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Effect of sintering temperature on composition, microstructure and electrical properties of $K_{0.5}Na_{0.5}NbO_3$ ceramics

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ABSTRACT

Lead free potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$) ceramic powders were synthesized by colloidal coating method. The calcined powders (800 °C) were sintered conventionally at three different temperatures (1050 °C, 1100 °C and 1150 °C) and the effect of sintering temperature on density, microstructure, composition and electrical properties was investigated. All the samples showed a single phase perovskite structure with orthorhombic symmetry similar to $KNbO_3$ ceramics. Microstructure examined under FEG-SEM revealed an optimum microstructure, in terms of grain size, porosity and uniformity, at the sintering temperature of 1100 °C, which also showed density of 92% of ρ_{Th}. As the sintering temperature increased the X-ray diffraction peaks shifted to lower 2θ values indicating excess volatilization of Na at higher temperature as compared to K. This was further confirmed through elemental Probe X-ray microanalysis and ICP–AES studies. Dielectric constant (ε_r), dielectric loss ($\tan\delta$), ferroelectric (*P–E* loop) and piezoelectric (d_{33}) properties showed considerable improvement and leakage current decreased with increasing sintering temperature. The sample sintered at 1100 °C showed marked improvement in maximum dielectric constant (573) at RT at 1 kHz, minimum tangent loss (0.04) at RT at 1 kHz, maximum remnant polarization (13.5 μC/cm^2), lower leakage current (7.6×10^{-7} A/cm^2) and maximum d_{33} value (100 pC/N).

1. Introduction

Lead zirconium titanate (PZT) and modified PZT-based ceramics are widely used for many industrial applications due to their superior performance in ferroelectric, piezoelectric, and pyroelectric applications [1,2]. It is well known and widely accepted that, use of lead-based ceramics raises serious environmental and safety concerns, due to the toxicity of lead oxide and its high vapour pressure during the sintering process [3,4]. Consequently, there has been growing interest in developing alternative lead-free ferroelectric and piezoelectric materials which could eventually replace the current lead-based ceramics. Extensive research all over the world in the last two decades has resulted in several lead free candidate materials such as $BaTiO_3$-based ceramics [5], Bi layered structures [4], alkaline niobate perovskites [4] and Bi-based perovskites [6], to name a few.

Alkaline niobate perovskites, in general, potassium sodium niobate (K, Na) NbO_3 (KNN) in particular has been widely studied. This is a potential candidate due to its high Curie temperature (420 °C) and promising ferroelectric and piezoelectric properties comparable with PZTs [7]. Further, KNN exhibits a morphotropic phase boundary (MPB) around 50% K and 50% Na, separating two orthorhombic phases and, as in PZT, an abrupt increase in piezoelectric coefficients near MPB [7,8]. Reports on successful processing of KNN ceramics have been with sintering using hot processing [8], spark plasma sintering (SPS) [9] and the use of sintering aids [3,10,11]. But these unconventional sintering methods are considered commercially rather nonviable. The difficulty and lack of success, in obtaining dense KNN ceramics with good electrical properties through conventional sintering has been attributed to volatilization of sodium (Na) during sintering and consequent deviation in MPB above 1100 °C as evidenced by XRD results [9]. Below 1100 °C there is no deviation from MPB, however densification is poor. Recently, we reported improvement in density, dielectric and ferroelectric properties of KNN obtained with conventional sintering of powders processed using colloidal coating method [12,13].

In this paper, we report correlation between density, microstructure, leakage current and piezoelectric properties as a function of sintering temperature for KNN ceramic powders synthesized by colloidal coating method and sintered by conventional method. Further, additional evidence for degradation of properties and deviation in MPB above 1100 °C are also examined.

2. Materials and methods

The starting materials used in this study were KNO_3, $NaNO_3$ (all 99% pure, Merck India) and Nb_2O_5 powder (99.9%, Aldrich USA). The raw materials were dried at 200 °C for 1 h prior to use. Single

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phase KNN powders were prepared by colloidal coating method as earlier reported [13,14]. The phase pure powders (obtained by calcination at 800 °C) were compacted and sintered at 1050 °C, 1100 °C and 1150 °C for 2 h in air. The experimental density of the sintered samples was determined using the Archimedes method (ASTM# C 373-88).

To determine the phase purity and lattice parameters of calcined powders and ceramic samples, X-ray diffraction data was recorded in the 2θ scan range of 10°–90° by X-ray diffractometer (PANalytical X-ray diffractometer). X-ray source was Cu-$K\alpha$ ($\lambda = 1.541$ Å) radiation. Microstructure of sintered and polished samples was observed using a JEOL (JSM-7600F) Field Emission Scanning Electron Microscope (FEG-SEM). For composition analysis EDX was performed on the samples with the help of an EDX detector (Oxford instruments) attached with FEG-SEM. Bulk composition analysis was carried out using inductively coupled plasma–atomic emission spectroscopy (ICP–AES) using ICP–AES Spectrometer (ARCOS, Germany). For ICP–AES measurement 0.1 g of sample was dissolved in a mixture of 8 ml of aqua regia and 2 ml of HF (hydrofluoric acid) in a microwave digester at 220 °C. The sample was diluted with Di-water to 25 ml volume. For electrical measurements of samples, silver paste was applied on both sides of the sample and dried at 100 °C for 1 h to remove organic solvent. The dielectric measurements of the samples were carried out over a temperature range from 50 °C to 500 °C by using a computer interfaced NovoControl dielectric Alfa analyzer in the frequency range 1 Hz to 1 MHz. Variation of electrical polarization as a function of electric field (P–E loop) at room temperature at 2 Hz was observed using ferroelectric test system (aixACT TF analyzer, Aachen, Germany). The mechanical displacement was measured using mechanical displacement sensor (SIOS). During the polarization measurement, an electric field of 10–50 kV/cm, based on the coercive fields of the samples, was applied. To prevent the breakdown from the edges of the sample, samples were immersed in silicone oil during the measurement. The I–V characteristics were measured in "switched triangular mode" with a maximum applied electric field of 20 kV/cm.

3. Results and discussion

3.1. Raw powders morphology

The morphology of pure Nb_2O_5 and precalcined (after coating) powders are shown in Fig. 1. The particle size distribution has been measured using Imge.J software and represented in inset of Fig. 1. The mean particle size of pure Nb_2O_5 powders is about ~0.230 μm and after coating the mean particle size increased to about ~0.240 μm. It can also be seen that the Nb_2O_5 particles are uniformly distributed and the Na and K precursors are homogeneously coated.

3.2. Phase analysis

Fig. 2 shows the room-temperature XRD patterns of KNN ceramic calcined at 800 °C for 6 h. It can be observed that the XRD patterns reveal a single phase perovskite structure. The diffraction peaks closely match with JCPDS card (PDF#71-0946) and all the peaks were indexed to orthorhombic perovskite unit cell. The peaks were fitted using pseudo-Voigt function in order to determine their angular positions and integral widths.

The room-temperature XRD patterns of KNN ceramics sintered at 1050 °C, 1100 °C and 1150 °C for 2 h are depicted in Fig. 3. It can be seen that the diffraction peaks have shifted to lower 2θ values as the sintering temperature increases from 1050 °C to 1150 °C. The shifting of peaks to lower 2θ values suggests that the stoichiometric ratio of K and Na has deviated from the nominal stoichiometry of KNN. Since the ionic radius of K^+ ($r_K = 1.38$ Å) is larger than Na^+ ($r_{Na} = 1.02$ Å), the decrease in 2θ value or increase in d value means the K/Na ratio increases with increasing sintering temperature. This result suggests that the volatilization of Na is higher than that of K at higher temperatures. This is consistent with the reported results by Zhang et al. [9] in which K/Na ratio was tailored and found that as the K content increases the value of 2θ decreases (d value increasing) for KNN ceramics.

3.3. Density measurements

It is well known that density and porosity have pronounced effect on properties of most electro-ceramics. The density and porosity of the samples sintered at different temperatures are listed in Table 1. It may be noted that the sample sintered at 1050 °C showed density of 3.78 g/cm^3 which corresponds to 84% of the theoretical density ($\rho_{Th} = 4.51$ g/cm^3) [15]. The observed density for 1100 °C and 1150 °C sintered samples were 4.15 g/cm^3 (92% of ρ_{Th}) and 4.25 g/cm^3 (94% of ρ_{Th}), respectively. This shows that there is no appreciable difference in the density of samples sintered at 1100 °C and 1150 °C for 2 h. The improvement in density of 1100 °C and 1150 °C sintered samples over 1050 °C sintered sample can be attributed to an increase in grain size and presence of fairly uniform microstructure as described in the next section.

3.4. Microstructure of sintered KNN ceramics

The effect of sintering temperature on the microstructure was examined on polished and thermally etched surface using Field Emission Scanning Electron Microscopy (FEG-SEM). Fig. 4(a)–(c) shows microstructure of pure KNN ceramics sintered in air at 1050 °C, 1100 °C and 1150 °C for 2 h, respectively. All the samples showed well developed grains and grain size increased with increasing temperature. The sample sintered at 1050 °C, having lower density, shows apparent porosity in the microstructure. The

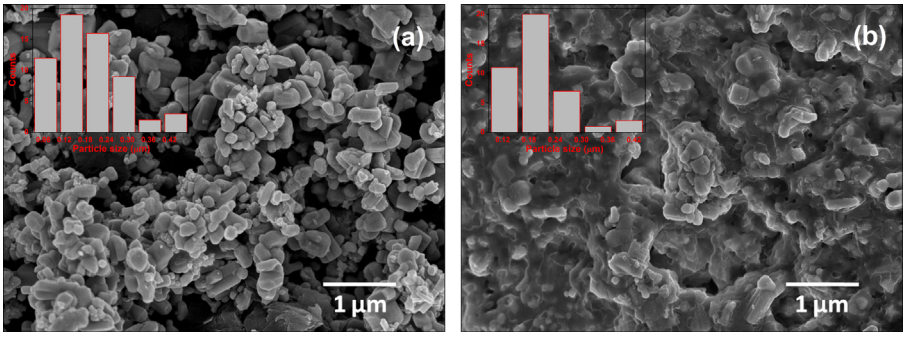

Fig. 1. FEG-SEM Morphology of (a) Pure Nb_2O_5 and (b) Precursors after coating (precalcined).