Journal of Alloys and Compounds 581 (2013) 446–451

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Letter

Enhanced d_{33} value in $(1-x)[(K_{0.50}Na_{0.50})_{0.97}Li_{0.03}Nb_{0.97}Sb_{0.03}O_3]-xBaZrO_3$ lead-free ceramics with an orthorhombic–rhombohedral phase boundary

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ARTICLE INFO

Article history:
Received 7 May 2013
Received in revised form 25 June 2013
Accepted 27 June 2013
Available online 16 July 2013

Keywords:
Lead-free piezoelectric
Rhombohedral–orthorhombic phase boundary
Piezoelectricity

ABSTRACT

In this work, the rhombohedral–orthorhombic (R–O) phase boundary and the composition-induced piezoelectric properties have been observed in the $(1-x)[(K_{0.50}Na_{0.50})_{0.97}Li_{0.03}Nb_{0.97}Sb_{0.03}O_3]-xBaZrO_3$ $[(1-x)KNLNS-xBZ]$ lead-free ceramics prepared by the conventional solid-state method. Effects of BZ content on the phase structure, microstructure, and electrical properties of $(1-x)KNLNS-xBZ$ ceramics are studied. The R–O phase coexistence is found in these ceramics with the compositional range of $0.04 \leqslant x \leqslant 0.06$, which is further confirmed by the XRD and the temperature dependence of the dielectric behavior. With increasing BZ content, their grains become smaller and much more uniform, the T_{O-T} and T_C drops, the remanent polarization decreases, and the dielectric constant increases. The ceramic with $x = 0.05$ has an enhanced piezoelectric behavior because of the involvement of R–O together with the addition of Li and Sb as well as a higher $\varepsilon_r P_r$, and an optimum electrical behavior of $d_{33} \sim 235$ pC/N, $k_p \sim 0.44$, $2P_r \sim 42.0\ \mu C/cm^2$, $2E_c \sim 27.6$ kV/cm, $\varepsilon_r \sim 1567$, tan $\delta \sim 3.3\%$, $T_C \sim 267$ °C, $T_{O-T} \sim 85$ °C, and $T_{R-O} \sim 5$ °C is observed in such a ceramic, showing the material system is a promising lead-free piezoelectric candidate.

1. Introduction

$(K,Na)NbO_3$ (KNN) lead-free piezoelectric ceramics endure some continuous phase transitions with increasing temperatures: rhombohedral to orthorhombic phase transition (T_{R-O}) at ∼−123 °C, orthorhombic to tetragonal transition (T_{O-T}) at ∼200 °C, and tetragonal to cubic transition (T_C) at ∼410 °C [1,2]. In the past, most researches have focused on the modification of the O–T phase transition in KNN-based ceramics for enhancing its piezoelectric properties, that is, the O–T phase boundary is shifted to be room temperature by doping some additives [3–12]. The R–O phase transition of a pure KNN ceramic is located at a very low temperature of ∼−123 °C, and thus such a phase boundary is always ignored [13–16]. Some additives (i.e., $LiNbO_3$, $LiTaO_3$, $LiSbO_3$, and etc.) can decrease the T_{O-T} to be room temperature [3–12,17,18], while the T_{R-O} is difficult to increase up to be room temperature by few additives [$CaZrO_3$, $BiBO_3$(Co, Fe, and Sc)] [13–16,19]. Some results also show that a low d_{33} value of <200 pC/N is always observed in KNN-based ceramics with an R–O phase boundary, as shown in Table 1. For example, Zuo et al. has reported that a morphotropic phase boundary between orthorhombic and rhombohedral phases is formed in the solid solution of $Na_{0.5}K_{0.5}NbO_3$ and $BiFeO_3$, and a low d_{33} value of ∼185 pC/N is induced [15]. Similar phenomena have also been demonstrated in the material systems of $Na_{0.5}K_{0.5}NbO_3$–$BiCoO_3$ and $(Na,K)(Nb,Sb)O_3$ with R–O [14,16]. Although the $Na_{0.5}K_{0.5}NbO_3$–$BiScO_3$ and $(Na,K)(Nb,Sb)O_3$ systems with R–O have a high d_{33} of 210 and 230 pC/N [13,14], respectively, an expensive Sc and a low T_c of ∼220 °C are inferior in such ceramics.

In this work, we hope to get a large d_{33} and a high T_c of KNN-based ceramics with R–O, and the $(1-x)[(K_{0.50}Na_{0.50})_{0.97}Li_{0.03}Nb_{0.97}Sb_{0.03}O_3]-xBaZrO_3$ $[(1-x)KNLNS-xBZ]$ material system without expensive elements is designed. Effects of BZ content on the phase structure, microstructure, and electrical properties of $(1-x)KNLNS-xBZ$ ceramics have been importantly studied, and the underlying physical mechanisms have been clearly illuminated.

2. Experimental procedure

$(1-x)KNLNS-xBZ$ (x = 0, 0.02, 0.03, 0.04, 0.05, 0.06, and 0.08) ceramics have been prepared by the normal sintering method, and the starting raw materials were Na_2CO_3 (99.5%), K_2CO_3 (99.0%), Nb_2O_5 (99.5%), Li_2CO_3 (99%), Sb_2O_3 (99%), $BaCO_3$ (99%), and ZrO_2 (99%). These weighed powders were ball mixed in a nylon jar with anhydrous ethanol as the medium, and these dried powders were calcined at 850 °C for 6 h. Subsequently, these calcined powders were ball milled again for 24 h in ethanol, and then were pressed in some disked samples with a diameter of ∼1.0 cm and a thickness of ∼1.0 mm. All samples were sintered in air in the temperature range of 1040–1130 °C for 3 h, and well sintered samples were obtained in the

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http://dx.doi.org/10.1016/j.jallcom.2013.06.165

Table 1
Piezoelectric properties of KNN-based ceramics with an R–O phase boundary.

Materials System	Phase Boundary	d_{33} (pC/N)	k_p	Comments	Ref.
$Na_{0.5}K_{0.5}NbO_3$–$BiScO_3$	R–O	210	0.45	Expensive Sc	[13]
$Na_{0.5}K_{0.5}NbO_3$–$BiFeO_3$	R–O	185	0.46		[15]
$Na_{0.5}K_{0.5}NbO_3$–$BiCoO_3$	R–O	165	0.40		[16]
(Na,K)(Nb,Sb)O_3	R–O	230	–	Low T_c of ~220 °C	[14]
$(1 - x)$KNLNS – xBZ	R–O	235	0.44		This work

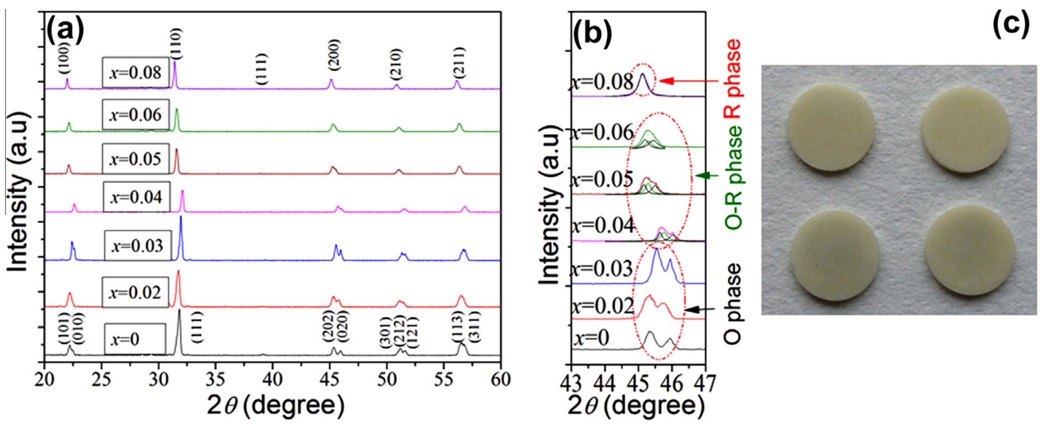

Fig. 1. XRD patterns of $(1 - x)$KNLNS – xBZ ceramics in the 2θ range of (a) 20–60°, (b) 43–47°, and (c) Photos for the sintered $(1 - x)$KNLNS – xBZ ceramics with $x = 0.05$.

Table 2
Electrical properties of $(1 - x)$KNLNS – xBZ ceramics.

x	T_{Poling} (°C)	d_{33} (pC/N)	k_p	ε_r (1 kHz)	tan δ (1 kHz)	$2P_r$ (μC/cm²)	$2E_c$ (kV/cm)
0	120	80	0.26	424	0.163	56.4	19.8
0.02	100	131	0.38	706	0.048	34.9	27.9
0.03	70	103	0.24	925	0.114	53.2	27.9
0.04	60	205	0.48	1126	0.031	39.5	26.5
0.05	55	235	0.44	1567	0.033	42.0	27.6
0.06	50	203	0.37	2343	0.060	31.6	21.5
0.07	45	145	0.21	2698	0.053	23.0	15.5

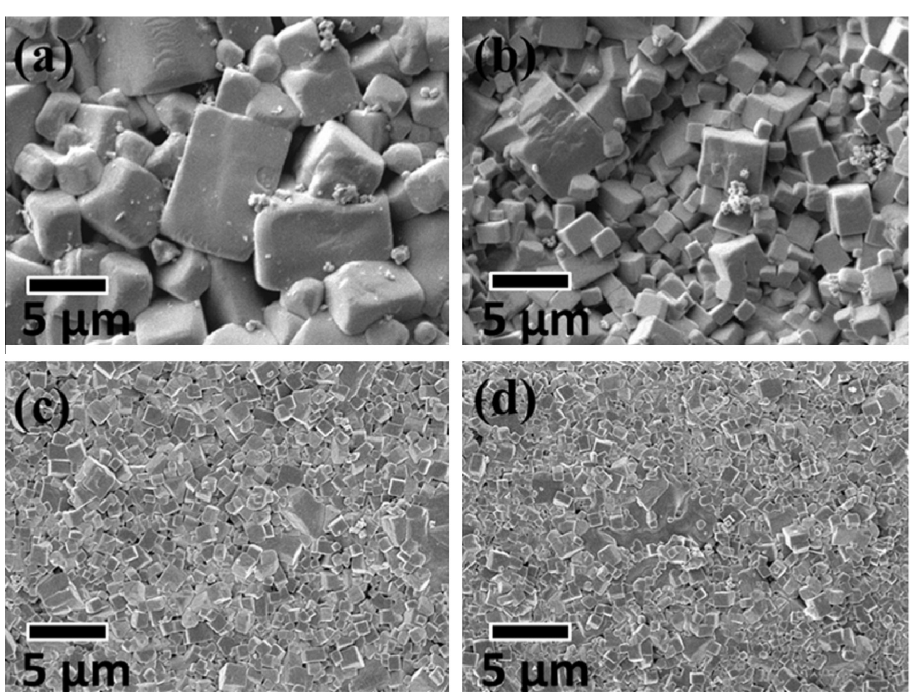

Fig. 2. SEM surface morphologies of $(1 - x)$KNLNS – xBZ ceramics: (a) $x = 0$, (b) $x = 0.03$, (c) $x = 0.05$, and (d) $x = 0.08$.