Raman and Dielectric Studies on Lead free \((K_{0.5}Na_{0.5})\) NbO\(_3\) Piezoelectric Ceramics

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Abstract. The present study demonstrates the preparation of \((K_{0.5}Na_{0.5})\)NbO\(_3\) (KNN) ceramics at low temperatures by using mechanochemical synthesis process. The effect of calcination temperature on structure, and dielectric properties of KNN ceramics have been studied systematically. It is found that both the dielectric constant and tan\(\delta\) of KNN ceramics as a function of temperature exhibited two sharp phase transitions indicating orthorhombic to tetragonal \((184^\circ C)\) and ferroelectric tetragonal to paraelectric cubic phases \((385^\circ C)\). It was observed that the ceramics calcined at 700\(^\circ\)C and sintered at 1000\(^\circ\)C shows the high Curie temperature, high dielectric permittivity and low dielectric loss. Further with increase in calcination temperature, the ferroelectric tetragonal to paraelectric cubic phase shifted to lower temperatures. Raman spectra of KNN ceramics were obtained and the three characteristic Raman peaks in the spectra of KNN are related to the internal vibrations of the NbO\(_6\) octahedron. The effect of processing parameters on dielectric properties and phase transitions studied systematically.

1. Introduction

Lead-free piezoelectric materials have been studied due to the environmental and biological advantages and almost equivalent piezoelectric properties to PZT [1, 2]. Despite its excellent piezoelectric properties, one of the major disadvantages of PZT is potential lead volatility at higher temperatures. It is known that lead poisoning can result in adverse effects on health such as reduced IQ, slowed body growth, and kidney damage [3].

\((K_{0.5}Na_{0.5})\)NbO\(_3\) (KNN)-based piezoelectric materials have drawn great attention due to their competitive piezoelectric properties among lead-free ceramics and broad operation temperature range. \((K_{0.5}Na_{0.5})\)NbO\(_3\) (KNN) is currently considered as a potential candidate of lead-free piezoelectric materials. KNN is a solid solution of ferroelectric KNbO\(_3\) and antiferroelectric NaNbO\(_3\) [4]. KNN exhibits an orthorhombic structure at room temperature. Saito et al. reported that most of the piezoelectric properties are comparable to those of PZT [1]. Pure KNN-ceramics have difficulty becoming fully dense using ordinary sintering methods. This is because the Na\(_2\)O and K\(_2\)O easily evaporate at high temperatures. However, densification of KNN ceramics is reported to be difficult at low temperatures. The present study demonstrates the preparation of KNN ceramics at low temperatures by using solid state reaction process. The effect of calcination temperature on structure, and dielectric properties of KNN ceramics as a function of temperature have been studied systematically.

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2. Experimental Procedure
Samples of KNN ceramics were prepared by conventional solid-state reaction method from individual high purity powders (>99.99%) of $\text{K}_2\text{CO}_3$, $\text{Na}_2\text{CO}_3$, and $\text{Nb}_2\text{O}_5$. The starting materials were mixed in accordance with desired stoichiometry of the KNN ceramics. A planetary ball mill (Fritsch GmbH, Germany) was used to prepare these powders. The powders were mixed with propanol and the mixed powders were dried and calcined at different temperatures (600°C, 700°C, 800°C and 900°C) for three hours. The calcined powders again grounded for 5 hours and are uniaxially pressed into cylindrical samples of diameter 13mm and height 2mm isostatically. These pellets were sintered at temperature 1000°C for 5 hours. The phase purity of the calcined powders and the sintered pellets was identified by X-Ray Diffractometer (Bruker D8). The dielectric constant and dielectric loss were measured using LCR meter (Wayne Kerr Electronics Pvt. Ltd., Model 1J43100). A PID temperature controller is used to control the temperature of the heating assembly up to 500°C. The Raman spectra of the samples were collected using a LABRAM HR800 Raman spectrometric analyzer developed by JOBIN YVON with a He-Ne source.

3. Results and Discussions
Figure 1 shows the XRD patterns of the KNN ceramics, calcined at different temperatures and sintered at 1000°C for 5 hours. It is observed that all the samples exhibited single orthorhombic phase and the sample calcined at 600°C exhibited the secondary phase peaks but the single phase has been confirmed at 650°C. Chang et al [5] reported the single phase for the KNN ceramics at 850°C. This shows the importance of mixing the initial mixing reagents by high energy milling in reducing the initial particle size and uniform mixing for the low temperature synthesis of KNN ceramics. The basic principle of processing temperature by high energy milling is that this synthesis not only makes the material finer but also includes structural changes, phase transformations and even solid-state reactions among the solid reagents. These physicochemical changes occur due to the efficient transformation of the mechanical energy of the grinding media to the material particles and the intensive mechanochemical force during the milling process. The smaller particle sizes would accelerate the chemical reaction between the initial reagents and also reduces the reaction temperature. It is also observed that as the calcination temperature increases the peaks are broadened and peak position shifted to lower side. The average crystallite sizes of the KNN ceramics are in the range of 60nm to 20nm.

![Figure 1. XRD patterns of the KNN ceramics calcined at different temperatures and sintered at 1000°C for 5 hours.](image-url)
Figure 2. SEM image of the KNN ceramics calcined at (a) 600°C, (b) 700°C and sintered at 1000°C for 5hrs.

The SEM micrograph of the KNN samples sintered at 1000°C for 5 hours is shown in Figure 2. The surface morphology shows the rectangular size of the grains with dense packing with an average grain size of 1.2μm. The densities of the KNN ceramics were in the range of 84-90%.

Figure 3. Raman spectra for the KNN ceramics calcined at different temperatures and sintered at 1000°C for 5 hours.

The Raman spectroscopy is an extremely sensitive tool to study at a local scale the structural deformations of perovskites, which are induced both by the tilting of octahedra and by the cationic displacements. These structural modifications induce large changes in internal modes associated with NbO\textsubscript{6} octahedron and thus a modification of the Raman spectra. Figure 3 shows the Raman spectra of KNN powders recorded at room temperature. The spectra measured are similar to those reported earlier [6, 7]. The Raman spectrum can be described by means of internal vibrations of the octahedral NbO\textsubscript{6} molecular group. The free NbO\textsubscript{6} group exhibits cubic O\textsubscript{h} symmetry, whose dynamics is characterized by 15 internal vibrational degrees of freedom or six normal vibrations $\nu$:

$$\Gamma_{\text{vib}} = A_{1g}(\text{Raman}) + E_{g}(\text{Raman}) + 2T_{1u}(\text{IR}) + T_{2g}(\text{Raman}) + T_{2u}(\text{silent}).$$

The $\nu_1$ vibration is related to symmetric $A_{1g}$ type mode, which represents the Nb-O bonds vibration, $\nu_2$ means doubly degenerated $E_g$ vibrations of the O-Nb-O bonds and $\nu_3$ is triply degenerated $T_{1u}$ vibration of the Nb-O bonds. The $\nu_{1}$, $\nu_{2}$, $\nu_{3}$ vibrations are the stretching modes of the NbO\textsubscript{6} octahedral group. The other three normal vibrational modes: triply degenerated $\nu_{4}$ of $T_{1u}$ symmetry of the O-Nb-O bonds, triply degenerated $\nu_{5}$ with $T_{2g}$ symmetry of the O-Nb-O and triply degenerated $\nu_{6}$ with $T_{2u}$ symmetry of the O-Nb-O bonds are all the bending vibration modes. Thus there are three characteristic Raman peaks ($\nu_{1}=870 \text{ cm}^{-1}$, $\nu_{2}=620 \text{ cm}^{-1}$ and $\nu_{3}=250 \text{ cm}^{-1}$) in the spectra of KNN which are related to the internal vibrations of the NbO\textsubscript{6} octahedron. The broad Raman bands peaking at 250 and 620 cm\textsuperscript{-1} in the cubic phase shown in Figure 3 are a clear signal of disorder, for Raman activity in cubic perovskites is symmetry forbidden. These features are common in the cubic phase of perovskite ferroelectrics and they signal local static and/or dynamic disorder reminiscent of the distortions in ferroelectric phases [7].

Figure 4 (a) shows the temperature dependence of dielectric constant of KNN ceramics calcined at different temperatures and sintered for 5 hours. It is observed that two sharp phase transitions are
observed in dielectric constant versus temperature curve corresponding to the phase from orthorhombic to tetragonal (184°C) and tetragonal to cubic (385°C) respectively. The phase transition around 184°C is the ferroelectric phase transition temperature whereas the transition around 385°C is the ferroelectric to paraelectric transition temperature which is also called as the Curie temperature (T_C). It is observed that the KNN sample calcined at 600°C exhibited lowest Curie temperature, low dielectric constant and high dielectric loss attributed to the presence of secondary phases on the other hand KNN sample calcined at 700°C exhibited the highest dielectric constant and lowest loss. Further with increasing the calcination temperature dielectric properties as well as Curie temperature decreases, this may due to the volatilization of alkali elements. The dielectric anomaly, near the T_C, can be explained by the fact that soft mode frequency softens, giving rise to large value of dielectric constant [10]. The variation in tanδ as a function of temperature for the KNN samples calcined at different temperatures and sintered at 1000°C was shown in Figure 4(b).

![Figure 4](image)

**Figure 4.** Temperature Variation of (a) relative dielectric permittivity and (b) tanδ of KNN ceramics calcined at different temperatures and sintered at 1000°C.

The variation in tanδ as a function of temperature is also similar to the behaviour of the dielectric constant. In the present study it is interesting to note that the observed tanδ values are much lower and can be attributed to the higher densities and uniform microstructure and the obtained tanδ values were in the range of 0.006 to 0.14. The higher loss in the case of the sample calcined at 600°C may be due to the secondary phases which are identified by XRD patterns. It is well known that the dielectric loss is heavily influenced by the secondary phases. In the present study the obtained lower dielectric properties compared to the reported values in the literature and can be attributed to the lower densities and the smaller grain sizes [5]

4. Conclusions
In conclusion, KNN ceramics are prepared by solid state reaction method. The effect of calcination temperature on structure and dielectric properties of KNN ceramics are investigated. The phase pure KNN ceramics were formed at 700°C itself with the initial small particles size. The Phase transitions from orthorhombic to tetragonal (184°C) and ferroelectric tetragonal to paraelectric cubic (385°C) phase transitions are observed in the present study. The KNN ceramics calcined at 700°C and sintered at 1000°C exhibited the highest dielectric constant and lowest dielectric loss. The obtained lower dielectric constant values can be attributed to the lower densities and the smaller grain sizes

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