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Electrical Properties of lead free ceremics $Na_{1-X}K_xNbO_3$ at x=0.305.

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By solid state reaction method, ceramic pellets of $Na_{0.695}K_{0.305}NbO_3$ have been prepared. X-ray- diffraction, Piezo properties, scanning electron microscope, and temperature dependence of dielectric constant and loss tangent of the prepared samples have been studied. It has been observed that, at the transition temperature, dielectric constant peak shifts to lower temperature, and the dielectric constant and loss tangent peak heights decrease, with increasing frequency, and show three structural phase transitions.

Keywords: Ferroelectrics, solid state reaction, dielectric constant, dielectric conductivity.

1 Introduction

Lead-based ferroelectric and piezoelectric materials, such as $PbTiO_3$-$PbZrO_3$ (PZT), are most widely used in acoustic transducers, actuators, and other electromechanical fields because of their electromechanical and high piezoelectric properties[1]. However, despite the toxic nature of PbO (which comprises 60–70 wt% of ceramic) it is most commonly used in PZT-based materials, therefore an urgent demand is to find lead-free materials to replace Pb-based ceramics in future. One of the most excellent candidates is sodium potassium niobate, (Na, K)NbO_3 (NKN), based solid solutions due to the high piezoelectric response, good ferroelectric properties, and especially high Curie temperature. Guo *et al.* [2] prepared the (1-x)KNN-x$LiNbO_3$ ceramics, exhibiting excellent piezoelectric properties, d_{33} ~ 235 pC/N, kt ~ 48%, and TC ~ 460 °C, which is in the vicinity of the morphotropic phase boundary (MPB) of $(K_{0.5}Na_{0.5})NbO_3$ and $LiNbO_3$ binary solid solution system. In addition, some modified NKN ceramics prepared by conventional solid-state sintering method have been investigated[3-6].

The low dielectric constant of perovskite $Na_{1-x}K_xNbO_3$ ceramics, coupled with fine structure and improved piezoelectric activity, especially near the equimolar composition of Na and K, make these materials desirable for transducer and certain solid ultrasonic delay line applications, which require the use of thin-section transducers[7]. Dielectric measurements were first reported, by Matthias and Remeika[8] on end members of $Na_{1-x}K_xNbO_3$ system, *i.e.*, on $NaNbO_3$ and $KNbO_3$, single crystals and observed three transitions at 80, 370 and 480°C for $NaNbO_3$; and two transitions, at 224 and 434°C, for $KNbO_3$, at 10 KHz. Afterwards several investigators studied this system[9-11]. However, these studies were restricted to low range single frequencies.

The aim of our work is to study the crystal structure, dielectric properties of (NaK)NbO_3 system.

2 Experimental Details

Pellet samples of $Na_{1-x}K_xNbO_3$ ($0.250 \le x \le 0.350$) were prepared by solid-state reaction method, using the powders of Na_2CO_3, K_2CO_3, Nb_2O_5 (all with purity ≥ 99.9%, from MERK, Germany). At first the raw powders were separately dried, at 200 °C for 2 hours, to remove the absorbed moisture and weighed in stoichiometric ratio. The weighed powders were dry mixed and ground for 4 hours, and then wet mixed with acetone and ground for 2 hours, using a gate mullet mortar and pestle. The mixture was calcined in an alumina crucible, in ambient atmosphere, at 900 °C, for 4 hours, to remove the present carbon dioxide. When the furnace was switched off and cooled to room temperature the calcined mixture was weighed to ensure the complete carbon dioxide removal from the mixture. The calcined mixture was further ground for half an hour and then pressed into pellets of 8 mm diameter and about 2 mm thickness, using 0.4 GPa uniaxial pressure. These pellets, with

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x = 0.250, 0.300, 0.310, 0.315, 0.320, 0.325, 0.330 and 0.350, were sintered, each composition for 4 hours in the order of their melting points, at 1170, 1165, 1160, 1156, 1152, 1150, 1148 and 1145 °C, respectively, in a high temperature muffle furnace. The crystal structures of the sintered samples were examined using an X-ray diffractometer (PANalytical X'PERT PRO) with Cu K_{α} radiation (wavelength, λ = 1.540598 Å)[10]. X-ray diffraction (XRD) patterns of all the prepared samples were taken with 2Θ in the range from 20 to 70°, at ambient temperature. Surface morphology, grain size and energy dispersive X-ray analyses (EDAX) of the prepared pellets were studied using a scanning electron microscope (CARL ZEISS, MA15/EVO18)[11]. Measurement of Polarization characteristics and piezoelectric parameters of the prepared samples, using a ferroelectric- (PE loop tracer) and piezo- meter (AixACCT Systems, GmbH). For dielectric measurements sintered pellets were electroded, using air drying silver paste, in parallel-plate capacitor configuration. Temperature, frequency and composition ($0.250 \leq x \leq 0.350$) dependence of dielectric constant (K), loss tangent (tan δ) and dielectric conductivity (σ) of the prepared samples were measured in MIM configuration, in the 1 to 1000 KHz frequency range, using an RCL meter (Fluke– PM6306); and the temperature ranging from RT to 150 °C, using a temperature controller having an accuracy of ±1 °C.

3 Results and Discussion

Figure 1 presents the observed XRD patterns of the prepared $Na_{1-x}K_xNbO_3$ (0.305) pellet samples. Peak indexing was done with the help of Ceramic Inorganic Data Cards[12]. The X-ray patterns show polycrystalline behavior of the prepared samples and were consistent with reference with the Inorganic Crystal Structure Database (ICSD) (code 00-061-0310) data of $(Na,K)NbO_3$ with peaks corresponding to (100), (110), (200), *etc*.

The cell parameters were refined by High Score Plus software, using the Rietveld method[13], and the background was modeled using the Legendre polynom and the peaks' profiles were refined by a pseudo-Voigt function. The monoclinic Pm6 space group was chosen in these refinements. Values of calculated subcell parameters are a = 3.963, b=3.901, c= 3.937 and β angle is 90.35 is closely agree with the reported results[14, 15], Fig. 2 shows the scanning electron micrographs (SEM) of the prepared samples. The density and porosity greatly affect the dielectric properties of the samples[16].

The observed energy dispersive X-ray analysis (EDAX) results, show significant escaping of alkali (Na and K) ions in the sintered pellets,

The observed polarization- electric field (P-E) hysteresis loops at room temperature, for unpoled NKN samples under an applied electric field of 22 kV/cm and 1 Hz, have been shown in Fig. 3. and the strain (%) at RT, under an applied electric field of 22kV/cm and 1Hz, have been shown in Fig. 4. All the

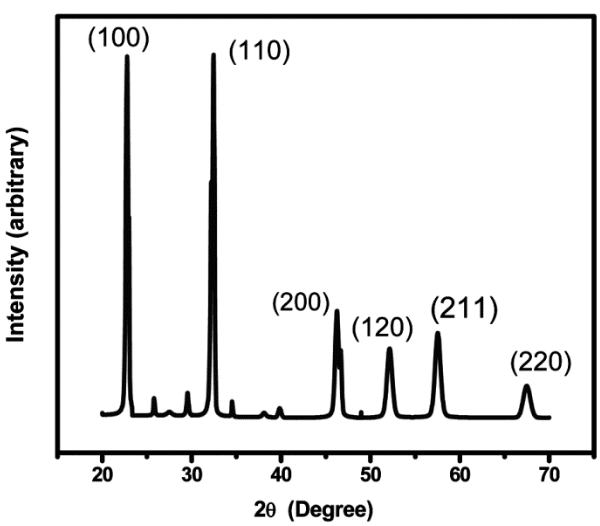

Fig. 1 — XRD patterns for $Na_{0.695}K_{0.305}NbO_3$ samples

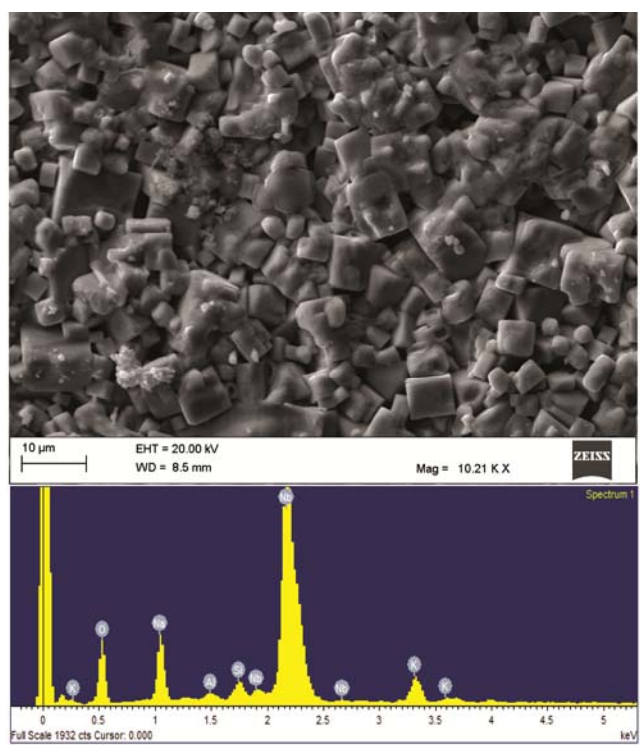

Fig. 2 — SEM photographs and EDAX of $Na_{1-x}K_xNbO_3$ sample

samples show a normal hysteresis loop confirming ferroelectric nature of all the prepared NKN ceramics. Shape of the P-E hysteresis loop depends on the microstructure, stress, defects, and processing conditions [17]. It has been reportedly observed that the ferro- and piezo- electric properties not only depend on the preparation conditions, but also on the type of the manufacturing company and the grain size of the starting materials[18,19].

The temperature dependence of dielectric constant for different frequency has been shown in Fig. 5. , at 10, 100 and 1000 kHz, respectively. Three structural phase transitions, at about 180, 400 and 458 °C have been observed. Between these temperatures $K_xNa_{1-x}NbO_3$ is in monoclinic, tetragonal, rombhohedral and cubic phase, as observed in the previously reported studies [20-23]. Similar behavior is observed for the loss tangent, as shown in Fig. 6. The temperature dependence of conductivity for composition has been shown in Fig. 7, at 10, 100 and 1000 kHz, respectively. The figures show that the conductivity of the $K_xNa_{1-x}NbO_3$ system increases with the increase of temperature. It is also observed that the conductivity increases with increasing concentration of K in the mixed system.

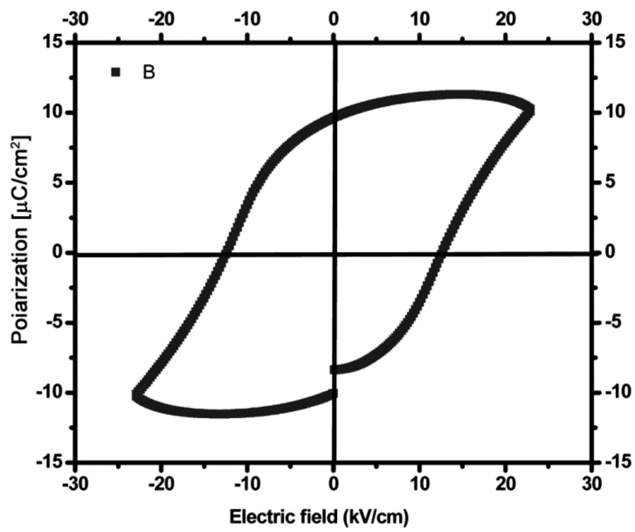

Fig. 3 — P-E loop for different composition(s) of $Na_{1-x}K_xNbO_3$, at applied field 22 kV/cm.

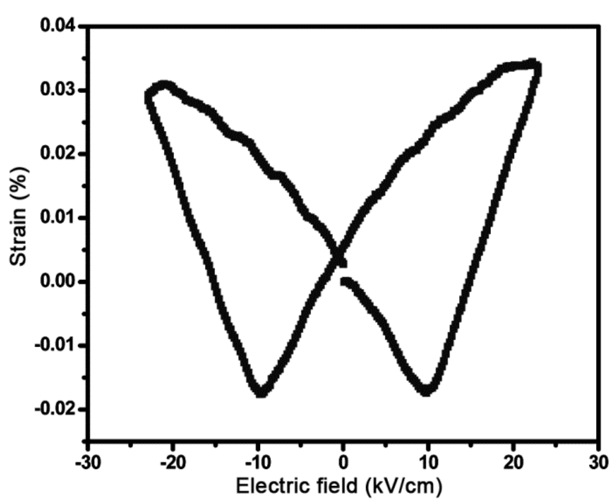

Fig. 4 — Variation of strain (%) with electric field, in $Na_{1-x}K_xNbO_3$,at applied field 22 kV/cm.

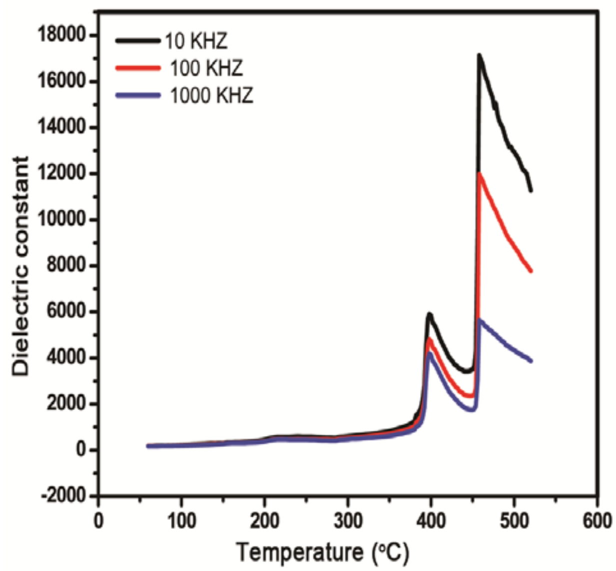

Fig. 5 — Temperature variation of dielectric constant (K) of $Na_{1-x}K_xNbO_3$, for different frequency.

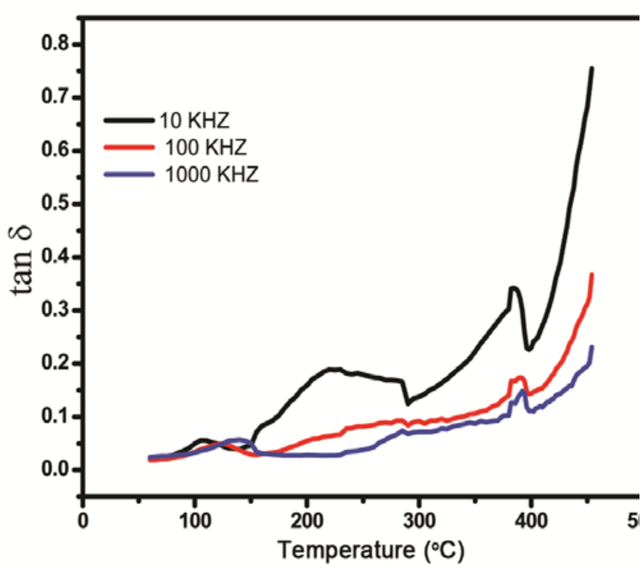

Fig. 6 — Temperature variation of dielectric loss (tan δ) of Na_{1-x} K_xNbO_3, for different frequency.

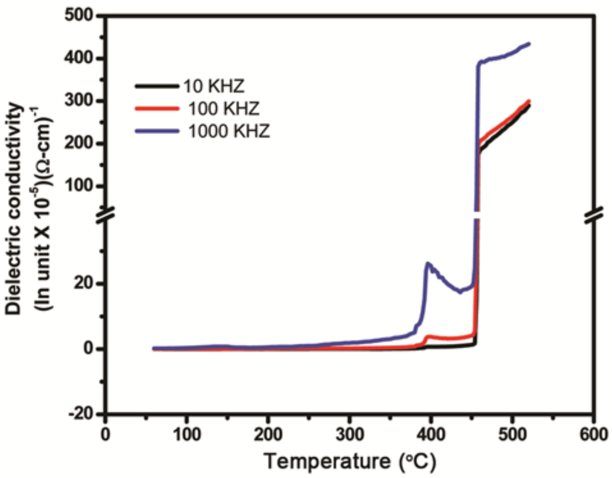

Fig. 7 — Temperature variation of dielectric conductivity (σ) of $Na_{1-x}K_xNbO_3$, for different frequency.

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