Materials and Design 136 (2017) 119–126

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Composition design and electrical properties of $(K_{0.48}Na_{0.52})NbO_3$-$x$$LiSbO_3\}$-$y\{(Bi_{0.5}Na_{0.5})(Zr_{1\text{-}z}Sn_z)O_3\}$ ceramics

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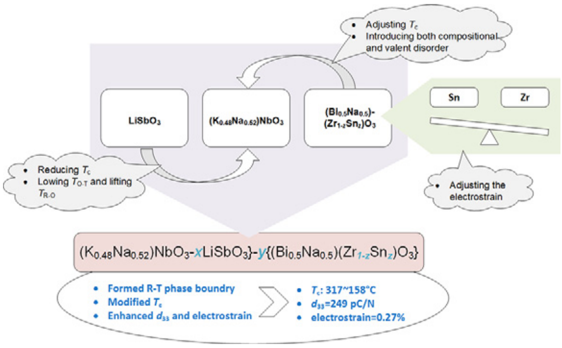
HIGHLIGHT

- A new KNN ceramics system with Tc from 158 °C to 317 °C and multi-phase coexistence at room temperature.
- Large electrostrain with d_{33}* of 675 pm/V which even rival that of 250 pm/V from hard-PZT ceramics.
- Large d_{33} of 249 pC/N, the large planar coupling factor k_p of 37.3% and high Curie temperature of 271 °C were achieved.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 March 2017
Received in revised form 15 September 2017
Accepted 18 September 2017
Available online 23 September 2017

Keywords:
Piezoelectric ceramics
Lead-free
Ferroelectrics
Electrostrain
Potassium sodium niobate

ABSTRACT

In the present study, we designed a new system, $(K_{0.48}$Na0.5$_2)NbO_3$-$x$$LiSbO_3\}$-$y\{(Bi_{0.5}Na_{0.5})(Zr_1$-$zSnz)O_3\}$ and systemically investigated both the piezoelectric performance under weak field and the electrostrain under large electric field. Here the isovalent additive $LiSbO_3$ (LS) was employed to pinch the three ferroelectric phases together, while the aliovalent dopant $(Bi_{0.5}Na_{0.5})(Zr_{0.8}Sn_{0.2})O_3$ (BNZS) was introduced to further lower the Curie temperature (T_c). The enhanced piezoelectric properties were achieved by pinching the phases with different symmetries together; hereinto the ceramic with LS content of 0.05 and BNZS content of 0.03 exhibited large piezoelectric coefficient (d_{33}) of 249pC/N. Besides the high piezoelectric performance under weak field, the present ceramics also exhibited large electrostrain under large electric field, ascribing to the Zr^{4+} and Sn^{4+} in BNZS. The electrostrain reached 0.27% under the electric field of 4 kV/mm (with the converse piezoelectric coefficient d_{33}* of 675 pm/V), even superior to the widely used hard PZT.

1. Introduction

For over half a century lead based piezoelectric ceramics, represented by $Pb(Zr, Ti)O_3$ (PZT), has played an important role in many devices like sensors, transducers, actuators, and so on [1–3]. However, lead, the main element in PZT, is toxic and threatens environment and human health. Therefore lots of efforts have been made on developing the lead-free piezoelectric substitutes, such as $BaTiO_3$ based, $(K,Na)NbO_3$ (KNN) based, $(Bi,Na)TiO_3$ based ceramics, and etc. [4–14]. Among them, KNN based ceramics have manifested themselves as the most promising candidate, due to their moderate Curie temperature (>250 °C) and considerable piezoelectric performance with d_{33} of 200–550 pC/N [15–17].

Both in Pb-based and Pb-free piezoelectric systems, the common solution to achieve high piezoelectric performance is to place materials at their phase transition boundaries, either paraelectric to ferroelectric phase boundary or multi ferroelectric phases coexisting boundary (including the most famous morphotropic phase boundary, i.e. MPB),

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https://doi.org/10.1016/j.matdes.2017.09.036
0264-1275/

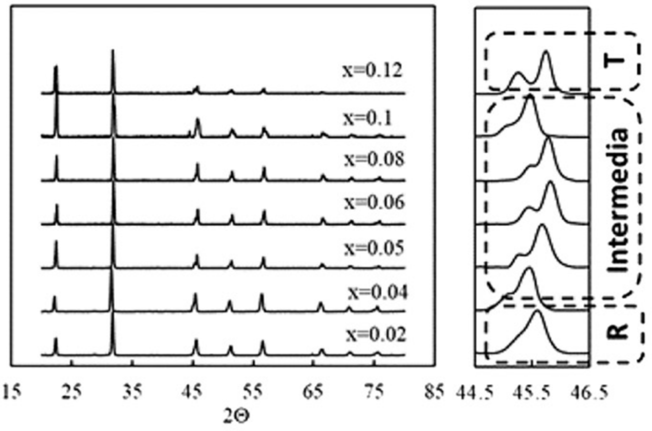
since the instability of the polarization at phase boundaries allows a significant polarization variation under an external stress or electric field. For KNN based ceramics, it is an effective way to enhance the piezoelectric performance by reaching multiphase coexistence at room temperature with the decrease of the transition temperature from tetragonal (T) to orthorhombic (O) phase while increase the transition temperature from rhombohedral (R) to O phase [6,18,19]. Extensive doping was employed to achieve the multiphase coexistence state (i.e. Li^+, Sb^{5+}, Ta^{5+}, $Bi_{0.5}Na_{0.5}ZrO_3$) [20–24]. Wu JG and his co-researchers have reported many promising results in recent years and their latest research work provided a high piezoelectric performance of d_{33} of 550 pC/N as well as a high T_c of 237 °C achieved in $(1–x–y)K_{1–w}Na_wNb_{1–z}Sb_zO_3–xBiFeO_3–yBi_{0.5}Na_{0.5}ZrO_3$ (KNwNSz-xBF-yBNZ) which showed large potential for senior applications [15].

Previous study pointed out that a T-O-R phase coexistence give totally flat polarization rotation energy landscape, while T-O or O-R single phase boundary has relatively large energy barriers. It is highly possible for $KNbO_3$ based ceramics, who has a T to O to R ferroelectric transition sequence originally. This can be achieved by doping. In the present study, we designed a new system, $(K_{0.48}Na_{0.52})NbO_3$-$x$$LiSbO_3$}-$y${$(Bi_{0.5}Na_{0.5})(Zr_{1-z}Sn_z)O_3$} and systemically investigated both piezoelectric performance under weak field and electrostrain under large electric field. Here $LiSbO_3$ was employed to lower the transition temperature from orthorhombic to tetragonal phase ($T_{O\text{-}T}$) and raise the transition temperature from rhombohedral to orthorhombic phase ($T_{R\text{-}O}$), i.e. to pinch the three ferroelectric phases together. Besides the inclusion of Li^+ would also contribute to sintering process and benefit the condensed ceramics [25–27]. This would give more polarization instabilities as well as phase similarities and consequently decrease the polarization anisotropy and energy barriers for both polarization rotation (intrinsic contribution) and domain wall motion (extrinsic contribution). On the other hand, we chose $(Bi_{0.5}Na_{0.5})(Zr_{0.8}Sn_{0.2})O_3$ as the aliovalent doping to lower the T_c [19,28,29]. According to the Landau theory of phase transition, when the temperature is close to T_c, the energy barrier for polarization switching decreases and may benefit the enhanced dielectric, ferroelectric and piezoelectric properties at room temperature. Besides, considering Zr^{4+} and Sn^{4+} could promote electrostrain [30,31], different ratio of Zr/Sn was designed for further investigation. The results demonstrated that the electric, ferroelectric and piezoelectric properties would be tailored by compositional design in the ternary materials system; hereinto good piezoelectric performance under both small field (with d_{33} of 249 pC/N) and large field (with electrostrain of 0.27% under 3 kV/mm) indicated the present system is very promising as the lead-free substitute.

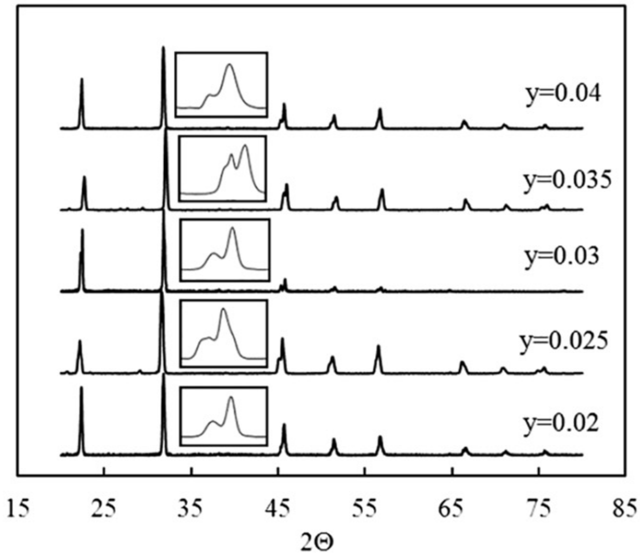
2. Samples and tests

The designed sample $(1\text{-}y)\{(1\text{-}x)(K_{0.48}Na_{0.52})NbO_3\text{-}xLiSbO_3\}\text{-}y\{(Bi_{0.5}Na_{0.5})(Zr_{1\text{-}z}Sn_z)O_3\}$ (abbreviated as of KNN-xLS-y(BNZ$_1$-zSz)) were fabricated by the conventional solid state reaction method. To reveal the effect of each dopant respectively, three groups of the ceramics were designed. In group-1, the LS content (x) was set as 0.02, 0.04, 0.05, 0.06, 0.08, 0.1 and 0.2, while the BNZS content (y) was fixed to 0.04 and the Sn^{4+} content (z) in BNZS was fixed to 0.2. In group-2, the BNZS content (y) was set as 0.02, 0.025, 0.03, 0.035 and 0.04, while the LS content (x) was fixed to 0.05 and the Sn^{4+} content (z) in BNZS was fixed to 0.2. In group-3, the Sn^{4+} content (z) in BNZS was set as 0, 0.1, 0.2, 0.3 and 0.5, while the LS content (x) was fixed to 0.05 and the BNZS content (y) was fixed to 0.04.

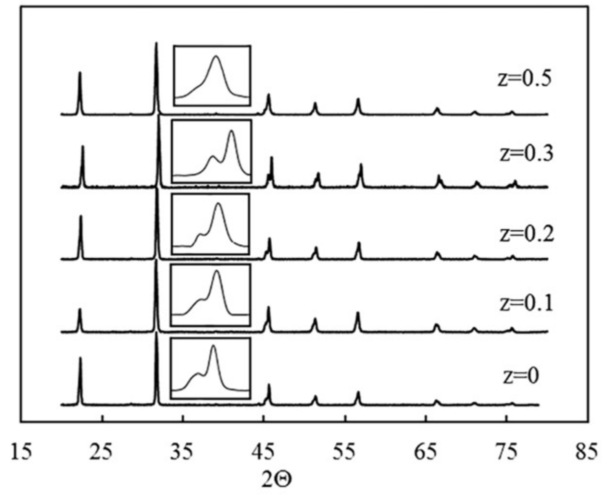
Raw materials of Na_2CO_3 (99.8%), K_2CO_3 (99%), Li_2CO_3 (99.9%), Sb_2O_5 (99.99%), Nb_2O_5 (99.5%), SnO_2 (99.9%), ZrO_2 (99%), and Bi_2O_3 (99.999%) were used here for the chemical reaction of $Na_2CO_3 + K_2CO_3 + Li_2CO_3 + Sb_2O_5 + Nb_2O_5 + SnO_2 + ZrO_2 + Bi_2O_3 \rightarrow (K_{0.48}Na_{0.52})NbO_3\text{-}xLiSbO_3\}\text{-}y\{(Bi_{0.5}Na_{0.5})(Zr_{1\text{-}z}Sn_z)O_3\}$. They were mixed according to the stoichiometric ratio and then ball milled by planetary mill for 4 h. After dried out, the mixed powder was calcined



a) XRD patterns of different $LiSbO_3$ concentration



b) XRD patterns of different BNZS concentration



c) XRD patterns of different Sn^{4+} concentration

Fig. 1. XRD patterns.