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Average vs. local structure and composition-property phase diagram of $K_{0.5}Na_{0.5}NbO_3$-$Bi_{1/2}Na_{1/2}TiO_3$ system

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ABSTRACT

Phase diagram of the solid solution system $K_{0.5}Na_{0.5}NbO_3$- $Bi_{1/2}Na_{1/2}TiO_3$ [(1-x)KNN-xBNT] has been established from dielectric permittivity measurement and structure analyses. The unit cell volumes continuously decrease depending on the composition, while the local structure maintains distortions away from the cubic average structure in the range $0.10 \leq x \leq 0.90$. No clear correspondence for the temperatures of phase transition exists between structural studies and physical properties. The dielectric behavior is depicted successively from normal ferroelectric, diffuse phase transition, re-entrant-like relaxor, relaxor + dipolar glass-like relaxor, BNT-like relaxor with the increase of BNT. A comprehensive composition-property phase diagram for this system has been given to understand the various ferroelectric phenomena. The result could be mainly elucidated by the nanoclusters and the disorder driven nucleation of polar nanoregions contributed by a valence mismatch at one of the cation sites.

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1. Introduction

Both sodium potassium niobate ($K_{0.5}Na_{0.5}NbO_3$, abbr. KNN) and sodium bismuth titanate ($Bi_{1/2}Na_{1/2}TiO_3$, abbr. BNT) have been considered as a potential replacement for $PbZr_xTi_{1-x}O_3$(PZT) because of their relatively high piezoelectric properties. KNN shows cubic (C) symmetry in space group $Pm\bar{3}m$ above 690 K (T_{C-T}) and tetragonal (T) symmetry ($P4mm$) in the temperature range 470–690 K. The transition from a tetragonal phase to an orthorhombic(O) phase ($Amm2$) occurs at 473 K (T_{T-O}), which in turn transforms to a rhombohedral (R) phase ($R3m$) at ~110 K (T_{O-R}) [1]. Most work on KNN is focused on lowering the high-temperature ferroelastic phase transition (T → O) towards room temperature by the addition of various

extra dopants, which is now frequently termed the polymorphic phase transition (PPT) [2–5]. Wang et al.[6] suggested that the main reason for the rapid decrease of T_{C-T} and the deviation for T_{C-T} from the Vegard's law is attributed by valence mismatch. Meanwhile, T_{T-O} and T_{O-R} are mainly affected by the B-site cations, whereas T_{C-T} is mainly affected by the A-site cations [6].

The solubility of dopant ions in the KNN lattice is connected with (i) the crystallographic site in which the dopant ion is incorporated and (ii) the charge compensation mechanism for aliovalent dopant ions. In order to maintain electrical neutrality, aliovalent doping often is accompanied by the creation of electronic or ionic defects. Basically ionic conduction leads to increased loss, and results in electrical degradation of the ceramic capacitor. Therefore, acceptor/donor co-doping have proven to be effective mechanisms to overcome this problem.

The structure change of $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) with temperature is more complex. At room temperature (RT), it shows a ferroelectric (FE) rhombohedral (R) with a polar $R3c$ space group. Recent studies

showed that the *R* phase is actually monoclinic with space group *Cc* [7,8]. Afterwards referred to as the RT or low temperature phase. X-ray or neutron diffraction indicate that two phase transitions occur above room temperature [9–12]. Firstly, the *R* phase changes to a tetragonal (*T*) one over a broad temperature range (500–700 K), during which the two phases coexist. Vakhrushev et al. considered that the coexistence of the two phases consists of rhombohedral clusters dispersed within tetragonal matrix that grows as temperature decreases, until the rhombohedral phase becomes stable [13]. The tetragonal ferroelastic domain structure is unchanged on cooling from 800 K to 300 K [14]. The cubic (*C*) phase appears at about 800 K up to the melting point.

Isupov [15] has given the physical properties of BNT in detail and emphasized the good convergence of all the results from literature. The temperature dependence of the dielectric permittivity $\varepsilon_{i}\ddot{a}(T)$ shows two anomalies associated with the two phase transitions in BNT [16]. A frequency dependent small hump near 500 K exhibits the relaxor behavior of BNT, then a very broad dielectric maximum situates near 600 K which does not depend on the frequency [17]. It is suggested that a ferroelectric (FE) −antiferroelectric (AFE) phase transition could occur near 500 K. The main dielectric anomaly and depolarization near 600 K originate in the dynamic nature of ferroelectric clusters in the coexisting rhombohedral/tetragonal phases according to neutron diffuse scattering [18]. Above 700 K, the Curie-Weiss law is fulfilled and BNT is clearly paraelectric (PE). The investigation of phase transitions in BNT by transmission electron microscope (TEM) [19] shows that a long-range ordering occurs within the tetragonal phase. The order is still visible in the cubic phase. Therefore, BNT is one of the rare perovskites in which local structure plays an important role on macroscopic physical properties.

Aliovalent substitution in KNN was paid much attention in recent years. Gao et al. [20] reported perovskite $(K_{0.5}Na_{0.5})_{1-3x}La_xNbO_3$ ceramics with $0 \le x \le 0.0175$ possess a orthorhombic symmetry. The observed T_C linearly decreases from 711 to 651 K at a rate of ~34 K/at% as *x* increases from 0 to 0.0175, while T_{O-T} changes slightly, only having a value of 5 K/at% in 462–501 K. La^{3+}/Ti^{4+} co-doped KNN ceramics [21] show a depressed dielectric peak corresponding to the phase transition from ferroelectric to paraelectric. The transition exhibits the characteristics of a normal diffuse phase transition with an incipient relaxor behavior. Therefore, understanding the solubility mode in co-doped KNN is an important factor to control their electrical properties.

The literature is scarce on studies devoted to the structure-composition-property relationships of co-doped KNN, especially for high concentration doping. Zuo et al. reported a morphotropic phase boundary (MPB) between ferroelectric orthorhombic and rhombohedral phases in the $(1-x)$KNN-xBiFeO₃ solid solution near $x = 0.01–0.02$ [22]. Guo et al. found the crystal structure changed from orthorhombic to tetragonal at $x \sim 0.04$ in $(1-x)$KNN-xSrTiO₃ ceramics, and the dielectric relaxor behavior was induced by doping of TiO₂ and SrO into KNN [23]. The dielectric response shows a typical relaxor/glass-like behavior in the $(1-x)$KNN-xSrZrO₃ system[24]. According to Zuo et al. the $(1-x)$KNN-xBNT solid solution shows symmetries of orthorhombic at $x \le 0.02$, of tetragonal at $0.03 \le x \le 0.09$, of pseudocubic at $0.09 < x \le 0.20$ and of rhombohedral phases at $x > 0.20$ at room temperature. The MPB between *O* and *T* ferroelectric phases was identified in the composition range of $0.02 < x < 0.03$ [25]. In BNT-rich composition, Kounga et al. reported another MPB between a rhombohedral FE phase ($x > 0.93$) and a tetragonal AFE phase ($x < 0.93$) was found at $x \sim 0.93$ [26]. However, the phase structure is not clear from $x = 0.20$ to $x = 0.90$. The literature provides no information about how the phase structure evolves from rhombohedral ($x \sim 0.20$) to tetragonal ($x \sim 0.93$) and back to rhombohedral ($x \sim 1.00$) with increasing *x*.

Recently, we have investigated the structural phase diagram of the $(1-x)$KNN-xBNT system [27]. Synchrotron X-ray diffraction (SXRD) data show the co-solubility of Bi^{3+}/Ti^{4+} into K^+/Nb^{5+} to be infinite. The phase diagram was established by neutron diffraction (ND) and electron diffraction (ED). The room-temperature structures of the orthorhombic ($x \le 0.02$), monoclinic + tetragonal ($0.02 < x \le 0.14$), tetragonal + pseudocubic ($0.14 < x \le 0.87$), tetragonal + rhombohedral ($0.87 < x \le 0.96$) and rhombohedral ($x > 0.96$) phases have been confirmed and subtle changes in the underlying structures were observed. The origin of this change in crystal symmetry was attributed to tilting of octahedra.

More recently, we found that the correlation between the properties and the structure of this system is not yet understood. Furthermore, in the high-concentration substitution range, the physical properties are determined by local structure. Therefore, in this study, we investigate the dielectric behavior of the solid solution $(1-x)$KNN-xBNT in details. The origin of ferroelectricity in the system is believed to arise from the displacement of the Ti^{4+}/Nb^{5+} octahedra (and of the cations away from a centrosymmetric position within the TiO_6/NbO_6 octahedra). Ti^{4+} and Nb^{5+} have ionic radii of 0.605 and 0.64 Å, respectively. A more pronounced off-center shift of the smaller Ti atoms is observed in their oxygen octahedral cage in comparison to the larger Nb atom [28]. Then the substitutions of K^+ with Bi^{3+} (exhibiting a stereochemically active lone electron pair) and Nb^{5+} with Ti^{4+} not only disturbs the long-range Nb^{5+} displacement, but also results in substantial local lattice strain, which promotes the appearance of polar nanoregions (PNRs). A detailed investigation on the average/local structure-property relationship for the co-doped $(1-x)$KNN-xBNT system is carried out. Average and local structure of the infinite solid solution have been determined using a combination of techniques, including Raman spectroscopy, SXRD, ND and transmission electron microscopy (TEM). Finally, a comprehensive composition-property correlation of $(1-x)$KNN-xBNT ceramics has been investigated to exhibit the various ferroelectric phenomena in the whole phase diagram.

2. Experiment

The preparation of $(1-x)$KNN-xBNT ($x = 0.00, 0.005, 0.02, 0.04, 0.06, 0.10, 0.20, 0.30, 0.50, 0.70, 0.90, 0.92, 0.94, 0.96, 0.98, 1.00$) has been shown in Ref. [27] in detail. The apparent density of the ceramic samples was determined by applying the Archimedes method. The grain size was determined by averaging over the total number of grains in a scanning electron microscopy (SEM) (JSM EMP-800). Silver paste was painted on polished disk-shaped specimens about 0.7 mm thickness and electrodes were fired at 650 °C for 30 min for dielectric measurement. Electrical property measurements were taken with an applied voltage of 500 mV over the frequency range 40 Hz to 1 MHz from 100 K to 800 K using an impedance analyzer (Agilent 4294A).

A Thermo Scientific DXR Raman microscope (Waltham, MA) controlled by the software (Thermo Scientific Omnic) for dispersive Raman measurements was employed. Raman spectra were measured using a 5.0 mW laser emitting at 532 nm, a high-resolution grating with 1200 lines per mm and a confocal pinhole size of 25 μm. The microscope was set to 50 × magnification. Temperature-dependent (*in situ*) Raman experiment was carried out in the range 300–800 K by means of a Linkam MDS600 (Linkam, Tadworth, UK) heating-cooling stage.

High-resolution X-ray diffraction was carried out at the Beamline P02.1 (PETRA III) at HASYLAB (DESY, Hamburg, Germany) [29]. The beamline operates at a fixed energy ~60 keV. The wavelength is 0.20724(5) Å determined by a LaB₆ NIST standard. Powder neutron diffraction was done on the SPODI powder diffractometer at the research reactor FRM-II (Garching, Germany) at an incident wave-