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Effect of NiO Sintering Aid on the Electrical Properties of KNN-LST Lead-free Piezoceramics

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ABSTRACT

The current research focuses on the synthesis and characterization of sodium potassium niobate (KNN), a lead-free piezoelectric compound. The objective is to replace lead-based compounds like PZT using KNN-LST, which is sodium potassium niobate piezoceramic powder doped with lithium, antimony, and tantalum. To this end, solid-state method was employed to sinter the samples at 1110 °C with varying percentages of NiO sinter aid (0%, 0.75%, 1.5%, and 2.25%). X-ray diffraction analysis confirmed the formation of pure KNN-LST perovskite phase at 1110 °C with a composition containing 1.5% NiO. Scanning electron microscope images also demonstrated that cubic particles inherent in KNN were observed in samples with no NiO addition as well as those containing 0.75% and 1.5% NiO; however, these particles were transformed into cylindrical grains when incorporating 2.25% NiO. With an increase in the sintering percentage from zero NiO content to higher amounts, sample density also increases from approximately 85% up to its peak at around 94%, followed by a slight decrease by about 91%. Similarly, the dielectric coefficient increased from approximately850 without any contribution from NiO sinter addition up to1500 upon addition of 1.5%NiO sinter but then, it decreased again by approximately 1200 followed by addition of 2.25% NiO sinter. Conversely, dielectric loss initially reduced from roughly 0.14% during no NiO sinter addition by merely 0.04% during 1.

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1. INTRODUCTION

The most important piezoelectric ceramic (lead titanate zirconate) has great applications in transducers, sensors and actuators because of its remarkable ferroelectric properties and high electromechanical nature (Chermahini et al., 2020) (Schmid, 2008) (Chermahini et al., 2018). Investigation of the lead-free piezoelectric materials gains significance particularly because of the undeniable damages of Pb to the environment (Surowiak et al., 2001) (Shieh et al., 2007) (Sushkov et al., 2008) (Yamamoto, 1996) (Cross, 1987). In addition, a great deal of attention has been paid to the sodium-potassium niobate (KNN) as the most important candidate for lead free material. It is an atomic mixture of NaNbO3 (NN) and KNbO3 (KN) ceramics (Yamamoto, 1996) (Cross, 1987) (Shafiee et al., 2019). The special torsion of octahedral voids in the NN ceramics makes its crystal structure more complicated than KN symmetry (Liu & Ren, 2009) (Halliday, 2005) (Kumar & Pattanaik, 2013) (Marandian Hagh et al., 2007) mainly due to the unfitting size of Na cations for corners of perovskite structure (Cross, 1987). Therefore, from the energy point of view, the structure of KN is more stable than the NN symmetry (Li et al., 2013) (Ye, 2008) (Nan et al., 2008) (Eerenstein et al., 2006). It is expected that the structure of KNN be similar to KN due to its high stability (Pullar, 2012). Up to 220 °C, the KNN

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piezoceramics show a duplicated unit cell with orthorhombic system (Shafiee et al., 2019). This orthorhombic structure of KNN (at room temperature) transforms into tetragonal symmetry at 220 ˚C. This effective phenomenon is known as Polymorphic Phase Transition (PPT) (Merz, 1956). It is established that the great electromechanical nature of the KNN system is a function of PPT behavior as well as Morphotropic Phase Boundary (MPB) (Bibes & Barthélémy, 2008) (Franke et al., 1994). The latter occurs when two types of piezoelectric symmetries are simultaneously present in the individual composition (Halliday, 2005). In the KNN case, the PPT phenomenon occurs at about 220 ˚C, and the MPB is detected in the K0.5Na0.5Nb2O5 composition (Franke et al., 1994). In order to decrease the PPT temperature in the application area, use of some additives such as lithium, tantalum, and antimony are frequently recommended (Schmid, 2008) (Chermahini et al., 2018) (Surowiak et al., 2001) (Shieh et al., 2007) (Sushkov et al., 2008) (Yamamoto, 1996) (Cross, 1987) . In addition, some sintering aids such as NiO, MnO_2, and Y_2O_3 that are frequently used in KNN based piezoceramic to improve the densification of bulk ceramics (Chermahini et al., 2018) (Surowiak et al., 2001) (Shieh et al., 2007) (Sushkov et al., 2008) (Yamamoto, 1996) (Cross, 1987) . This study aims to address the synthesis challenges throughout the production process of ceramic powders based on sodium-potassium niobates to achieve high-quality tablets with the desired electrical properties. Key considerations include precise initial mixing techniques and preventing evaporation of volatile elements such as sodium, potassium, and lithium. The traditional ceramic methods were employed in the present study to prepare lead-free piezoceramic powders to subsequently investigate their dielectric and piezoelectric characteristics.

2. MATERIALS AND METHODS

High-purity primary powders including Na2Co3, Ta2O5, Sb2O3, Nb2O5, K2Co3, and Li2Co3 were purchased from Aldrich company and then, they were utilized to synthesize piezoceramic powder using sodium-potassium niobate doped with antimony (Sb), lithium (Li), and tantalum (Ta) through the ceramic method. To mitigate moisture absorption by sodium and potassium carbonate powders during synthesis, a pre-drying step was conducted at 110 °C for one day. The solid-state approach was employed for the synthesis process at 900 ºc for 2 h. The synthesis materials were combined with 0 to 2.25 % wt. Ni0. Then, the resulting powder was mixed with a weight ratio of 3% PVA solution. Tablets of approximately13 mm in diameter and 0.7 mm in thickness were prepared under the pressure of 300 MPa using uniaxial press. The tablets were sintered at 1120 ºC for 2 h. The relative density of the sintered samples was determined based on Archimedes' method. Subsequently, X-ray diffraction analysis was carried out using Philips device within two-theta range between 20° and 80°. CuKα X-ray wavelength production was verified with the step size of 0.02º and scan rate of 0.5 step/s. Scanning Electron Microscope (SEM, PHILIPS XL30) was employed for microstructural characterization, investigating the particle morphology and porosity in the KNN-LST piezoceramic. Dielectric properties were measured using an LCR meter (CHY 41R) at the frequency of 10 KHz.

3. RESULTS AND DISCUSSION

Figure 1 illustrates the X-Ray Diffraction (XRD) pattern of the synthesized piezoceramic based on sodium potassium niobate doped with lithium (Li), antimony (Sb), and tantalum (Ta) at the synthesis temperature of 1110 °C.

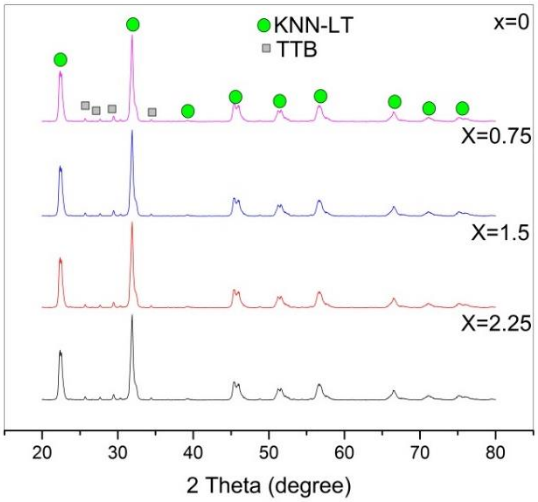

Figure 1. The XRD pattern of sintered samples at 1110 oC with various NiO content (x)

The analysis was conducted using Xpert software, enabling phase and structure investigations on the synthesized powder. The observed peaks correspond to both the main peaks of sodium potassium niobate and additional peaks attributed to the impurity phases , i.e., Tetragonal Tungesten Boronze (TTB), formed during the synthesis process of KNN-LST piezoceramics. In Figure 1, the circles represent the main peaks while the squares show the impurity peak symbols. The desired structure for piezoelectric sodium potassium niobate ceramic doped with Li, Sb, and Ta is a perovskite structure without central symmetry. However, the presence of an impurity phase in sodium potassium niobate-based piezoelectrics has a detrimental effect that causes a sharp decline in electrical properties (Schmid, 2008). In case the concentration of impurities exceeds an optimal value specific to electroceramic applications, it can even render the electrical properties ineffective (Chermahini et al., 2020). The identified impurity phase known as tungsten-bronze exhibits a chemical formula K3LiNb6O17 (Sushkov et al., 2008). Its formation results from the incomplete reaction between raw materials during the synthesis process. This tungsten-bronze impurity phase forms at lower temperatures and remains stable up to 850°C; therefore, its removal from the system becomes essential to enhance the electrical properties in piezoceramic samples. Overall, these results highlight not only successful synthesis of sodium-potassium niobate-based piezoceramics but they emphasize the necessity of careful control over impurities to achieve desirable electrical characteristics essential for effective utilization in various electroceramic applications.

The SEM images provided in Figure 2 verify the presence of piezoelectric phase formation across different percentages of sintering agent.

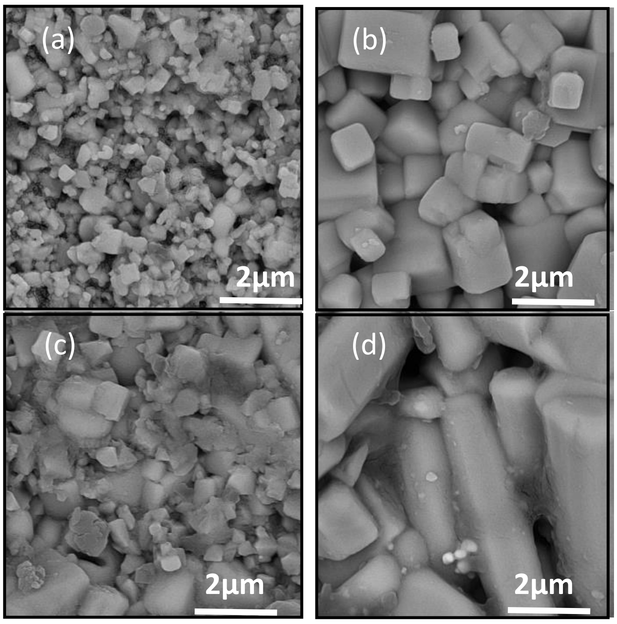

Figure 2. The SEM migrograph of sintered samples at 1110 oC for various NiO content (x)

The captured images taken by a scanning electron microscope (FESEM) on the fractured surfaces of these samples illustrate the size and shape of piezoceramic particles in sodium potassium niobate doped with lithium, antimony, and tantalum at various sintering agent percentages ranging from 0% to 2.25%. Figure 2 clearly shows the cubic morphology characteristics of KNN-LST piezoceramics in samples containing 0% and 0.75% sintering aids, indicating successful formation of the desired phase. Comparisons made between these observed morphologies and previous studies are noteworthy (Surowiak et al., 2001). In samples with 1.5% sinter addition, apart from grains exhibiting cubic morphology, the presence of a molten phase is visibly evident as well. As observed in the SEM micrographs, from 0 to 1.5% sintering aids, the whole porosity of ceramics decreases. It can be expected that in the mentioned range, the sample density decreases. This observation aligns with the typical characteristics seen in piezoceramic samples where increasing percentage of sinter aid results in larger grain growth for greater structural uniformity ultimately leading to higher density. As depicted by their considerable distribution within each sample composition, all piezoceramic compositions exhibit cubic particle morphology when varying amounts of sinter assistance are employed. Moreover, the absence of defects along boundaries indicates that agglomerates have been successfully broken down during pressing, resulting in the presence of KNN-LST cubic particles within the powder structure. The sample containing 2.25% displays a change in seed morphology accompanied by specific outward growth tendencies.

Figure 3 illustrates the relationship between composition and relative density in various percentages of NiO sinter contribution, ranging from 0% to 2.25%.

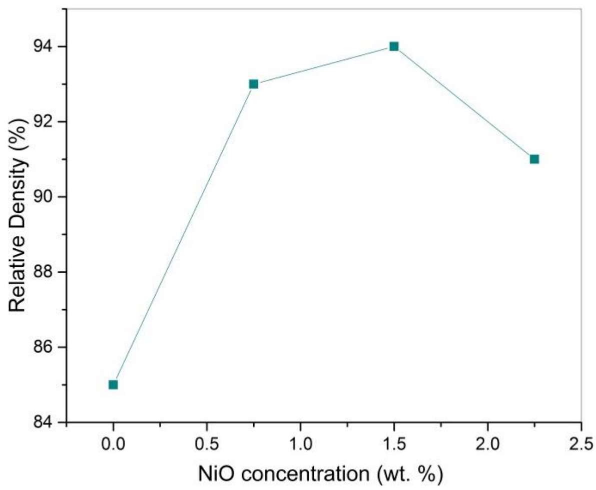

Figure 3. The relative density of sintered samples at 1110 ºC for various NiO content (x)

In the piezoceramic sample of sodium potassium niobate doped with lithium, antimony, and tantalum, the relative density increased gradually from 85% at 0%. NiO sintering aid to a peak value of 94% at 1.5% NiO sintering aid before declining to 2.25%. These findings indicate that the relative density of this particular piezoceramic is highly sensitive to the percentage of sintering aid used. Notably, a relative density above 90%, achieved at the content of 1.5%, signifies excellent quality for sodium potassium niobate-based piezoceramics. This increase can be attributed to the formation of an intermediate phase (Madab phase) between grains during sintering, which promotes proper grain-to-grain bonding and enhances piezoelectric properties.

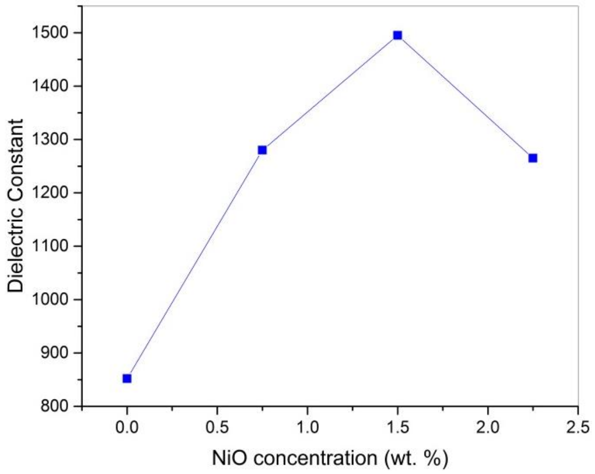

Figure 4. The dielectric constant of sintered samples at 1110 ºC as afunction of NiO content (x)

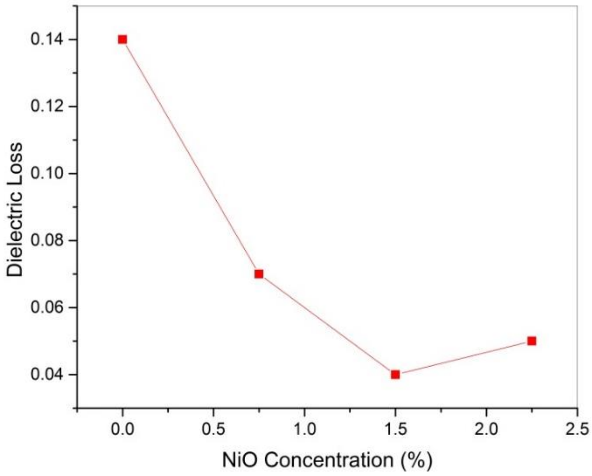

Figure 5. The dielectric loss of sintered samples at 1110 ºC as afunction of NiO content (x)

Further increment in the sintering aid content from 1.5 to 2.25 % causes a decrease in the relative density probably due to the abnormal grain growth during sintering caused by higher amount of sintering aids content (Surowiak et al., 2001) (Sushkov et al., 2008) (Sushkov et al., 2008) (Sushkov et al., 2008) (Shafiee et al., 2019). Figure 4 shows variations in dielectric constant (Ɛr) across different percentages of NiO sinter contribution in sodium potassium niobate samples doped with lithium, antimony, and tantalum.

4. CONCLUSION(S)

The synthesis of KNN-LST compound with a perovskite structure was successfully achieved using the solid-state method and calcination process, and the findings are summarized in the following. The solid-state method proved effective in eliminating the impurity peaks caused by incomplete raw material reactions, leading to improved piezoelectric and dielectric properties in the samples. Upon employing the solid-state method along with ball milling, the particle size was reduced by 2 micrometers, thus enhancing the overall quality of the synthesized KNN-LST compound. The dielectric constant of the produced KNN-LST composition initially increased and then decreased as the percentage of sintering aid contribution was raised, implying that there was an optimal percentage for achieving maximum dielectric constant. Similarly, as the sintering aid contribution percentage increased, the dielectric loss of the produced KNN-LST compound first decreased and then increased, highlighting an optimal range for minimizing dielectric loss again. Based on our findings, it can be concluded that an ideal sintering aid contribution percentage to achieve the desired properties is 1.5% for KNN-LST combination. Sintering aids at the concentration of 1.5% NiO resulted in complete formation of KNN-LST composition during the sintering process. Overall, these results provide valuable insights into optimizing synthesis methods and identifying critical factors influencing key properties such as piezoelectricity and dielectrics within KNN-LST compounds.

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