ $(Ba_{0.8}Sr_{0.2})_{0.08}$ TiO_3+x mol% La_2O_3(x=0, 0.1, 0.3, 0.5, 0.8) were synthesized by conventional solid state reaction. The crystal structure of all compositions is mono-perovskite ascertained by XRD. The grain size decreased and diffuse phase transition behavior was more evident with the increasing amount of La_2O_3. The piezoelectric constant d_{33} and the electromechanical coupling factor k_p showed the maximum value of 165 pC/N and 0.322 at 0.3% and 0.1% La_2O_3 addition, respectively, and rapidly decreased when La_2O_3 addition over 0.5%. The loss tangent tanδ linearly increased and the mechanical quality factor Q_m linearly decreased with the increasing amount of La_2O_3.

Keywords Piezoelectric ceramics · Lead-free · Perovskite structure · Dielectric properties

1 Introduction

The piezoelectric properties play an important role for electronics and mechatronics materials. The most widely used piezoelectric materials are Pb(Zr, Ti)O_3(PZT)-based three component system. However, volatilization of toxic PbO during high temperature sintering not only causes environmental pollution but also generates unstability of composition and electrical properties of products. Therefore, it is necessary to develop environment-friendly lead-free piezoelectric ceramics to replace PZT based ceramics.

Bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$, abbreviate as BNT), discovered by Smolensky et al. in 1960, is one of important lead-free piezoelectric materials with perovskite structure [1]. As BNT shows a strong ferroelectricity and high Curie temperature Tc=320°C, it has been considered to be a promising candidate of lead-free piezoelectric materials to replace the widely used piezoelectric ceramics. However, this ceramic has drawbacks such as high conductivity and large coercive field of 73 kv/cm, to cause problems in poling process. As a result of those, a lot of work to modify and improve piezoelectric properties of BNT ceramics have been done by substitution of $BaTiO_3$, $K_{0.5}Bi_{0.5}TiO_3$, $NaNbO_3$ [2–4]. Among them, it was known that $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$(abbreviate as BNBT) system ceramics with morphotropic tetragonal-rhombothedral phase boundary (abbreviate as MPB) showed excellent piezoelectric properties. The further enhancement on the piezoelectric properties of BNBT system ceramics by substitution and addition of $SrTiO_3$, La_2O_3, Co_2O_3, Nb_2O_5, $MnCO_3$ is reported by Li et al. [5–8].

Our preliminary research results showed that the composition of $(Bi_{0.5}Na_{0.5})_{0.92}(Ba_{0.8}Sr_{0.2})_{0.08}TiO_3$(abbreviate as BNBST) had excellent electrical properties. Therefore, in this paper, the composition of $(Bi_{0.5}Na_{0.5})_{0.92}$ $(Ba_{0.8}Sr_{0.2})_{0.08}TiO_3$ was selected as a base composition. The purpose of this paper is to present the effect of La_2O_3 addition on improving the electrical properties of the composition ceramic. The effect of La_2O_3 on microstructure, diffuse phase transition behavior were also investigated.

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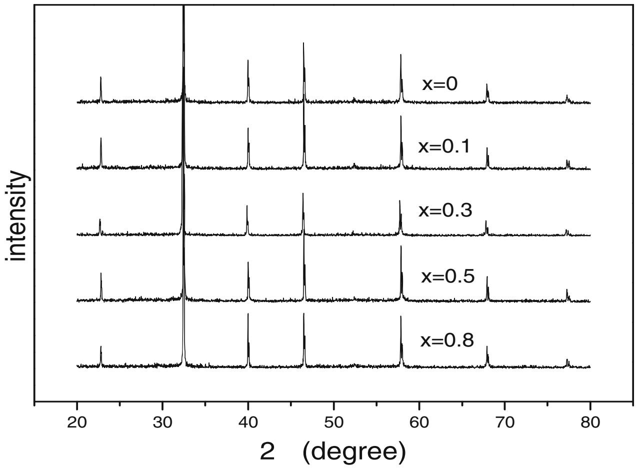

Fig. 1 XRD pattern of sintered samples

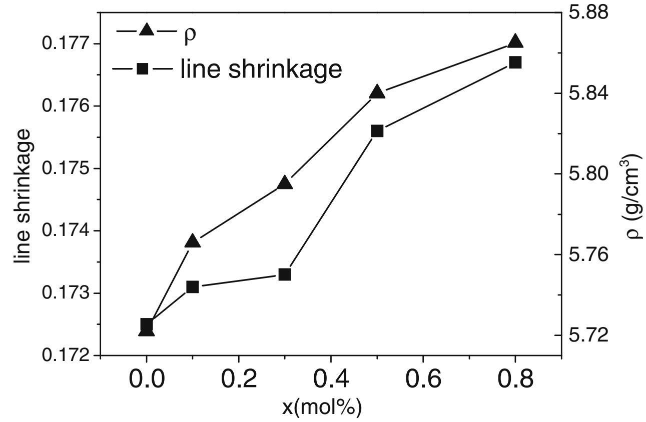

Fig. 3 Line shrinkage and density of BNBST ceramics as a function of La_2O_3 concentration x

2 Experimental procedure

The $(Bi_{0.5}Na_{0.5})_{0.92}(Ba_{0.8}Sr_{0.2})_{0.08}TiO_3$+xmol% La_2O_3(x=0, 0.1, 0.3, 0.5, 0.8) ceramics were prepared by the conventional ceramic fabrication technique. Bi_2O_3, Na_2CO_3, TiO_2, $SrCO_3$, and La_2O_3 with the purity of over 99.5% were used as starting materials. The powders were ball-milled for 12 h and calcined at 900°C for 2 h. After calcinations, the mixture was ball-milled for 24 h, dried and granulated with PVA as a binder. The granulated powders were pressed into

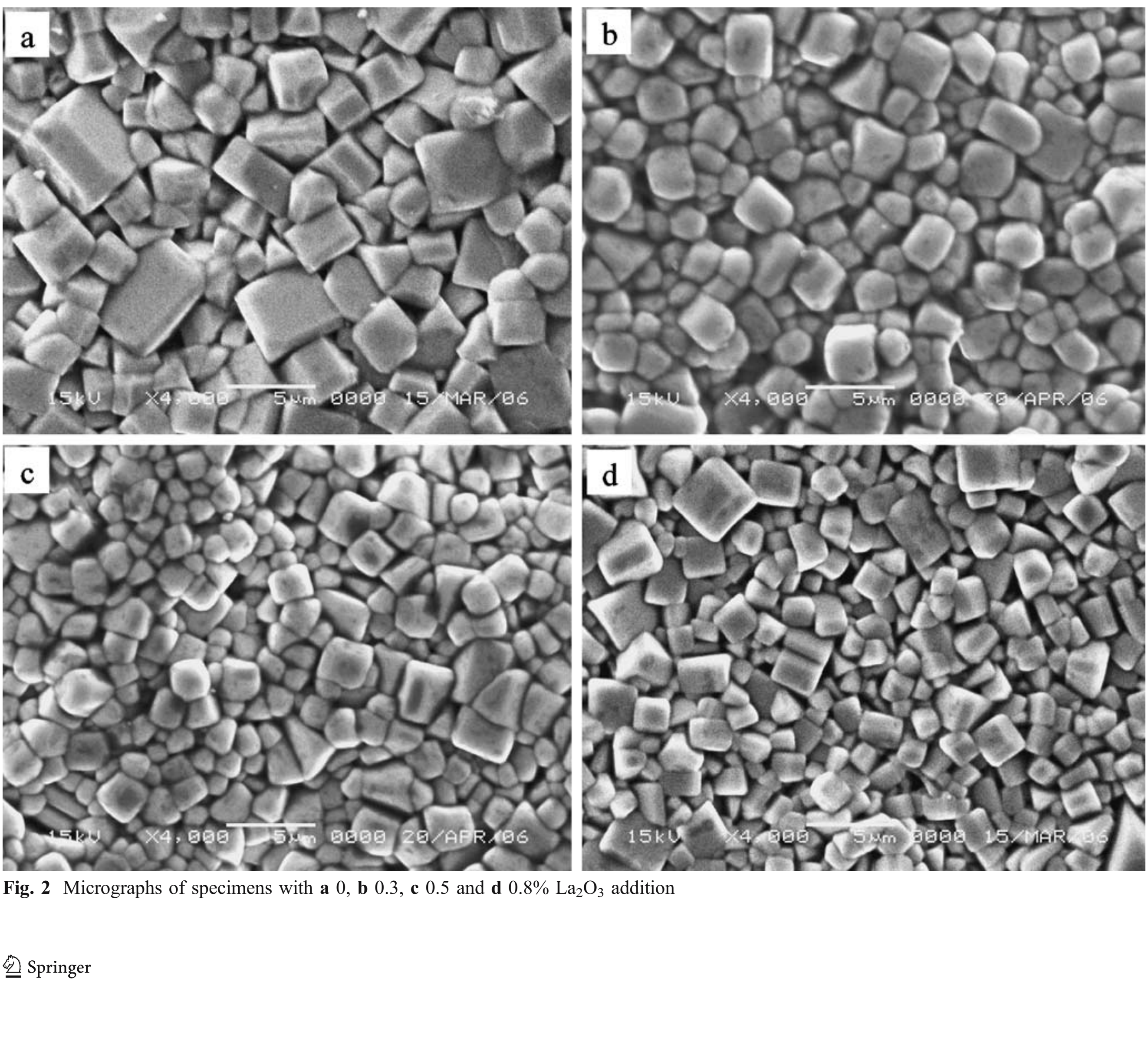

Fig. 2 Micrographs of specimens with **a** 0, **b** 0.3, **c** 0.5 and **d** 0.8% La_2O_3 addition

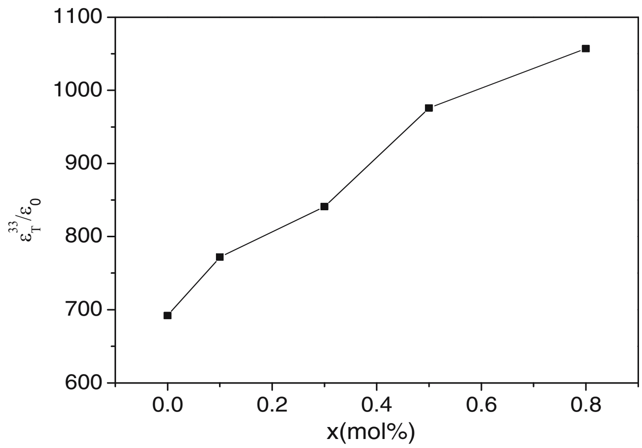

Fig. 4 Dielectric constant $\varepsilon_{33}^{T}/\varepsilon_0$ of BNBST ceramics as a function of La_2O_3 concentration x

disc with diameter 18 mm and thickness 1.2 mm. The compacted discs were sintered at 1,190°C for 2 h in air. Silver paste was fired on both faces of the discs at 650°C for 30 min as electrodes. The specimen with dimension Φ14.6×1.0 mm for measurement of piezoelectric properties was poled in silicon oil at 80°C under 4 kv/mm for

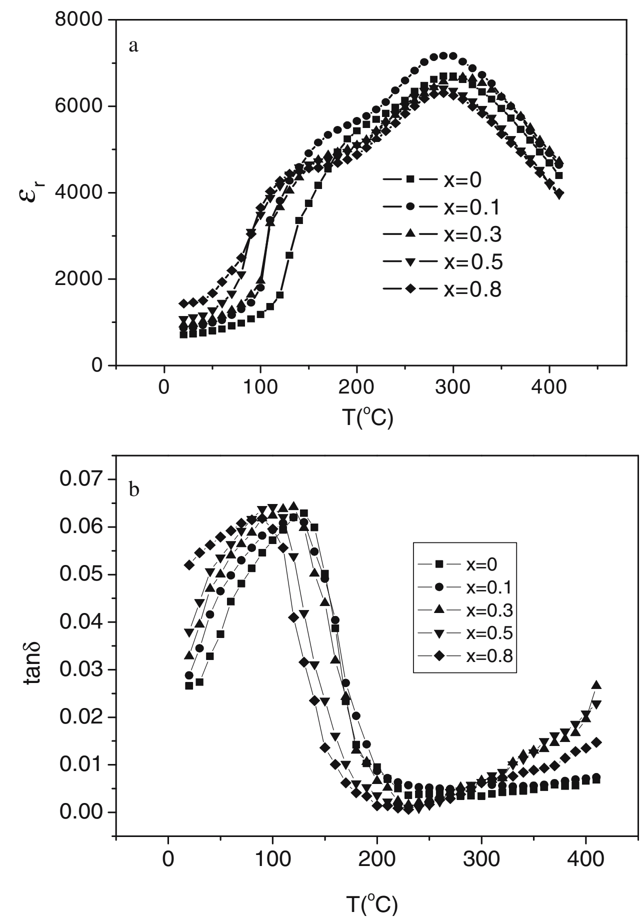

Fig. 5 Temperature dependence of dielectric constant ε_r (**a**) and dissipation factor tanδ (**b**) of BNBST ceramics as a function of La_2O_3 concentration x

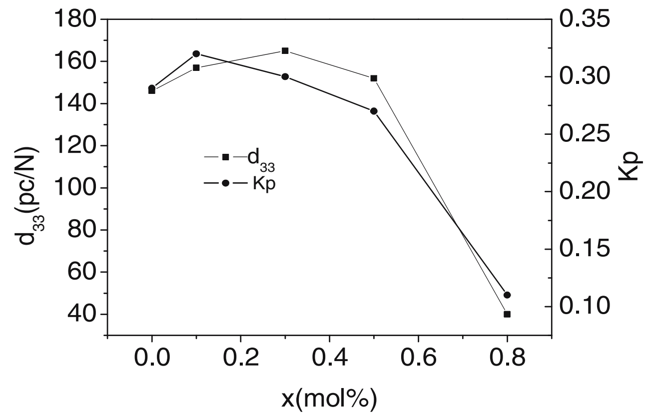

Fig. 6 Piezoelectric constant d_{33} and electromechanical coupling factor k_p of BNBST ceramics as a function of La_2O_3 concentration x

15 min. After 24 h, piezoelectric properties were measured using an impedance analyzer (Agilent 4294A) by resonant and anti-resonant method, and microstructure and crystal structure were measured by SEM(JSM-5610LV) and X-ray diffractometer (Bruker D8-Advance), respectively. Piezoelectric constant d_{33} was measured using a d_{33} meter (ZJ-3A) and the temperature dependence of dielectric constant and dissipation factor were investigated using LCR meter (TH2818) in the temperature rang 20–410°C at 1 KHz.

3 Results and discussion

Figure 1 shows the X-ray diffraction patterns of sintered samples in the 2θ ranges 20–80°. A pure perovskite structure without any secondary impurity phases could be confirmed.

Figure 2 shows the microstructure of the fabricated samples. It can be seen that the average size of grain slightly decreased with the increasing amount of La_2O_3. It can be contributed to that some of the La^{3+} ions probably segregated at grain boundaries that would inhibit grain growth.

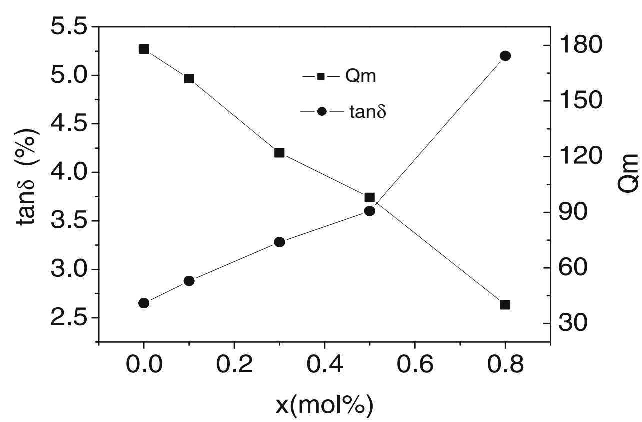

Fig. 7 Dissipation factor tanδ and mechanical quality factor Q_m of BNBST ceramics as a function of La_2O_3 concentration x

Figure 3 shows line shrinkage and density of BNBST ceramics as a function of the amount of La_2O_3. It can be seen from Fig. 3 that the line shrinkage and density of BNBST ceramics increased with the increasing amount of La_2O_3. It attributed to the addition of La_2O_3 significantly improves the sintering performance, and greatly assists in densification of the BNBST ceramics.

Figure 4 shows the dielectric constants $\varepsilon_{33}^{T}/\varepsilon_0$ at room temperature as a function of the amount of La_2O_3. It can be seen that the dielectric constants $\varepsilon_{33}^{T}/\varepsilon_0$ gradually increased with the increasing amount of La_2O_3.

Figure 5a and b show the temperature dependence of dielectric constants ε_r and dissipation factor tanδ of the ceramics as a function of the amount of La_2O_3 at 1 kHz. From the curves, it can be evidently seen that there are two abnormal dielectric peaks with the increasing temperature. The two dielectric peaks can attribute to the reason caused by the phase transitions from ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric phase, which is consistent with the previous reports of NBT, NBT-BT, NBT-KBT lead-free ceramics system [2–5]. Here, the temperature where the transition between ferroelectric phase and anti-ferroelectric phase is called as depolarization temperature (T_d) and the temperature corresponding to maximum value of dielectric constant is named as maximum temperature (T_m) [6]. It is evident that T_d decreased with the increasing amount of La_2O_3 addition. That is because the La_2O_3 additives in BNBST composition cause vacancies and lattice deformation, and they facilitate the domain movement leading to decreasing T_d.

It can be also found from Fig. 5 that all samples have diffuse phase transition behavior with broad peaks. The diffuse phase transition behavior of specimens became more evident with increasing content of La_2O_3. It mainly attributed to the increase of the cations disorder degree induced by La_2O_3 doped [6–11].

The dissipation factor tanδ as a function of temperature shown in Fig. 5b indicates that all specimens only have one dielectric loss peak corresponding to T_d. In ferroelectric phase, the dissipation factor probably comes from domain wall movement. When phase transition from ferroelectric to anti-ferroelectric which corresponds with macro-domain break into micro-domains occurred at T_d, the domain wall movement enhancement brings to the dissipation factor peak. Above T_m, the sharp dissipation factor increase was caused by the high conductivity of ceramics at high temperature [6, 10].

The piezoelectric constant d_{33} and the electromechanical coupling factor k_p as a function of the amount of La_2O_3 are showed in Fig. 6. The piezoelectric constant d_{33} and the electromechanical coupling factor k_p first increased and then decreased as La_2O_3 concentration increased, showed the maximum value of 165 pC/N and 0.322 at 0.3 and 0.1% La_2O_3 addition, respectively.

The dissipation factor tanδ and mechanical quality factor Q_m as a function of the amount of La_2O_3 are showed in Fig. 7. With increasing amount of La_2O_3, the dissipation factor tanδ linearly increased and mechanical quality factor Q_m linearly decreased. It seemed that these results were caused by La^{3+} ion (radius is 1.06 Å) substitution at Na^+ (radius is 0.97 Å) site of BNBST perovskite structure ceramics. The piezoelectric constant d_{33}, the electromechanical coupling factor k_p and the dissipation factor tanδ increased and mechanical quality factor Q_m decreased because softer effect of La_2O_3 doped [10, 11]. And it seemed that the decreased of kp were the decrease of polarization efficiency resulted from the weakness of ferroelectricity when the amount of La_2O_3 addition over 0.3 mol% [12].

4 Conclusion

The $(Bi_{0.5}Na_{0.5})_{0.92}(Ba_{0.8}Sr_{0.2})_{0.08}$ TiO_3 +x mol%La_2O_3(x= 0, 0.1, 0.3, 0.5, 0.8) ceramics were fabricated and their dielectric, piezoelectric properties were investigated. All samples exhibited single phase with perovskite structure without detectable secondary phase. The grain size decreased and the diffuse phase transition behavior was more evident with the increasing amount of La_2O_3. The piezoelectric constant d_{33} and the electromechanical coupling factor k_p showed the maximum value of 165 pC/N and 0.322 at 0.3 and 0.1% La_2O_3 addition, respectively, and rapidly decreased when La_2O_3 addition over 0.5%. The loss tangent tanδ linearly increased and the mechanical quality factor Q_m linearly decreased with the increasing amount of La_2O_3.

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