



Synthesis of nano-crystalline potassium sodium niobate ceramic using mechanochemical activation

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Abstract

Single phase nano-crystalline $K_{0.5}Na_{0.5}NbO_3$ (KNN) ceramic has been successfully synthesized by the mechanochemical activation method. High energy ball milling was carried out on a mixture of K_2CO_3 , Na_2CO_3 and Nb_2O_5 powders for different times (6 h, 12 h, 24 h and 32 h). The 32 h mechanically activated sample was calcined at 550 °C for 2 h. This is about 300 °C lower as compared with conventional solid state reaction. X-ray diffraction pattern of calcined sample revealed single phase perovskites structure with orthorhombic phase. Particle size of these powders was measured using DLS. The Morphology of mixture powder, before and after calcination, was examined under FEG-SEM. Dielectric, ferroelectric and piezoelectric properties were evaluated and compared with reported results using other competing techniques.

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1. Introduction

Perovskite $Pb(Zr,Ti)O_3$ (PZT) and doped PZT-based ceramics are widely used in many Industrial applications due to their superior performance in ferroelectric, piezoelectric and pyroelectric properties [1,2]. However, PZT contains more than 60 wt % lead that raises serious environmental and safety concerns, due to the toxicity of lead oxide and its high vapor pressure during the sintering process [3,4]. Therefore, there has been a growing interest to develop lead-free ceramics for ferroelectric and piezoelectric applications. Extensive research all around 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. Among them, much attention has been paid to the alkaline niobate perovskites. In particular, potassium sodium niobate (K, Na) NbO_3 (KNN) is

considered to be an important lead free candidate material due to its high Curie temperature (420 °C) and promising ferroelectric and piezoelectric properties comparable with PZTs [7,8].

The conventional synthesis of KNN ceramic requires high-temperature and long time for calcination, which leads to the volatilization of the alkali metal and consequent, non-stoichiometric and undesirable secondary phase formation. Furthermore, this method results in products with large and inhomogeneous particle sizes, due to particle coarsening that deteriorates the piezoelectric response [9]. In order to overcome these drawbacks, many wet chemical-based processing techniques have been developed, such as, sol-gel [10], citrate gel [11], co-precipitation [12], hydrothermal [13], to name a few. However, these techniques require high-purity inorganic materials that are typically much more expensive than the widely available oxides and carbonates.

Mechanochemical activation involves high energy ball milling of a mixture of powders and is accompanied by chemical reaction. Initially this technique was used for synthesizing metallic alloys and inter-metallic compounds [14]. The main

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advantage of this method is that it permits the synthesis of nano-materials, in bulk, at an ambient temperature and in a very short processing time [15]. In the past few years, several attempts have been made to synthesize various perovskites ceramic powders using mechanochemical activation starting from a powder mixture of carbonates and oxides, such as BaTiO₃ [16], LiFeO₂ [17], NaNbO₃ [18], PZT [19] and KNN [9]. However, earlier reported literature on synthesis of KNN by the mechanochemical activation method did not result in single phase KNN during milling [9]. Even prolonged milling resulted in an amorphisation of the reactants.

In this paper, we report synthesis of single phase nanocrystalline KNN ceramic, using mechanochemical activation, in an effort to decrease the calcination temperature as compared to conventional solid state reaction. The morphology, structure and electrical properties of the ceramics so obtained are presented.

2. Materials and methods

The starting materials used in this study were K₂CO₃, Na₂CO₃ (all 99% pure, Merck India) and Nb₂O₅ powder (99.9%, Aldrich, USA). The alkaline carbonate powders were first dried at 200 °C for 1 h prior to use due to their hygroscopic nature. High energy ball-milling was carried out in a high energy mill, SPEX8000D, for mechanochemical activation of the samples. The milling speed was 875 cycles (back and forth) per minute. The milling was interrupted at regular intervals (6 h, 12 h, 24 h and 32 h) to collect samples for analysis. The 32 h milled sample was calcined and sintered at 550 °C and 1100 °C for 2 h, respectively, in air. The density of the sintered samples was determined using the Archimedes method of fluid displacement (ASTM #C 373-88).

Thermogravimetric analysis (TGA) was performed, in flowing air, at a heating rate of 10 °C/min using PerkinElmer Pyris 1 Thermo-gravimetric analyzer. To determine the phase purity and lattice parameters of calcined powders, X-ray diffraction data was recorded in the 2θ scan range of 10–90° using X-ray diffractometer (PANalytical X-ray diffractometer) and Rietveld refined using Fullprof program. X-ray source was Cu-Kα (λ=1.541 Å) radiation. The morphology of mechanically activated powders was examined using a JEOL (JSM-7600F) Field Emission Scanning Electron Microscope (FEG-SEM). For electrical measurements, silver paste was applied on both sides of the sample and dried at 100 °C for 1 h to remove organic solvent. Dielectric measurements of the samples were carried out over a temperature range of 50–500 °C using a computer interfaced NovoControl dielectric Alfa analyzer in the frequency range from 1 Hz to 1 MHz. Variation of electrical polarization as a function of electric field (P–E loop) at room temperature and at 2 Hz was observed using ferroelectric test system (aixACT TF analyzer, Aachen, Germany). Mechanical displacement was measured using mechanical displacement sensor (SIOS). During the polarization measurement, an electric field of 10–50 kV/cm was applied. To prevent the breakdown from the edges, samples were immersed in silicone oil during the measurement.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows results of Thermo-gravimetric analysis (TGA), and its corresponding derivative, for the mixture powders mechanochemically activated for 32 h. The experiment was carried out from room temperature to 1000 °C. From the figure it can be seen that the powder mixture goes through two main stages of thermal decomposition. In the initial stage, from room temperature to about 150 °C, the weight loss (7.61%) is mainly due to moisture and water with maximum weight loss rate at 135 °C. In the second stage, the main part of the curve from 400–550 °C, the weight loss (19.38%) is due to the decomposition of carbonates. The peak at 450 °C in the derivative curve indicates the starting of carbonate decomposition. The major peak at 510 °C corresponds to the highest rate of decomposition. Absence of a peak after 550 °C suggests that the reaction is completed at 550 °C.

3.2. Phase analysis (XRD)

The XRD pattern of mixture of powders, mechanically activated for different times, is shown in Fig. 2. It can be seen that before activation both the alkaline carbonates, [K₂CO₃ (JCPDS #87-0730) and Na₂CO₃ (JCPDS #19-1130)], and Nb₂O₅ (JCPDS #27-1313) phase is present [20–22]. However, after 32 h mechanochemical activation only Nb₂O₅ phase (JCPDS #27-1313) was detected and no peak belonging to alkaline carbonates has been observed. This suggests the loss of the long-range periodicity in the carbonates crystal structure to the point at which it is undetectable using the XRD [23]. The loss of long-range periodicity in the carbonates when milled together with Nb₂O₅ is an evidence of an interaction between the reactants and confirms that the chemical reaction occurs during milling [23]. Further, no new peak has been detected after mechanical activation. However, the peak intensity decreases as milling time increases. The decrease in intensity and increase in background is related to the formation of an amorphous phase. This amorphous phase has formed due to the reconstruction of the CO₃²⁻ ions into a carbonate

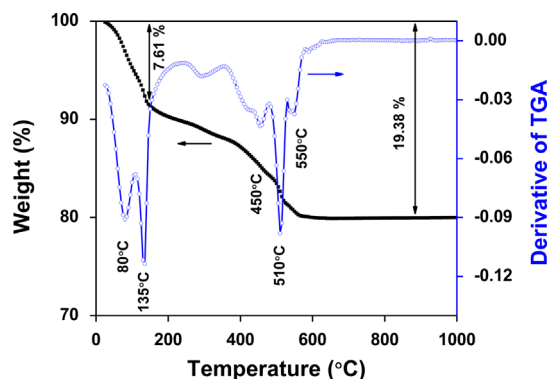


Fig. 1. TGA and derivative of TGA curve for 32 h mechanically activated mixture powders.

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