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Short communication

Effect of sintering temperature on ferroelectric properties of $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LNbO_3$ system

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Abstract

Lead free $0.94(K_{0.5}Na_{0.5}NbO_3)$–$0.06(LiNbO_3)$ (KNN–LN) system was synthesized by conventional solid state reaction route (CSSRR). The KNN–LN system was calcined at 850 °C for 6 h for the formation of single perovskite phase whereas the sintering was done at 1050 °C, 1080 °C and 1100 °C for 4 h, respectively. The KNN–LN samples sintered at 1080 °C show better properties: room temperature (RT) dielectric constant (ε_r) ~936, dielectric loss (tan δ) ~0.016 at 1 MHz, a relatively high bulk density (ρ) ~4.385 g/cm^3, which is 97.5% of the theoretical density (TD ~ 4.51), remnant polarization (P_r) ~6.4 μC/cm^2 and coercive field (E_c) ~9.6 kV/cm have been observed.

Keywords: A. Powders: solid state reaction; A. Sintering; C. Dielectric properties; C. Ferroelectric properties

1. Introduction

Ferroelectric ceramics are the heart and soul of several multibillion dollar industries, ranging from high-dielectric-constant capacitors to later developments in piezoelectric transducers, positive temperature coefficient devices and electro-optic light valves [1]. Among lead oxide-based ferroelectrics, lead zirconate titanate (PZT) system was intensively studied for many years [2]. A noticeable feature of PZT material is the occurrence of a morphotropic phase boundary (MPB) [2–5]. The compositions close to the MPB show excellent piezoelectric and ferroelectric properties and hence, they have been widely used for piezoelectric actuators, sensors and transducers applications [6]. However, the high toxicity of lead oxide has caused serious environmental problems. Therefore, investigations have been extensively carried out to develop lead free systems with potentially good piezoelectric and ferroelectric properties [7].

Lead free ferroelectric materials with perovskite structure have attracted much attention since they are easy to prepare and the structure is simple compared to other structures [1]. Many lead free ferroelectric materials such as barium titanate (BT), bismuth sodium titanate (BNT), potassium niobate (KN), potassium sodium niobate (KNN) and potassium tantalate niobate (KTN) have a perovskite structure [8,9]. Among all the lead free ferroelectric materials $(K_{0.5}Na_{0.5})NbO_3$ (KNN) based systems have attracted much attention because of having high piezoelectric properties, high Curie temperature (T_c) and environmental friendly nature [10–19]. A major problem concerning KNN system is difficulty in obtaining high density by conventional solid state reaction route (CSSRR) for several reasons [20,21]. One is that for KNN phase stability is limited to 1140 °C [22]. In addition, a deviation from stoichiometry can result in the formation of extra phases [23]. Therefore, in order to solve the above problems, various synthesis techniques have been utilized, such as hot pressing and spark plasma sintering process [24,25]. Although these methods can yield high densities and better properties compared to KNN synthesized by CSSRR, but still careful investigation and optimization of sintering parameters are needed to obtain reproducible and high quality materials. Additionally, since they are more expensive routes compared to the CSSRR, efforts have been made to find new systems based on KNN that can be synthesized by CSSRR with improved electrical properties.

In this work, the lead free KNN–LN system has been synthesized by conventional solid state reaction route. The

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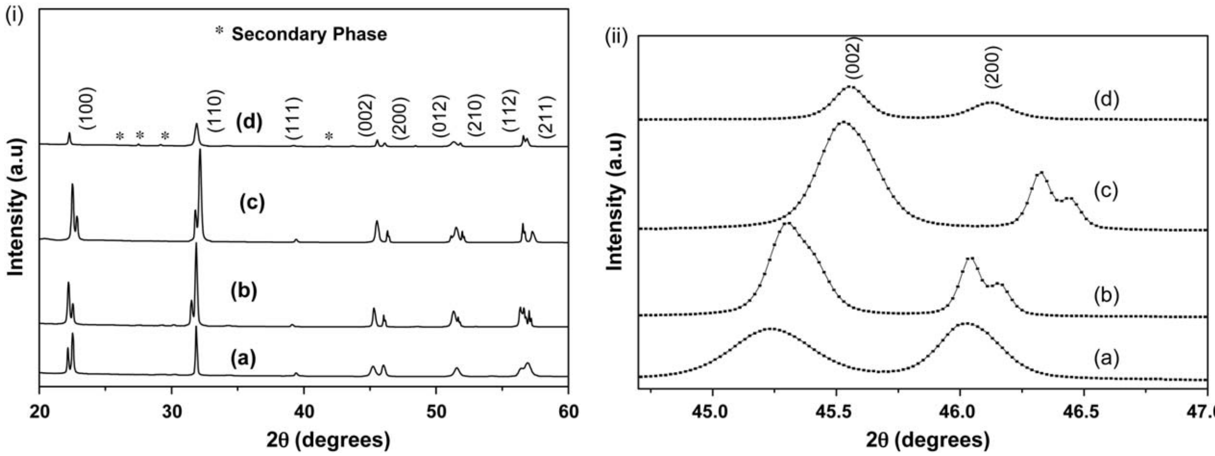

Fig. 1. (i) XRD patterns of KNN–LN system calcined at (a) 850 °C, sintered at (b) 1050 °C. (c) 1080 °C and (d) 1100 °C. (ii) Enlarged XRD pattern.

effects of sintering temperature on density, remnant polarization and dielectric properties have been studied.

2. Experimental procedure

Lead free KNN–LN ceramics were prepared by a conventional solid state reaction route. Sodium carbonate (Na_2CO_3, 99% purity), potassium carbonate (K_2CO_3, 99% purity), lithium carbonate (Li_2CO_3, 99% purity), and niobium pentoxide (Nb_2O_5, 99% purity) were used as starting materials. Stoichiometric weights of all the powders were mixed and ball milled with acetone for 8 h, using zirconia balls as the grinding media. After drying the slurry in oven, the calcination was carried out at 850 °C for 6 h and single phase formation was confirmed by the X-ray diffraction (XRD) technique. The calcined mixture was mixed thoroughly with 2 wt% polyvinyl alcohol (PVA) binder solution and then pressed into disks of diameter of 10 mm and a thickness of 1.5 mm under ~60 MPa pressure. The sintering of the samples was carried out at 1050 °C, 1080 °C and 1100 °C for 4 h, respectively with a

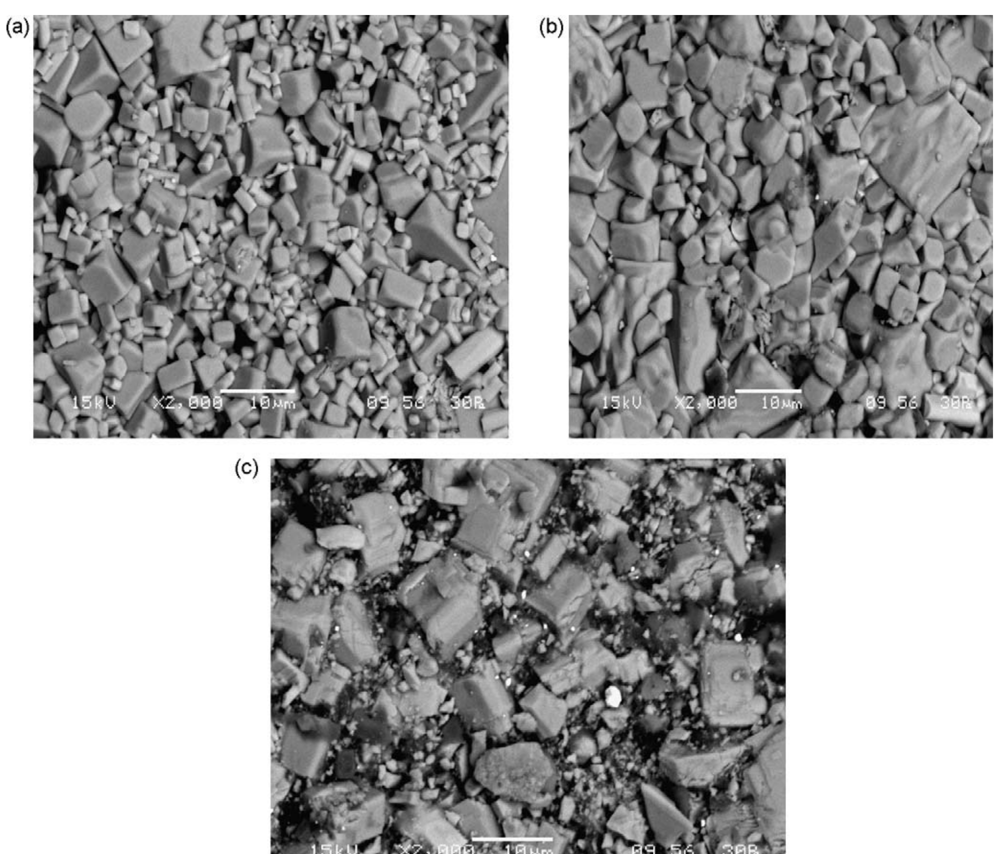

Fig. 2. SEM micrograph of KNN–LN samples sintered at (a) 1050 °C, (b) 1080 °C, and (c) 1100 °C.

heating rate of 5 °C/min in air. XRD analysis of the pellets was performed on a PW 3020 Philips diffractometer using Cu Kα (λ = 0.15405 nm) radiation in order to examine the phases present in the system. The sintered microstructures were observed using a JEOL T-330 scanning electron microscope (SEM). The bulk densities of the samples were measured by the Archimedes method. Silver paste was applied on both sides of the samples for the electrical measurements. Dielectric constant (ε_r) and dielectric loss (tan δ) were measured as a function of frequency using a computer interfaced HIOKI 3532-50 LCR-HITESTER. A conventional Sawyer–Tower circuit was used to measure the polarization hysteresis (P–E) loop at 20 Hz frequency.

3. Results and discussion

Fig. 1(i) shows the room temperature X-ray diffraction (XRD) patterns of KNN–LN samples calcined at 850 °C for 6 h and sintered at different temperatures. The XRD peaks are found to be sharp and distinct indicating good homogeneity and crystallinity of the samples [26]. Single perovskite phase is developed at 1050 °C and 1080 °C sintering temperature, whereas at 1100 °C sintering temperature secondary phase along with the perovskite phase is developed in KNN–LN samples. The development of secondary phase in KNN–LN samples sintered at 1100 °C may be due to the evaporation of potassium oxide since the volatilization temperature of potassium oxide (K_2O) is at ~800 °C [27,28]. The existence of mixed structure is confirmed by indexing the XRD patterns of KNN–LN ceramics with JCPDS card no. 71-2171 (orthorhombic) and 77-0037 (tetragonal). Fig. 1(ii) shows the enlarged XRD patterns of KNN–LN system sintered at different temperatures. The splitting of peaks between 44.5° and 47° at 1050 °C and 1080 °C sintering temperature confirms the MPB nature of the system [29].

Fig. 2 shows the SEM micrographs of KNN–LN samples sintered at different temperatures. It is distinctly observed that as the sintering temperature increases from 1050 °C to 1080 °C, the grain size increases from 3.2 μm to 5.3 μm and pore size decreases. It can be explained according to the phenomenological kinetic grain growth equation that with the increase in sintering temperature grain size increases [30]. It can also be observed that as the sintering temperature further increases to 1100 °C, the grain size of the sample decreases, which may be due to the evaporation of potassium oxide.

Fig. 3 shows the density of the KNN–LN samples as a function of sintering temperature. The density of KNN–LN samples first increases with the increase in sintering temperature, and then decreases at 1100 °C sintering temperature. Maximum density of ~4.385 g/cm^3 is obtained for the KNN–LN sample sintered at 1080 °C. The decrease in density of KNN–LN sample sintered at 1100 °C may be due to the evaporation of potassium oxide [31].

Fig. 4 shows the frequency dependence of ε_r and tan δ of KNN–LN samples sintered at different temperatures. The room temperature value of ε_r at 1 MHz frequency of KNN–LN samples sintered at 1050 °C, 1080 °C and 1100 °C are found to be ~820, 936 and 653 whereas values of tan δ are ~0.008, 0.016, and 0.007, respectively. The increase in ε_r with the

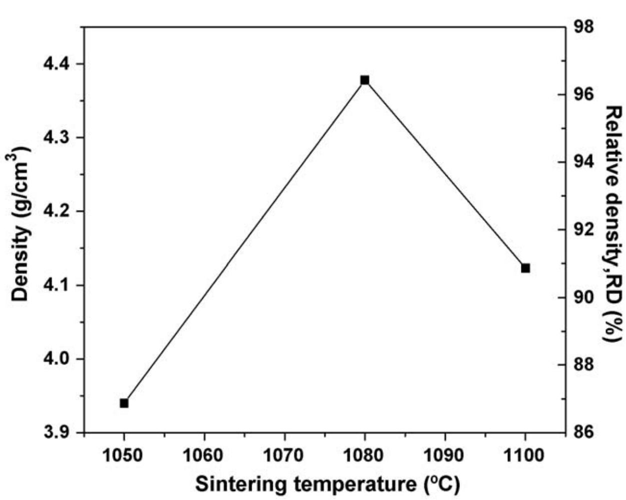

Fig. 3. Bulk density (BD) as a function of sintering temperature.

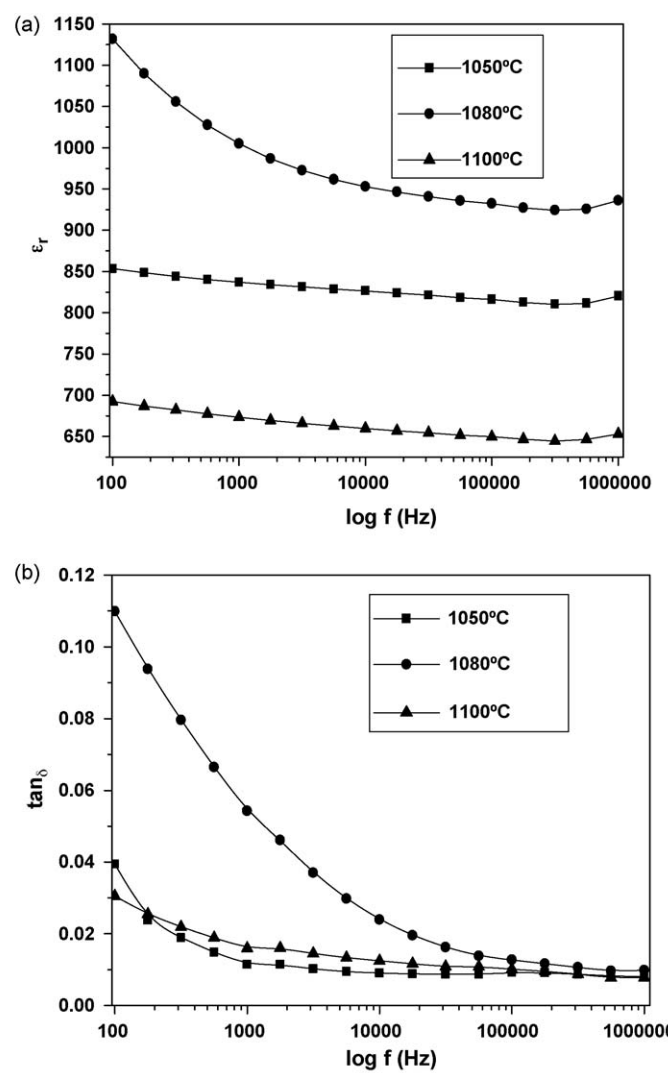

Fig. 4. (a) Frequency dependence of dielectric constant (ε_r). (b) Frequency dependence of dielectric loss (tan δ).

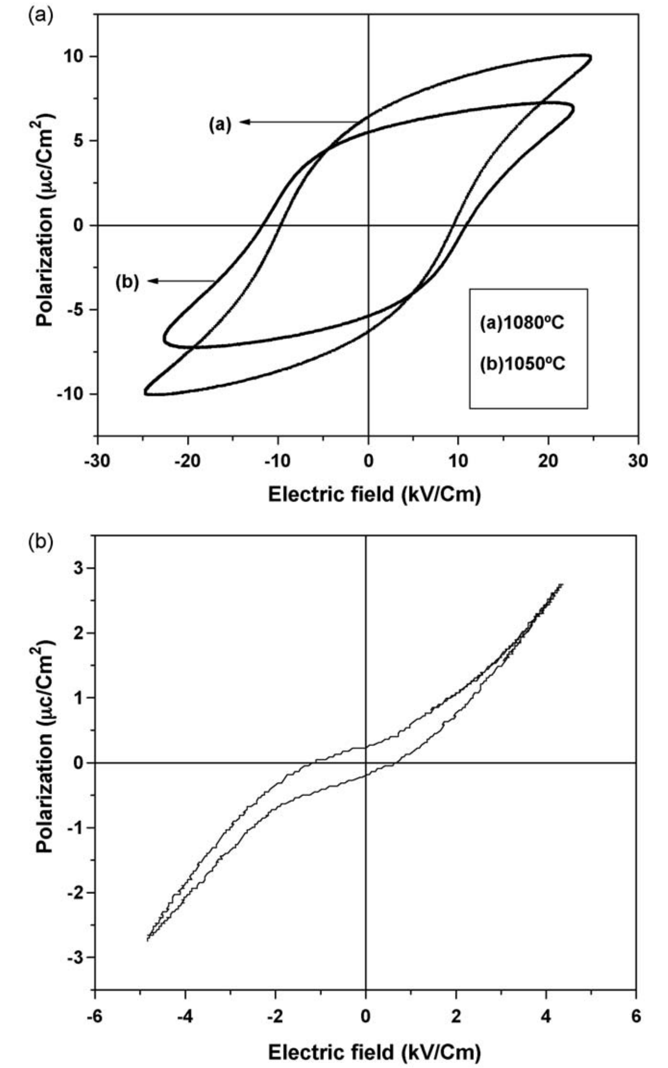

Fig. 5. (a) P–E loop of KNN–LN samples sintered at 1080 °C and 1050 °C. (b) KNN–LN sample sintered at 1100 °C.

increase in sintering temperature can be attributed to the increase in grain size. Now, the increase in grain size leads to a decrease in thickness of the relatively more insulating grain boundary layer [32] and therefore ε_r value increases with the increase in grain size. It is distinctly observed that ε_r and tan δ of all the KNN–LN samples decreases with the increase in frequency. The decrease in the value of ε_r can be explained on the basis of decrease in polarization with the increase in frequency. Polarization of a dielectric material is the sum of the contributions of dipolar, electronic, ionic and interfacial polarizations [33]. At low frequencies all the polarizations respond easily to the time varying electric field but as the frequency of the electric field increases different polarization contributions filters out, as a result, the net polarization of the material decreases which leads to the decrease in the value of ε_r. Further, the decrease of tan δ with the increase in frequency can be explained by Debye formula [34]. According to this formula, at lower frequencies tan δ is inversely proportional to frequency which explains the decrease in tanδ with frequency [34].

Fig. 5 shows the polarization vs. electric field (P–E) loops of KNN–LN samples sintered at different temperatures. It is clearly observed that the shapes of P–E loop greatly vary with the sintering temperature. The P–E loops of the samples sintered at 1050 °C and 1080 °C are well developed whereas abnormal P–E loop is obtained for the KNN–LN sample sintered at 1100 °C. Maximum remnant polarization (P_r) ~6.4 μC/cm^2 and minimum coercive field (E_c) ~9.6 kV/cm has been found for the sample sintered at 1080 °C. The increase in P_r for the KNN–LN sample sintered at 1080 °C can be associated with the increase in domain wall motion with the increase in grain size which helps in switching the domains and hence affects the polarization [35]. The appearance of abnormal P–E loop at 1100 °C may be due to the non-uniform grain size, evaporation of potassium oxide and development of non-ferroelectric secondary phase.

4. Conclusions

Dense KNN–LN samples have been synthesized by conventional solid state reaction route. With the increase in sintering temperature, the grain growth, densification and the ferroelectric properties were enhanced however at 1100 °C sintering temperature, the structure and ferroelectric properties were deteriorated. The KNN–LN samples sintered at 1080 °C showed excellent microstructural and ferroelectric properties, i.e. $\rho \sim 4.385$ g/cm^3, $P_r \sim 6.4$ μC/cm^2, $E_c \sim 9.6$ kV/cm, $\varepsilon_r \sim 936$ and tan $\delta \sim 0.016$. The results in this study indicated that KNN–LN system can be a suitable candidate to replace the lead-based materials.

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