Advanced Ceramics Progress: Vol. ?, No. ?, (Season 202?) ??-??

Materials and Energy Research Center
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Advanced Ceramics Progress

Journal Homepage: www.acerp.ir

Original Research Article

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

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ARTICLE INFO

Article History:

Received? Month 202?
Received in revised form? Month 202?
Accepted? Month 202?

Keywords:

Piezoelectric
KNN
Solid-state
microstructure

ABSTRACT

The paper 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 by utilizing KNN-LST, which is sodium potassium niobate piezoceramic powder doped with lithium, antimony, and tantalum. The solid-state method was employed to sinter samples at 1110 °C with varying percentages of NiO sinter aid (0%, 0.75%, 1.5%, and 2.25%). X-ray diffraction analysis revealed the formation of pure KNN-LST perovskite phase at 1110 °C with a composition containing 1.5% NiO. Scanning electron microscope images 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 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 exhibited an upward trend from approximately 85% to its peak at around94%, followed by a slight decrease to about91%. Similarly, the dielectric coefficient increased from approximately850 without any contribution from NiO sinter addition up to1500 when using1.5%NiOsinter addition but then decreased again reaching around1200with a2.25%NiOsinter addition. Conversely, dielectric loss initially reduced from roughly0.14%during no NiOsinter addition down to merely0.04%during1.

https://doi.org/10.30501/acp.2018.90833

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 [1-3]. Lead-free piezoelectric materials are essentially investigated because of the undeniable damages of Pb for the environment[4-8]. The sodium-potassium niobate (KNN) as the most important candidate for lead free materials have been greatly paid attention. It is an atomic mixture of NaNbO3 (NN) and KNbO3 (KN) ceramics[7-9]. The special torsion of octahedral voids in NN ceramics makes its crystal structure more complicated than KN symmetry[10-13]. The unfitting size of Na cations for corners of perovskite structure causes this phenomenon [8]. Therefore, from the energy point of view the structure of KN is more stable than the NN symmetry[14-17]. It is expected that the structure of KNN be similar to KN due to its high stability [18]. Up to 220 oC, the KNN piezoceramics shows a duplicated unit cell with orthorhombic system [9]. This orthorhombic structure of KNN (at room temperature) converts to tetragonal symmetry (at 220 oC). This

Please cite this article as: Lastname1, F1., Lastname2, F2. A., Lastname3, F3. B., "Title must be Times New Roman, 14, Bold, Justify", ***Advanced Ceramics Progress***, Vol. ?, No. ?, (202?), ??-??. https://doi.org/10.30501/acp.2018.90833

effective phenomenon is known as polymorphic phase transition (PPT) [19]. It is established that the great electromechanical nature of KNN system is a function of PPT behavior as well as morphotropic phase boundary (MPB) [20-21]. The latter can be occurred with simultaneous existence of two types of piezoelectric symmetries at the individual composition) [11]. For KNN case, the PPT phenomenon is occurred at about 220 oC and the MPB reported in about K0.5Na0.5Nb2O5 composition [20]. In order to decrease in PPT temperature towards the application area, using of some additives such as lithium, tantalum and antimony are frequently reported [2-8]. In addition, some sintering aids such as NiO, MnO_2 and Y_2O_3 frequently used in KNN based piezoceramic to improved densification of bulk ceramics [3-8] This study aims to address synthesis challenges encountered during the production process of ceramic powders based on sodium-potassium niobates to achieve high-quality tablets with desired electrical properties. Key considerations include precise initial mixing techniques and preventing volatile element evaporation (sodium, potassium, lithium). In this project conducted using traditional ceramic methods, lead-free piezoceramic powders were prepared for subsequent investigation of their dielectric and piezoelectric characteristics.

2. MATERIALS AND METHODS

High-purity primary powders, sourced from Aldrich company, including Na2Co3, Ta2O5, Sb2O3, Nb2O5, K2Co3, and Li2Co3 were utilized to synthesize piezoceramic powder based on sodium-potassium niobate doped with antimony (Sb), lithium (Li), and tantalum (Ta) using 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 °c for 2 h. The synthesis materials was combined with 0 to 2.25 % wt. Ni0. Then the resulting powder was mixed with a weight ratio of 3% PVA solution. Tablets measuring approximately13 mm in diameter and 0.7 mm in thickness were prepared under pressure (300 MPa) using uniaxial press. The tablets were sintered at 1120 °C for 2 h. The relative density of sintered samples was determined utilizing Archimedes' method. 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 step size 0.02° and scan rate of 0.5 step/s. Scanning electron microscope (SEM, PHILIPS XL30) was employed for microstructural characterization, investigating particle morphology and porosity in the KNN-LST piezoceramic. Dielectric properties were measured using an LCR meter (CHY 41R) at a 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 a synthesis temperature of 1110 °C.

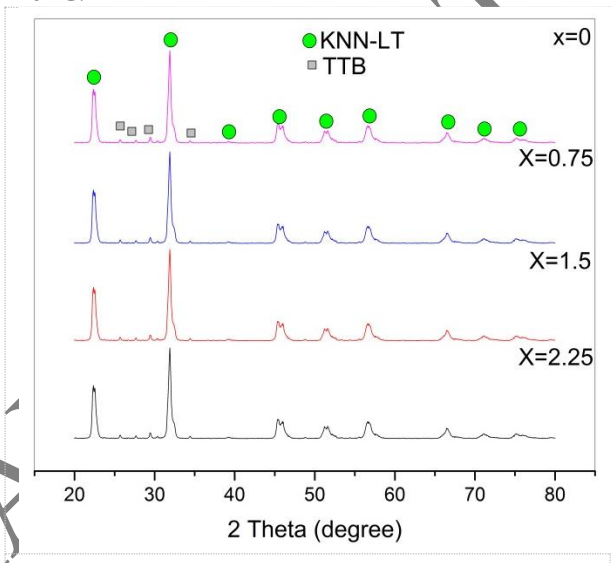

Figure 1. The XRD pattern of sintered samples at 1110 °C with various NiO content (x)

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 impurity phases (Tetragonal Tungesten Boronze(TTB)) formed during the synthesis process of KNN-LST piezoceramics. In Figure 1, circles represent main peaks while squares represent 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, it was found that the presence of an impurity phase in sodium potassium niobate-based piezoelectrics has a detrimental effect causing a sharp decline in electrical properties [2]. If the concentration of impurities exceeds an optimal value specific to electroceramic applications, it can even render the electrical properties ineffective [1]. The identified impurity phase known as tungsten-bronze exhibits a chemical formula K3LiNb6O17 [6]. Its formation occurs due to 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 crucial for enhancing electrical properties in piezoceramic samples. Overall, these results highlight not only successful synthesis of sodium-potassium niobate-based piezoceramics but also emphasize that careful control over impurities is necessary to achieve desirable electrical characteristics essential for effective utilization in various electroceramic applications.

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

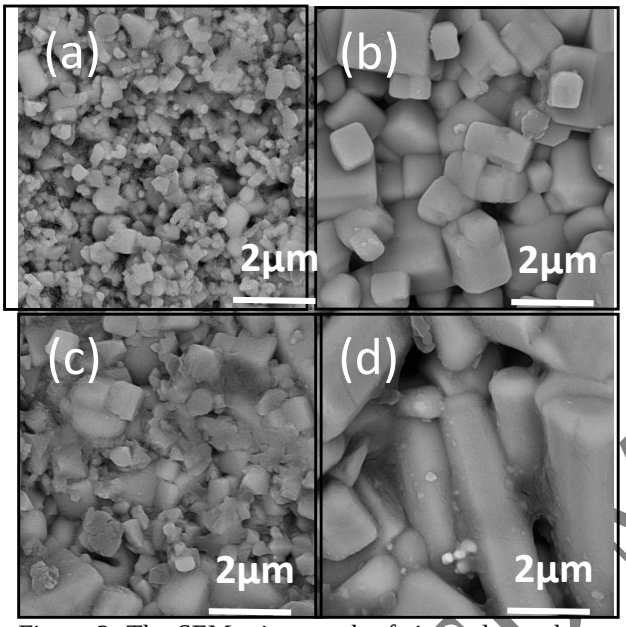

Figure 2: The SEM migrograph of sintered samples at 1110 oC for various NiO content (x)

Images captured using 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 characteristic 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 [4]. In samples with 1.5% sinter addition, apart from grains exhibiting cubic morphology, the presence of a molten phase is visibly evident as well. It can be observed in SEM micrographs that from 0 to 1.5% sintering aids the whole prosity of ceramics decreases. it can be expected that in mentioned range the density of sample decreases. This observation aligns with 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 KNN-LST cubic particles being present 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%.

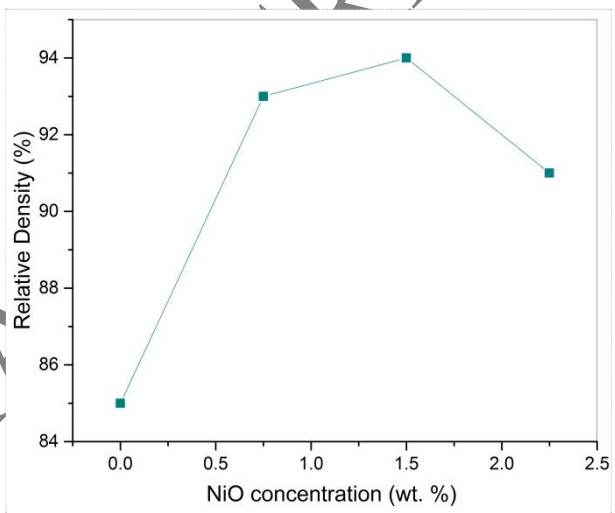

Figure 3. The relative density of sintered samples at 1110 ^{o}C for various NiO content (x)

For 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. Further increment in sintering aid content from 1.5 to 2.25 % causes decrease in relative density. It may be due to the abnormal grain growth during sintering caused by higher amount of sintering aids content [4, 6, 9]. In Figure 4, we observe variations in

dielectric constant (Ɛr) across different percentages of NiO sinter contribution in sodium potassium niobate samples doped with lithium, antimony, and tantalum.

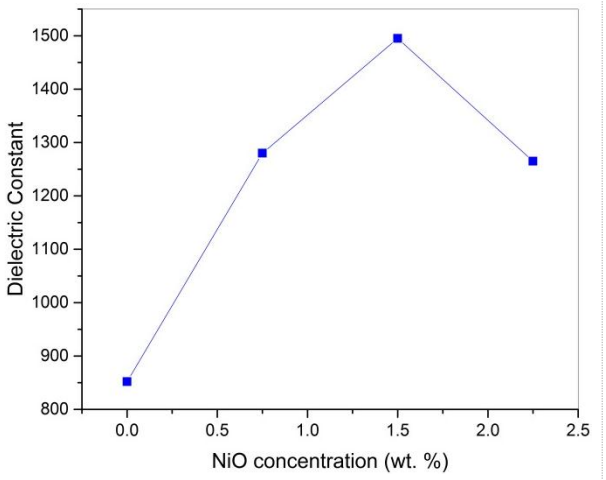

Figure 4. The dielectric constant of sintered samples at 1110 ºC as afunction of NiO content (x)

The dielectric constant initially increases from no added NiO sinter up until reaching its highest value at a contribution level of approximately 1.5%, after which it decreases as further contributions are made up to 2.25%. The maximum dielectric constant is observed when using a sintering aid concentration of around 1.5%. This increase can be attributed to grain growth facilitated by higher amounts of added sintering aid, resulting in the creation of molten phases between grains. Moreover, at this specific concentration level, the relative density increases while porosity decreases. Since porosity acts as a detrimental factor, the decrease leads to an increase in the dielectric constant [2, 3].

However, when sinter contribution exceeds 1.5%, grain morphology changes and growth becomes directional, hindering proper penetration and formation of a dense structure. Consequently, the desired grain-to-grain boundary structure is not achieved, resulting in a decrease in the dielectric constant. It is important to note that changing grain morphology and insufficient penetration hinder the formation of an optimal grain-to-grain boundary structure, leading to unsatisfactory results and lower dielectric constants. Figure 5 presents data on dielectric loss across different percentages of NiO sinter contribution (ranging from 0% to 2.25%). The dielectric loss constant decreases gradually from 0.14% at 0% NiO sintering aid to its lowest value of 0.04% at approximately 1.5% NiO sintering aid before slightly increasing again at 2.25%.

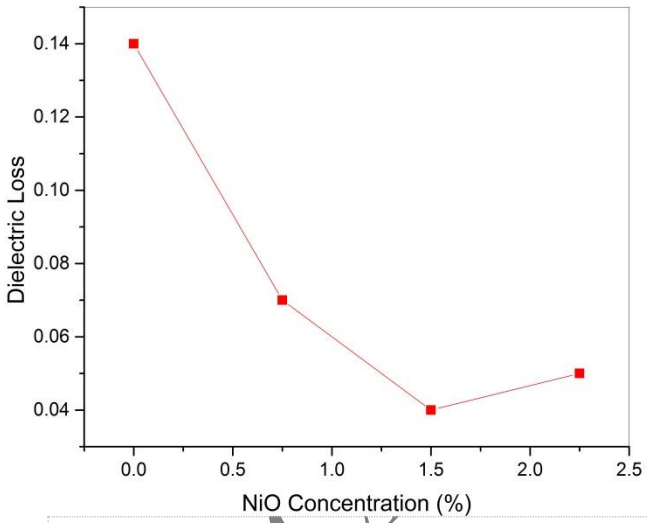

Figure 5. The dielectric loss of sintered samples at 1110 ºC as afunction of NiO content (x)

At 0% NiO concentration, where incomplete sintering occurs, a complete grain-boundary structure is not formed. As a result, there are fewer space charges and polarization within the structure, leading to increased dielectric loss. In higher percentages of sinter contribution, the grain-boundary structure is more developed, resulting in increased relative density as well as enhanced space charge distribution and polarization within the structure. This leads to reduced conductivity within grains and subsequently decreased dielectric loss [14]. The optimal percentage for minimum dielectric loss was found at approximately 1.5%, which corresponds with previous findings indicating improved capacitance properties with lower electrical losses. Beyond this point, at percentages higher than 1.5%, the decline in relative density leads to increased dielectric loss constant, rendering those samples less suitable.

Overall, these figures provide valuable insights into how varying percentages of NiO sinter contribute influence key properties such as relative density, dielectric constant (rɛ), and dielectric loss in sodium potassium niobate-based piezoceramics 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, yielding the following key findings: The solid-state method proved effective in eliminating impurity peaks caused by incomplete raw material reactions, leading to improved piezoelectric

and dielectric properties in the samples. By employing the solid-state method along with ball milling, particle size reduction down to 2 micrometers was achieved, enhancing the overall quality of the synthesized KNN-LST compound.The dielectric constant of the produced KNN-LST composition initially increased then decreased as the percentage of sintering aid contribution was raised. This suggests that there exists 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 then started increasing. Again highlighting an optimal range for minimizing dielectric loss. Based on our findings, it can be concluded that an ideal sintering aid contribution percentage in order to achieve desirable properties is 1.5% for KNN-LST combination. Sintering aids at a concentration of 1.5% NiO resulted in complete formation of KNN-LST composition during 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.

ACKNOWLEDGEMENTS

The authors appreciate the support of Mrs. N.pirkhalili during the present work.

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HIGHLIGHTS

- SEM Images Confirm Cubic Phase: SEM images validate successful formation of cubic phase in piezoceramics.

- Relative Density Increases Gradually: Relative density increases gradually with NiO sintering aid, indicating excellent quality.
- Dielectric Constant Varies with Sinter Aid: Dielectric constant initially increases, reaching a maximum at 1.5% sinter addition before decreasing.