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Piezoelectric and ferroelectric properties of lead-free (1-x)($Na_{1-y}K_y$)($Nb_{1-z}Sb_z$)O_3-xBaTiO$_3$ solid solution

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ABSTRACT

The solid solutions of lead-free (1-x)($Na_{1-y}K_y$)($Nb_{1-z}Sb_z$)O_3-xBaTiO$_3$ (with x=0.1, 0.2; y=0.03, 0.05; z=0.05, 0.1) (abbreviated as (1-x)NKNS-xBT) ceramics have been synthesized using conventional solid-state reaction method. The results of X-ray diffraction analysis show that all the grown specimens of NKNS display typical perovskite structure. With $BaTiO_3$ (BT) addition, a structural phase transition from tetragonal to cubic structure has been observed. The structural parameters of (1-x)NKNS-xBT powders were determined by profile refinements based on the analysis of X-ray powder diffraction. The charge density distributions of the prepared samples have been investigated by observed structure factors to understand the chemical bonding nature of (1-x)NKNS-xBT powders. The optical absorption of the ceramics has been investigated using UV–visible spectrophotometer. Scanning electron microscopic (SEM) measurements were performed to study the surface morphology of the prepared solid solutions. The elemental compositions of the (1-x)NKNS-xBT samples were analyzed by energy-dispersive X-ray (EDS) spectrometer. The dielectric constant versus temperature plots of the solid solutions exhibit ferroelectric to paraelectric phase transition, which is dependent on the $BaTiO_3$ content. The ferroelectric nature of the samples has been determined through polarization and electric field hysteresis measurements.

1. Introduction

Lead-based (PZT) ceramics are most widely used in sensors, actuators, transformers and other piezoelectric devices due to their excellent piezoelectric properties. However, they contain 60 wt% of PbO, which pollutes the environment strongly and also the health of humans. Therefore researches have been intensified to replace the toxic Pb-based materials [1–4]. The NKN-based ceramics exhibit poor piezoelectricity as compared to most of the lead-based ceramics. Hence, enhanced piezoelectric properties of NKN-based ceramics are needed to replace PZT [5,6]. Li, Ta, and Sb-modified (K, Na)NbO_3 ceramics grown by reactive-templated grain growth show a large d_{33} of ~416 pC/N [5,6]. Similarly, (1-x-y)$K_{1-w}Na_wNb_{1-z}Sb_zO_3$-$y$BaZrO$_3$-$xBi_{0.5}K_{0.5}HfO_3$ ceramics show high piezoelectric coefficient (d_{33}~570 pC/N) by designing new phase boundaries consisting of rhombohedral and tetragonal (R-T) [7]. The phase transition is the main reason for enhanced piezoelectric properties of NKN-based ceramics [8,9]. However, pure KNN ceramics are known to be difficult to densify fully by ordinary sintering methods due to the high volatility of alkaline elements at high temperatures, resulting in non-optimized properties [10,11]. There are two reasons for this problem, one being that the phase stability of pure KNN ceramics is limited a temperature of 1140 °C according to the phase diagram for $KNbO_3$-$NaNbO_3$ [12], and therefore, high sintering temperature cannot be employed. Secondly, in addition of Na_2O and K_2O compounds are easily evaporate at high temperature, which slightly changes stoichiometry of KNN ceramics and lead to the formation of extra phases [13]. Despite such difficulties in the sintering of pure KNN ceramics, the present authors have succeeded in the synthesis of dense KNN ceramics sintered in air owing to the careful control of processing conditions. Pure KNN ceramics have rather low piezoelectric properties, but different dopants (Li^+, Ta^{5+}, Sb^{5+}, Bi($Zn_{0.5}Ti_{0.5}$)O_3, $BaTiO_3$, etc.) are being substituted to improve their piezoelectric properties [14]. To improve the densification and piezoelectric properties of NKN-based ceramics a number of suitable dopants have been substituted in NKN ceramics to form new (Na, K)NbO_3 (NKN)-based ceramics, such as NKN-LiNbO$_3$ [15], NKN-LiSbO$_3$ [16,17], NKN-BaTiO$_3$ [18].

In the present work, (1-x)($Na_{1-y}K_y$)($Nb_{1-z}Sb_z$)O_3-xBaTiO$_3$ ceramics with x=0.1, 0.2; y=0.03, 0.05; z=0.05, 0.1 were prepared by the conventional solid-state method. The phase formation of the solid

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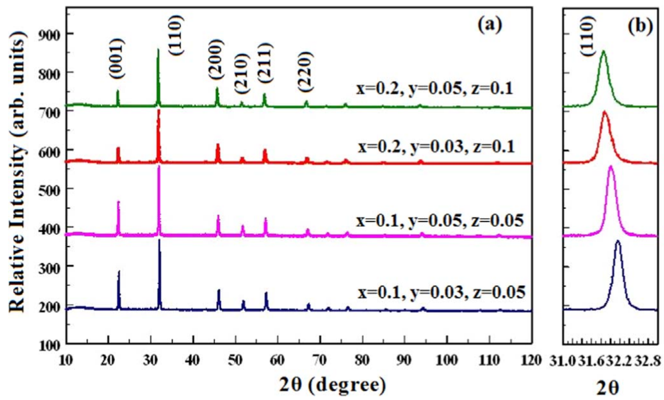

Fig. 1. (a) Powder XRD patterns of (1-x)($Na_{1-y}K_y$)($Nb_{1-z}Sb_z$)O_3-xBaTiO$_3$ ceramics x=0.1, 0.2; y=0.03, 0.05; z=0.05, 0.1 (b) enlarged (110) peak.

solutions was examined by powder X-ray data and Rietveld refinement [19] technique using JANA 2006 program [20]. This paper is mainly focused on the charge density distribution of tetragonal (x=0.1) and cubic (x=0.2) phases for (1-x)NKNS-xBT by the maximum entropy method [21] (MEM) based on the observed structural factors derived from the Rietveld refinement [19]. The objective of this paper analyses the electron density distribution in (1-x)NKNS-xBT and possible correlation of charge density with other physical measurements. The electron density distributions of (1-x)NKNS-xBT were obtained as a function of compositions x, y, z from the maximum entropy method analysis [21].

Table 1
Structural parameters of (1-x)($Na_{1-y}K_y$)($Nb_{1-z}Sb_z$)O_3-xBaTiO$_3$ through refinement of powder XRD data.

Parameters	x =0.1, y =0.03, z =0.05	x =0.1, y =0.05, z=0.05	x =0.2, y =0.03, z =0.1	x =0.2, y =0.05, z =0.1
a (Å)	3.9286(6)	3.93399(8)	3.9389(3)	3.9442(5)
b (Å)	3.9286(6)	3.9339(8)	3.9389(3)	3.9442(5)
c (Å)	3.9387(6)	3.9420(8)	3.9389(3)	3.9442(5)
α=β=γ (°)	90	90	90	90
c/a ratio	1.002	1.002	1	1
Volume (Å^3)	60.79	60.99	61.11	61.35
Density (gm/cc)	4.48	4.52	4.45	4.44
R_P (%)	6.32	6.74	6.56	7.67
R_{obs} (%)	2.04	3.79	2.58	5.49
GOF	0.22	0.22	0.21	0.24
$F_{(000)}$	76	77	76	76

R_P- Profile reliability factor; R_{obs}-Observed profile reliability factor; GOF- Goodness of fit; $F_{(000)}$- Number of electrons in the unit cell.

2. Experimental details

2.1. Sample preparation

High purity raw chemicals, Na_2CO_3 (99.99%), K_2CO_3 (99.99%), Nb_2O_5 (99.985%), Sb_2O_3 (99.99%) and BaTiO$_3$ were used to prepare the lead-free ceramics. The (1-x)($Na_{1-y}K_y$)($Nb_{1-z}Sb_z$)O_3-xBaTiO$_3$ with x=0.1, 0.2; y=0.03, 0.05; z=0.05, 0.1 powders were prepared by solid state reaction method. The powders were weighed in appropriate

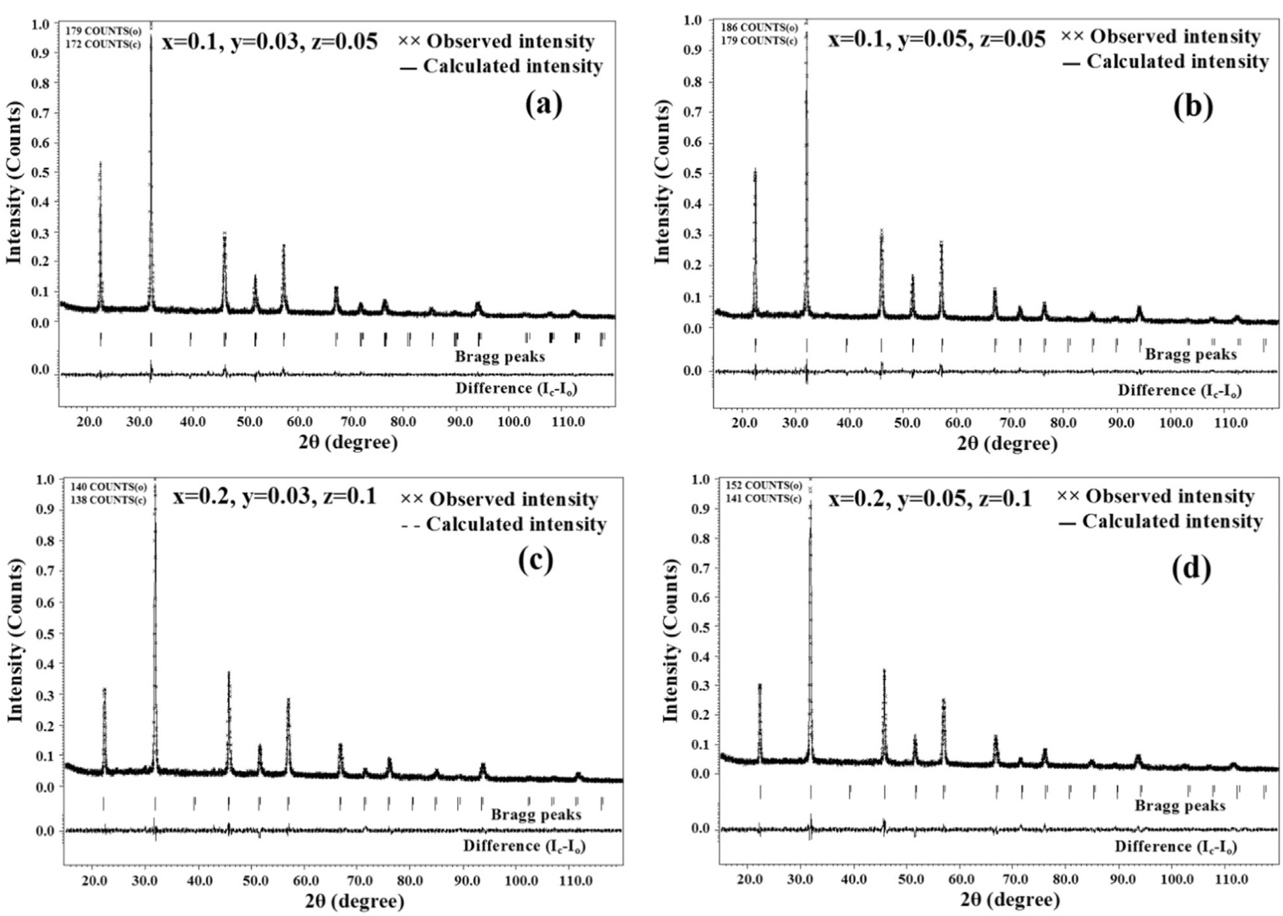

Fig. 2. Fitted powder XRD profile for (a) x=0.1, y=0.03, z=0.05 (b) x=0.1, y=0.05, z=0.05 (c) x=0.2, y=0.03, z=0.1 (d) x=0.2, y=0.05, z=0.1.