

Dielectric and piezoelectric properties of $\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3\text{--LiSbO}_3$ lead-free piezoelectric ceramics

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Abstract. The $(1-x)\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3\text{--}x\text{LiSbO}_3$ ($x = 0\text{--}0.03$) lead-free piezoelectric ceramics were fabricated by a conventional solid-state reaction method and the effect of LiSbO_3 addition on microstructure and electrical properties of the ceramics was investigated. The results of XRD measurement show that Li^+ and Sb^{5+} diffuse into the $\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3$ lattices to form a solid solution with a pure perovskite structure. The LiSbO_3 addition has no remarkable effect on the crystal structure. However, a significant change in grain size took place. Simultaneously, with increasing amount of LiSbO_3 , the temperature for an antiferroelectric to paraelectric phase transition clearly increases. The piezoelectric constant d_{33} and the electromechanical coupling factor k_p show an obvious improvement by adding small amount of LiSbO_3 , which shows optimum values of $d_{33} = 175$ pC/N and $k_p = 0.36$ at $x = 0.01$.

Keywords. Lead-free piezoelectric ceramics; ferroelectrics; perovskites structure; dielectric constant.

1. Introduction

Lead-free piezoelectric ceramics for replacing $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT)-based ceramics have recently become essential from the viewpoint of environmental protection. Therefore, recently various lead-free piezoelectric solid solutions, such as $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (abbreviated as BNT)-based materials (Xu *et al* 2008), Bi-layered structure materials (Noguchi *et al* 2008), tungsten bronze-type materials (Xie *et al* 2003), BaTiO_3 (abbreviated as BT)-based ceramics (Hiruma *et al* 2004), and alkaline niobate-based materials have been extensively investigated (Guo *et al* 2004). Among the solid solutions that have been developed so far, $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (abbreviated as BNKT) system has attracted considerable attention because of the existence of rhombohedral–tetragonal morphotropic phase boundary (MPB) near $x = 0.18$ (Zhou *et al* 2008).

However, the piezoelectric properties of this system are not good enough for most practical uses. In order to further enhance the properties of BNT-related ceramics and meet the requirements for practical uses, it is necessary to develop new BNT-based ceramics. It has been demonstrated that a ternary system is favourable to improving piezoelectric and ferroelectric properties (Lin *et al* 2008). Moreover, it was reported that introduction of

LiSbO_3 into the $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ solid solution could increase evidently the electrical properties (Lin *et al* 2007). Therefore, in this article, $0.82\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.18\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ was selected as a representative of MPB compositions in the $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ system, and LiSbO_3 was selected as the third component. A new perovskite type lead-free piezoelectric ceramics of $(1-x)\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3\text{--}x\text{LiSbO}_3$ was prepared by a conventional ceramic technique and effect of LiSbO_3 addition on the microstructure, dielectric behaviour, and piezoelectric responses was investigated.

2. Experimental

A conventional mixed oxide route was utilized to prepare $(1-x)\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3\text{--}x\text{LiSbO}_3$ (BNKT–LSx) ceramics ($x = 0, 0.5\%, 1\%, 2\%$ and 3%). Reagent grade oxide or carbonate powders of Bi_2O_3 , TiO_2 , Sb_2O_3 , K_2CO_3 , Li_2CO_3 and Na_2CO_3 were used as starting materials. The powders were ball-milled for 12 h and calcined at $800\text{--}900^\circ\text{C}$ for 2 h. After calcination, the mixture was ball-milled for 24 h, dried and granulated with PVA as a binder. The granulated powders were pressed into discs with diameter 18 mm and thickness 1.2 mm. The compacted discs were sintered at $1070\text{--}1100^\circ\text{C}$ for 2 h in air. Silver paste was fired on both faces of the discs at 650°C as electrodes. The specimens for measurement of piezoelectric properties were poled in silicon oil at $40\text{--}50^\circ\text{C}$ under $3\text{--}4$ kV/mm for 15 min.

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The crystalline phase of sintered ceramics was identified by the X-ray diffractometer (Bruker D8-Advance) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and graphite monochromator. The microstructure of sintered samples was observed by a scanning electron microscope (JSM-5610LV). Piezoelectric properties were measured using an impedance analyzer (Agilent 4294A) by the resonant and anti-resonant method. Piezoelectric constant d_{33} was measured by means of a quasi-static d_{33} meter (ZJ-3A, China) based on the Berlincourt method at 110 Hz. The dielectric properties were investigated using an impedance analyser (Agilent 4294A) in the temperature range of 30–500°C at 1 kHz.

3. Results and discussion

The XRD diffraction patterns of BNKT-LS x compositions are shown in figure 1. It can be seen that a single-phase perovskite structure was formed in the ceramics. The results suggest that Li^+ and Sb^{5+} have diffused into the BNKT lattices, with Li^+ entering the $(\text{Na}_{0.82}\text{K}_{0.18})^+$ sites and Sb^{5+} occupying the Ti^{4+} sites, to form a homogeneous solid solution and no secondary phase can be found with the sensitivity of XRD.

Figure 2 shows the scanning electron microscopy (SEM) micrographs of BNKT-LS x ceramics modified with different concentrations of LiSbO_3 sintered at 1100°C. It can be observed that all samples have a square grain shape and distinct pores appear in the sample with $x = 0$. The samples with $x > 0$ have dense microstructures, and the grain size increases as LiSbO_3 content increases. The Archimedes method gives a relative density of more than 96% of the theoretical values for samples with $x > 0$. It is clearly seen that the addition of LiSbO_3 can assist the

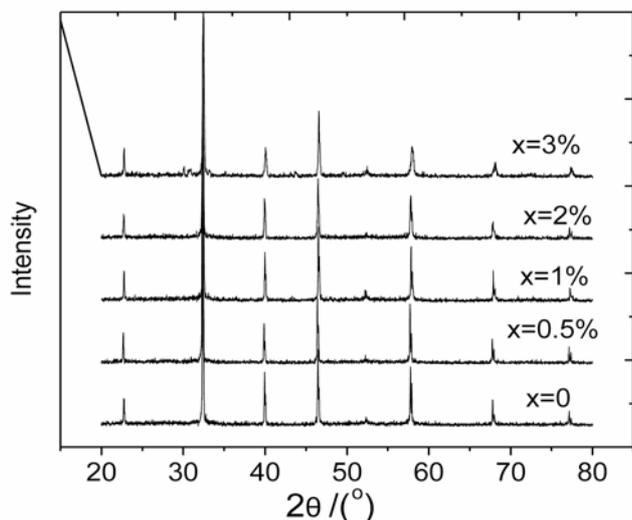


Figure 1. XRD pattern of BNKT-LS x ceramics with various amounts of LiSbO_3 .

densification of the BNKT ceramics and thus improves the sintering performance of the ceramics. Although the sintering temperature decreases with increasing the concentration of LiSbO_3 , the grain size increases and the ceramics become denser and can be sintered more easily. This may be attributed to the low melting temperature of Li compounds that appears to promote the formation of a liquid phase during sintering. The ceramics can be well sintered at 1070–1130°C, which is about 200°C lower than the sintering temperature for PZT ceramics.

Figure 3 shows the temperature dependence of dielectric constants ϵ_r of the ceramics as a function of the amount of LiSbO_3 at 1 kHz. The curves for different samples look similar, all exhibiting two two-phase transitions at T_f and T_m . The two dielectric peaks can attribute to the reason caused by the phase transitions from ferroelectric to anti-ferroelectric (T_f) and anti-ferroelectric to paraelectric phase (T_m), which is consistent with the previous reports of BNT-BKT-BT and BNT-BKT lead-free ceramics system (Nagata *et al* 2001; Li *et al* 2005a, b; Song *et al* 2006; Hiruma *et al* 2008). This feature intrinsically comes from pure BNT which was reported to have a diffuse structural phase transition from rhombohedral ferroelectrics to tetragonal antiferroelectrics at $\sim 200^\circ\text{C}$ and a Curie phase transition from the antiferroelectric to paraelectric phases at $\sim 320^\circ\text{C}$ (Smolenski *et al* 1961). BNKT-LS x ceramics may show similar phase transition behaviour. However, a clear difference was made by LiSbO_3 addition. First of all, with more LiSbO_3 addition, the dielectric maximum values become significantly lower. It is $\sim 11,000$ for BNKT-LS0 and only 3080 for BNKT-LS0.03 ceramic. Accordingly, the curves become flatter and the dielectric constants show lower and lower temperature dependence. LiSbO_3 seems to act as a suppressor. Secondly, the temperature for the second phase transition gradually shifts to higher temperature with LiSbO_3 addition. However, the first phase transition temperature seems to change little. This implies that LiSbO_3 addition makes the antiferroelectric zone larger and more stable.

Figure 4 shows the variation of piezoelectric constant d_{33} and the planar electromechanical coupling factor k_p as a function of the content of LiSbO_3 for BNKT-LS x ceramics. With the small addition, LiSbO_3 addition can increase d_{33} and k_p .

When the LiSbO_3 addition reaches 0.01, the best piezoelectric properties are realized: $d_{33} = 175 \text{ pC/N}$ and $k_p = 0.36$. However, further increase of LiSbO_3 addition worsen the piezoelectric properties of BNKT-LS x ceramics as can be seen in figure 4.

Generally, the piezoelectric properties of a piezoelectric ceramics are determined by the microstructure and the phase structure. Generally, Sb^{5+} ion prefers entering into the oxygenic octahedral centre of perovskite system substituting the B-site Ti^{4+} ions and Li^+ ion entering into A-site substituting the A-site $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ ions because

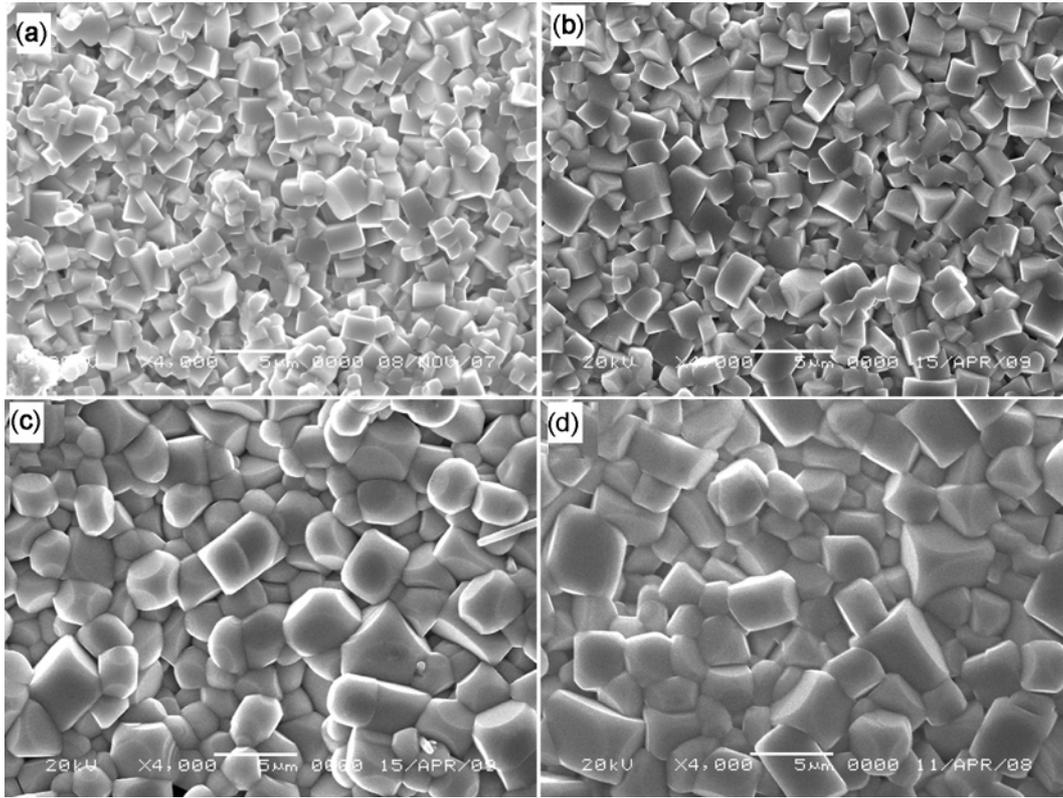


Figure 2. SEM images of BNKT-L x ceramics with various amounts of LiSbO $_3$: (a) $x = 0$, (b) $x = 1\%$, (c) $x = 2\%$ and (d) $x = 3\%$.

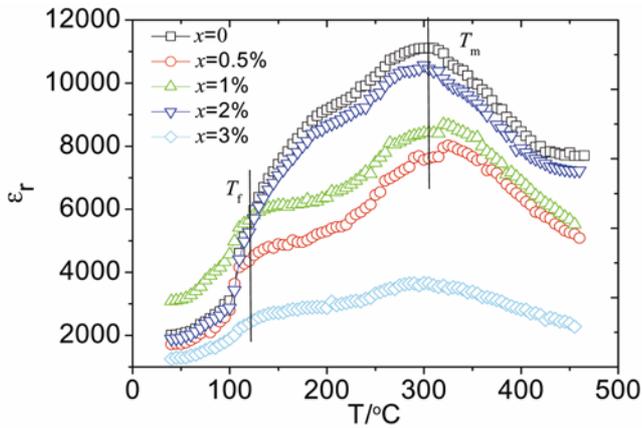


Figure 3. Temperature dependence of dielectric constants ϵ_r at 1 kHz for BNKT-L x ceramics.

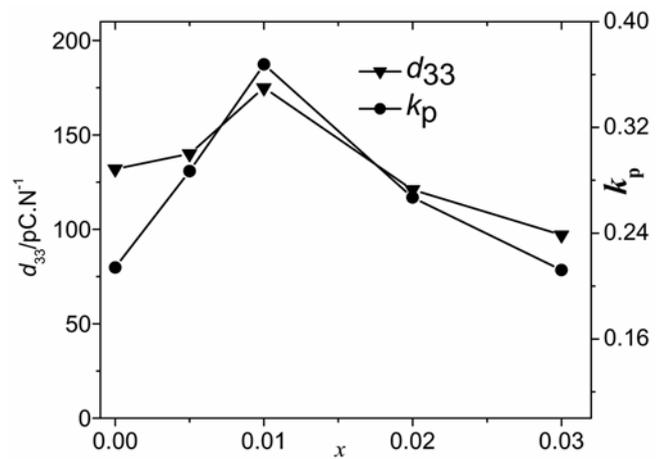


Figure 4. Piezoelectric constant d_{33} and planar electromechanical coupling factor k_p of the BNKT-L x ceramics as a function of LiSbO $_3$ concentration.

the radius of Sb^{5+} ion (0.62 \AA) and Li^+ ion (0.76 \AA) is close to that of Ti^{4+} (0.61 \AA) and $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ (1.28 \AA). The substitution of Ti^{4+} by Sb^{5+} will create an A-site vacancy and the substitution of $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ by Li^+ will create oxygen vacancies because of the imbalance of ion valence. For small addition of LiSbO $_3$, the increase of grain size is beneficial for the improvement of d_{33} (Zhu *et al* 2007). On the other hand, the creation of A-site vacancy induced by Sb^{5+} into the crystal lattice will

facilitate the movement of the ferroelectric domain and results in an increase of piezoelectric properties. The co-operation effect of grain size and the creation of A-site vacancy lead to an improvement in d_{33} and k_p . However, a large amount of addition of LiSbO $_3$ leads to drastic worsening of piezoelectric properties, which can be attributed to the clamping effect associated with oxygen vacancies

induced by Li^+ into the crystal lattice. The clamping effect pins the domain movement, which is considered to be responsible for the decrease of d_{33} and k_p .

4. Conclusions

Lead-free piezoelectric ceramics BNKT-LS x was prepared by a conventional ceramic technique. The crystal-line structure has no obvious change with minor LiSbO_3 additive and grain size increases obviously with increasing content of LiSbO_3 . The temperature dependence of dielectric properties suggests that the ceramics exhibit two two-phase transitions. The piezoelectric properties increase with trace LiSbO_3 addition and the optimum piezoelectric properties of $d_{33} = 175$ pC/N and $k_p = 0.36$ are obtained at $x = 0.01$.

Acknowledgements

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