Doping effect of SrZrO₃ on KNLN ceramics structure and their dielectric properties

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In this work, lead-free systems; $(1-x)(\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07})\text{NbO}_3-x\text{SrZrO}_3$ ($x = 0, 0.005, 0.050, 0.095$ and 0.14) were synthesized by the conventional solid-state reaction technique. XRD, SEM, densification parameter as well as dielectric parameters of the obtained KNLN ceramics were investigated. XRD analysis showed the formation of orthorhombic perovskite structure in all investigated specimens. SrZrO₃ (SZ) inhibited the grain growth and increased the distribution of grains uniformly in the microstructure. In addition, SZ changed the crystalline system of KNLN ceramics abnormally. As a consequence, the permittivity, dielectric loss as well as AC conductivity decreased remarkably. The ceramics of $x = 0.005$ are characterized by low conductivity (10^{-10} S/cm), low dielectric loss (0.005) and relatively high permittivity (34). They can be useful for the electrical capacitors fabrication and filtering out noise from signals in resonant circuits. At frequencies lower than 10^5 Hz, DC conductivity and separation of the charges at the interfaces were found to dominate the electrical behavior of ceramics, whereas at higher frequencies, a faster or dipole polarization may become more dominated. A broad peak has been observed in the imaginary part of electric modulus revealing to the non-Debye dielectric relaxation behavior. Quantum mechanical tunneling (QMT) was found to be the most suitable to characterize the electrical conduction mechanism in the ceramic compounds.

Keywords: Lead-free ceramics; KNLN; dielectric properties.

1. Introduction

Lead-based ceramics Pb(Zr, Ti)O₃ (PZT) are well-known ferroelectric materials that have piezoelectric response upon applying a mechanical force, i.e., compression or tension. In addition, they show the converse of piezoelectric effect when subjected to an electric field. These features enable them to apply in many fields: actuators, sensors, transformers and transducers.^{1,2} However, PZT is composed of about 60 wt.% of lead which is a toxic element that affects the human health and the environment. Therefore, demand is growing for lead-free or eco-friendly materials.³ Lead-free ferroelectric ceramics such as BaTiO₃, Na_{0.5}Bi_{0.5}TiO₃ (NBT), K_{0.5}Bi_{0.5}TiO₃ (KBT) have been applied in many fields: high permittivity capacitors, piezoelectric sonar, ultrasonic transducers, ultrasonic motors, memories, and cooling devices. In particular, (K_{0.5}Na_{0.5})NbO₃ (KNN) has been considered as one of the most important free lead piezoelectric ceramics because of its excellent electrical properties and high Curie temperature.^{4–16}

However, pure KNN ceramics have low piezoelectric activity due to its poor densification induced by high volatilization of potassium during sintering. In the literature, the density as well as the electrical properties of KNN ceramics has been improved upon adding ABO₃-type; BaTiO₃, SrTiO₃, CaTiO₃, LiSbO₃, LiTaO₃, LiNbO₃ and SrTiO₃.^{17,18} A study of 0.5% alkali earth doping showed that strontium and calcium improve sintering and magnesium oxide hinders it, and zirconia impedes grain growth.³

For the ceramic approach, a structuration process in the volume of materials can be induced to enhance the electrical and mechanical properties. Dielectric response of the ceramic materials depends on both complex permittivity of the constituting phases and the interfacial interactions. In the present contribution, we are investigating $(1-x)(\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07})\text{NbO}_3-x\text{SrZrO}_3$; where $x = 0, 0.005, 0.050, 0.095$ and 0.14 as a lead-free system synthesized by the conventional solid-state reaction technique. Then, the effect of microstructure and crystalline structure on the complex dielectric permittivity

($\varepsilon^* = \varepsilon' - i\varepsilon''$) of pure and SZ-doped KNLN ceramics have also been investigated. Where ε' is the permittivity, which expresses the amount of electrical energy stored by the material via polarization, whereas ε'' is the dielectric loss that determines the energy dissipated by the material. Properties as well as the electrical modulus and the conductivity of the ceramic samples were studied over a wide frequency range (10^{-1} – 10^6 Hz) and a temperature range of 25–175°C. Molecular relaxation processes will not be considered, being out of the scope of the current study, which is focused on the dielectric dispersions arising from the separation of free charges at the interfaces or Maxwell–Wagner–Sillars polarization (MWS) and DC conductivity.^{19,20}

2. Experimental Work

2.1. Materials and Methods

The conventional solid-state reaction technique was used to synthesize the lead-free ceramic compositions: $(1-x)$ ($\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07}$) NbO_3 – $x\text{SrZrO}_3$ ($x = 0, 0.005, 0.050, 0.095$ and 0.140). Chemically pure reagent powders of K_2CO_3 (99%), Na_2CO_3 (99%), Li_2CO_3 (99%), Nb_2O_5 (99.5%), $\text{Sr}(\text{NO}_3)_2$ (99%) and ZrO_2 (97%) were used as starting materials. A ($\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07}$) NbO_3 (KNLN) powder was prepared before adding SrZrO_3 (SZ) powder. The starting powders were weighed according to the stoichiometry formula and then ball-milled with the Zirconia grinding ball and ethanol for 24 h. To prepare SrZrO_3 from $\text{Sr}(\text{NO}_3)_2$ and ZrO_2 powders, the same procedure was applied. The slurries were dried in oven at 110°C for 24 h then calcined at 800°C for 6 h. After pulverization, the calcined powder batches were weighed according to the stoichiometry formula and ball-milled together in a planetary mill for 8 h to obtain compositions $(1-x)$ KNLN– x SZ. The resulted slurries were, then, dried and pulverized sequentially. These powders were mixed with 1 wt.% PVA (5 wt.% aqueous solution), then uni-axially pressed into a disk of 13 mm diameter under 300 MPa and dried. The samples were put in a closed ceramic box has excess stoichiometries powders of a similar composition, then subsequently sintered in air at 1100–1250°C, depending on SrZrO_3 content.

2.2. Characterization

The phase composition was analyzed by X-ray diffraction (XRD) analysis using CuK_α radiation (X' Pert, PANalytical). The bulk density of the sintered samples was determined by the Archimedes method. The surface microstructure of the samples was investigated using scanning electron microscopy (SEM) (FEI INSPECT 50S). The dielectric measurements were carried out using a high-resolution impedance analyzer spectrometer (Schlumberger Solartron 1260), provided with an electrometer amplifier and measuring cell over a wide frequency range (10^{-1} – 10^6 Hz) and at a temperature range of

25–175°C. The dielectric properties like the real (permittivity; ε') and imaginary (dielectric loss; ε'') part of complex permittivity as well as the real (σ') and imaginary (σ'') parts of complex AC conductivity were calculated from the output parameters i.e., the capacitance (C) and the dielectric loss tangent ($\tan\delta$) as follows:

$$\varepsilon' = C \frac{d}{\varepsilon_0 A}, \quad (1)$$

$$\varepsilon'' = \varepsilon' \times \tan\delta, \quad (2)$$

$$\sigma' = \varepsilon_0 \omega \varepsilon'' \quad (3)$$

$$\sigma'' = \varepsilon_0 \omega \varepsilon' \quad (4)$$

where C is the capacitance of the capacitor containing the dielectric material, ω is the angular frequency ($= 2\pi f$) and f is the frequency of the applied electrical field in Hertz. $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the vacuum permittivity. Further, the imaginary (loss modulus; M'') part of the complex electric modulus is given as

$$M'' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}. \quad (5)$$

The sample geometry is denoted as thickness (d) and cross section area (A). The error in ε' and ε'' amounts to $\pm 1\%$ and $\pm 3\%$, respectively. The reproducibility of the measurement was tested by re-measuring ε' and ε'' after performing the experiment once again.

3. Results and Discussion

3.1. XRD analysis

The phase composition and crystal structure of the sintered samples examined using XRD analysis are shown in Fig. 1. It can be seen that the investigated specimens composed mainly of KNLN ceramics with perovskite structure. A typical pure orthorhombic perovskite structure was obtained from KNLN powder fired specimens at 1100°C for 6 h, while tiny traces of impurities are observed in the 2θ range between 20° and

Fig. 1. XRD patterns of the $(1-x)$ ($\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07}$) NbO_3 – $x\text{SrZrO}_3$ ceramics in the range of 2θ from 20° to 70°.

40°. These impurities have the same d-spacing of the lithium potassium niobium oxide phase ($\text{K}_3\text{LiNb}_6\text{O}_{17}$).⁶

The addition of even 0.005 mol.% SZ decreases the orthorhombic distortion characteristic for KNLN and a mixture of orthorhombic and tetragonal phases is expected for samples with $x = 0.005$ at 1100°C. The diffraction peaks of the compositions with x from 0.050 to 0.140 correspond to the pseudo-cubic at 1200°C and 1250°C. Moreover, it was also found that the positions of the diffraction peak of the $(1 - x)$ KNLN- x SZ ceramics were shifted to lower angles with the increase of x .

3.2. Density

All samples sintered at optimum sintering temperatures (ST) are given in Table 1. It is commonly known that adding alkaline earth (AE) to substitute perovskite structure by creating A site vacancies in case of KNN leads to increase in the density.¹⁸ The addition of SZ to KNN also can promote densification. The obtained bulk densities (BD) of the investigated doped ceramics are in the range of 4.22–4.33 g/cm³, equivalent to the relative density (RD) of 94.2–95.1%, where the theoretical density is 4.51 g/cm³.

3.3. Microstructures

The unmodified KNLN surface morphology contains different shapes; cubic and rectangular. The size of the large rectangular grain is $\geq 7 \mu\text{m}$. In addition, smaller grains interspersed with large grain sizes of 3–4 μm are observed as shown in Fig. 2(a).

SEM micrographs of the fracture surfaces of $(1 - x)$ KNLN- x SZ samples with SZ contents of 0, 0.005, 0.05, 0.095 and 0.140 mol. % are shown in Fig. 2. Grain sizes slightly decreased and large grains of size $\geq 7 \mu\text{m}$ disappeared as shown in Fig. 2(b). Rod shapes with length of $\geq 10 \mu\text{m}$ are observed at $x = 0.095$ as seen in Fig. 2(c). With the increase of the SZ content, the grain size of the ceramics refines and becomes more homogeneous. This indicates that the addition of SZ promotes the nucleation but inhibits the growth of KNLN grains. Due to the addition of the SZ into KNLN, Sr^{2+} and Zr^{4+} ions distribute evenly in the KNLN ceramics and form nucleation points.

Table 1. The sintering temperature, density, permittivity and dielectric loss of lead-free $(1 - x)$ ($\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07}$) $\text{NbO}_3 - x\text{SrZrO}_3$ ($x = 0, 0.005, 0.050, 0.095$ and 0.14).

X content of SZ	ST (°C)	BD (g/cm ³)	RD (%)	ϵ' At 0 ⁵ Hz	ϵ''
0	1100	4.127	91.5	397	6
0.005	1100	4.248	94.2	34	0.005
0.05	1200	4.258	94.4	7	0.015
0.095	1200	4.228	93.7	9	0.047
0.14	1250	4.288	95.1	22	0.16

Fig. 2. SEM photographs of $(1 - x)$ ($\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07}$) $\text{NbO}_3 - x\text{SrZrO}_3$ ceramics Surfaces: (a) $x = 0.0$; (b) $x = 0.005$; (c) $x = 0.05$; (d) $x = 0.095$; (e) $x = 0.14$.

3.4. Dielectric study

3.4.1. Effect of frequency and temperature

The frequency and temperature-dependent permittivity (ϵ'), dielectric loss (ϵ''), conductivity (σ'), imaginary part of conductivity (σ'') and loss modulus (M'') were investigated for $(1 - x)$ ($\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07}$) $\text{NbO}_3 - x\text{SrZrO}_3$ ($x = 0, 0.005, 0.050, 0.095$ and 0.14). As a representative example, Fig. 3 shows the frequency dependence of ϵ' , ϵ'' and M'' for KNLN ceramics ($x = 0$) at different temperatures. Figure 3(a) shows that ϵ' has high values below $\sim 90 \text{ Hz}$ then becomes almost constant at higher frequencies. Similar behavior has been found for all investigated samples. At low frequencies, many types of polarizations (space charge, dipolar, ionic and electronic polarization) are possible,²¹ explaining why ϵ' increases. As the frequency increases, on the other hand, some of the polarizations became less effective and thus, ϵ' decreases. The frequency dependent ϵ' can also be explained

Fig. 3. The frequency and temperature dependence of permittivity (a), dielectric loss (b) and loss modulus (c) of pure KNLN ceramics.

on the basis of charge distribution effect by means of the carrier hopping on the lattice defects. At low frequencies, the charges on defects have enough time to redistribute so that the defects closer to the positive electrode of the applied field become negatively charged, while the defects closer to the negative electrode become positively charged. This results in reducing the applied electric field and hence, the electrical capacitance increases since it is inversely proportional to the field. According to Eq. (1), the permittivity (ϵ') is also increased. But at high frequencies, the defects have no longer enough time to rearrange themselves and follow the electric field. Based on this, the capacitance or permittivity decreases.

It can also be noticed from Fig. 3(b) that the dielectric loss (ϵ'') for all samples increases with decreasing frequency and increasing temperature. Further, ϵ'' shows high values at low frequencies, leading to DC-like imperfect charge transport, i.e., DC conductivity (σ_{dc}).²²

The plateau like behavior in the real part of conductivity, σ' (Fig. 4(a)) confirms such σ_{dc} effect. This effect found to be increased with temperature, showing thermally activated process. At high frequencies, σ' shows a significant increase with the frequency increase following the well-known power law of Jonscher²²:

$$\sigma_{ac} = \sigma_{dc} + A\omega^s \text{ S/cm}, \quad (6)$$

where $\omega = 2\pi f$ is the angular frequency, f is the electric field frequency and A is a temperature-dependent parameter

Fig. 4. The frequency and temperature dependence of the real (a) and imaginary (b) part of AC conductivity of pure KNLN ceramics.

determines the strength of polarizability, ω_p is hoping frequency at which the conductivity slope changes and s ($0 < s < 1$) is the frequency exponent.

The temperature-dependent s indicates the predominance of conduction mechanism for AC conductivity in addition the degree of interaction between mobile ions with the environments surrounding them. In the literature, different theoretical models have been suggested to determine the conduction mechanism.^{23–25} Hence, s values of all samples are plotted versus temperature as shown in Fig. 5. As clear in the figure, s values lie in the range 0.6–1 and increases with the temperature increase. This behavior suggests that the quantum mechanical tunneling (QMT) is the most suitable model to characterize the electrical conduction mechanism in the ceramic compounds $(1-x)(\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07})\text{NbO}_3-x\text{SrZrO}_3$ ($x = 0, 0.005, 0.050, 0.095$ and 0.14).

Further inspection of Fig. 4(b) shows that at $T > 75^\circ\text{C}$, the imaginary part of AC conductivity (σ'') increases with decreasing frequency, revealing to the contribution of electrode polarization (EP)¹⁹ which is manifested by the high values in both ϵ' and ϵ'' . For such a polarization, the charges are separated over considerable distances relative to the atomic and molecular sizes), and therefore its contribution to the dielectric loss can be orders of magnitude larger than those expected for molecular fluctuations so that information about the molecular or dipolar polarization would be missed.

Fig. 5. The temperature dependence of frequency exponent (s) for the ceramic compounds $(1-x)(\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07})\text{NbO}_3-x\text{SrZrO}_3$ ($x = 0, 0.005, 0.050, 0.095$ and 0.14).

This is evident from the absence of relaxation peak that describes the possible polarization types. Therefore, the dielectric data is suggested to be represented in terms of the imaginary part of the electric modulus, M'' (Fig. 2(c)) which suppresses the EP effect. Hence, one can clearly recognize a broad peak in M'' spectra whose maximum is shifted to higher frequencies with increasing temperature, showing thermally activated process. The appearance of peak in M'' while not in ϵ'' indicates the ionic conduction mechanism. The peak broadness indicates the non-Debye relaxation behavior. As the peak broadness extends to high frequencies up to 10^5 Hz, DC conductivity and EP will not be the only dominance of dielectric behavior. Instead, an additional polarization is expected to occur within this frequency range, may be the interfacial polarization.¹⁹ This arises from the local change in the electrical resistivity across the interfaces. The interfaces at which the charges are separated are represented here by the grain boundaries. As the interfaces increase, their resistivity increase and hence more charges are accumulated or decelerated at them. The interfacial polarization effect appears in the frequency region (10 and 10^5 Hz) as a step like increase in ϵ'' with increasing frequency and a strong bond between DC plateau and AC conductivity (Fig. 4(a)).²² However, such effect disappeared at temperatures higher than 150°C , while DC conductivity contribution becomes more dominated. Since, at high temperature, the charges acquire enough thermal energy enabling them to overcome the interfaces resistivity and then transport through the material exploring electric conduction. Also, we report a disappearance of the IP effect for SZ-doped KNLN ceramics with $x = 0.005\text{--}0.095$, leading to the improved homogeneity as reported in XRD analysis. This may be attributed to diffusion of SZ into KNLN lattice to form a new solid solution. However, the interfacial polarization effect appeared again at higher concentrations due to the formation of secondary phase potassium lithium niobium oxide; $\text{K}_3\text{LiNb}_6\text{O}_{17}$.⁶ In such a case, the free charge carriers suffer different resistances

across these different grains and thus they are accumulated at the interfaces upon applying the electric field. Both electrode and interfacial polarizations are well known as Maxwell–Wagner–Sillars (MWS) polarization.^{19,20} Based on the above description, the dielectric behavior of the pure and SZ-doped KNLN ceramics in the frequency range ($10^{-1}\text{--}10^5$ Hz), is generally explained on the basis of MWS polarization and DC conductivity. As an interesting result, we report here a good correlation between the sample microstructure and its electrical behavior. At frequencies higher than 10^5 Hz, a faster or molecular polarization may dominate the dielectric behavior. Such polarization will not be considered, being out of the scope of the current study.

The observed increase in permittivity (ϵ') and dielectric loss (ϵ'') with temperature is attributed to the creation of imperfections/disorders in the crystalline lattice and an increase in the mobility of charge carriers (ions and electrons). Furthermore, with the temperature increase, molecules are expected to be expanded causing some increase in the electronic polarization and hence an increase in both ϵ' and ϵ'' of the dielectric material.^{26–30} The increase of the electrical conductivity at high temperature is attributed to the impurities, which is located at the grain boundaries.^{26,29} These impurities lie below the bottom of the conduction band. The variation of the conductivity (σ') with temperature can also be explained on the basis of binding energy. So, as the temperature increases, the binding energy of the carriers in its localized states decreases due to an increase in the overlapping degree of Columbic potential wells.³⁰ The conductivity increase with temperature is probably due to decreasing of the binding energy.

3.4.2. Effect of SrZrO_3 doping

The effect of SZ-doping concentration on the electrical properties of KNLN ceramics is studied at constant frequency (10^5 Hz) and different temperatures and compared with those reported for pure KNLN ceramics as shown in Fig. 6. As a general description, the permittivity (ϵ'), dielectric loss (ϵ'') and imaginary part of AC conductivity (σ'') considerably decreased upon adding SrZrO_3 ; two possible reasons are suggested for such behavior. The first one is associated to reduction of the oxygen vacancies at the surface of grains and domain walls and thus these properties decreased. Taking into account, the oxygen vacancies are due to the existence of impurities reported by XRD mentioned above. The second reason is associated to the replacement of host ions i.e., K^+ ($1.64 \text{ \AA}$) and Na^+ ($1.39 \text{ \AA}$) by the smaller ions Sr^{2+} ($1.31 \text{ \AA}$) and Zr^{4+} ($0.72 \text{ \AA}$), respectively. As a consequence, the dipolar polarization or/and movements of free charge carriers would be hindered, thus the electrical properties of doped samples expected to be decreased. This kind of substitution is known as Frenkel defect in which either cation or anion leaves its site in the sublattice, creating the vacancy, and moves to another location to create an interstitial.³¹

Fig. 6. The temperature dependence of permittivity (a), dielectric loss (b) and real part of conductivity (c) for the ceramic compounds $(1-x)(\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07})\text{NbO}_3-x\text{SrZrO}_3$ ($x = 0, 0.005, 0.050, 0.095$ and 0.14) at 10^5 Hz.

On the other hand, the temperature dependence of permittivity (ϵ') for pure KNLN (Fig. 3(a)), shows an increase with increasing temperature up to 125°C (transition temperature) then a decrease at higher temperature showing ferroelectric property. The observed broad peak may be due to the formation of diffuse ferroelectric.³² With increasing SZ up to $x = 0.005$, the permittivity increases with increasing temperature up to 150°C then decreases at higher temperature. However, for the ceramics doped with $x = 0.05-0.14$, the peak cannot be clearly observed. Some authors have attributed this variation to the grain size decrease in doped samples, chemical composition and crystal imperfections.³³⁻³⁸

For more detailed discussion, both ϵ' and ϵ'' (dielectric properties) measured at room temperature (25°C) and constant frequency (10^5 Hz) are listed in Table 1 to compare their behavior with, SZ concentration sintering, temperature and bulk density of the pure and SZ-doped ceramics. The pure KNLN ceramics sintered at the lowest temperature have the lowest bulk density and highest dielectric properties. Both density and ϵ' show a decrease with increasing SZ concentration increases up to 0.095 , then they show an increase at higher concentration and higher STs. Interestingly, as the compounds of $x = 0.005-0.05$ are characterized with the lowest values of dielectric loss (~ 0.005) and relatively high permittivity (~ 34); they can be useful in the fabrication of the electrical capacitors and filtering out noise from signals as part of a resonant circuit.

4. Conclusion

Structure and electrical properties of the lead-free ceramics; $(1-x)(\text{K}_{0.465}\text{Na}_{0.465}\text{Li}_{0.07})\text{NbO}_3-x\text{SrZrO}_3$ ($x = 0, 0.005,$

$0.050, 0.095$ and 0.14), have been investigated. SrZrO_3 inhibits the grain growth and changes the crystalline system of KNLN ceramics abnormally due to its diffusion in KNLN lattice to form new solid solutions. The dielectric properties of the doped samples are significantly changed in accordance. For instance, the permittivity value of KNLN ($x = 0$) measured at 25°C and 10^5 Hz has been significantly decreased from 397 to 34 upon doping with SrZrO_3 ($x = 0.005$). Meanwhile, the dielectric loss of the compounds with $x = 0.005-0.05$, showed much lower values (~ 0.005). The characterizing features of these compounds make them useful in the fabrication of the electrical capacitors and filtering out noise from signals as part of a resonant circuit. The conduction mechanism of these compounds has been characterized by QMT model. Based on the above, the dielectric spectroscopy has been considered as a powerful technique that enabled us to find a correlation between the dielectric properties and structure and microstructure of the investigated ceramics.

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