# Structure and piezoelectric properties of CaZrO$_3$-modified (K,Na,Li)(Nb,Sb)O$_3$ ceramics prepared from powders synthesized by microwave heating

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## Abstract

*CaZrO$_3$-modified $(K_{0.48}Na_{0.48}Li_{0.04})(Nb_{0.95}Sb_{0.05})O_3$ (CZ-KNLNS) lead-free piezoelectric powders were synthesized by microwave method followed by conventional solid state sintering. Different amounts of CaZrO$_3$ were added (i.e. x = 0, 0.02, 0.03, 0.04, 0.06 mol) and their effects on the crystal structure, microstructure, as well as the electrical properties, were investigated. The results showed that CZ-KNLNS powders could be obtained by microwave heating at a relatively low temperature and short time of 650 °C and 10 min, respectively. The obtained CZ-KNLNS powders have cubic structure and good crystallinity with average particle size of 300–700 nm. The particle size gradually decreases with the increase of CaZrO$_3$ amount, indicating that addition of CaZrO$_3$ inhibits the growth of the particles. The powders were further sintered at 1120 °C for 4 h and CZ-KNLNS ceramics with homogeneous and highly dense microstructure were obtained. X-ray diffraction showed that, with increasing CaZrO$_3$ content, the phase structure gradually changed from orthorhombic to rhombohedral, which can be considered as the coexistence zone of orthorhombic-rhombohedral (O-R) phase in the range of 0.03 < x < 0.06. The optimized content of CaZrO$_3$ is x = 0.04, at which the CZ-KNLNS piezoelectric ceramics show good properties and maximum $d_{33}$ = 201.2 pC/N and $K_p$ = 36.8%.*

*Keywords: lead-free potassium sodium niobate ceramics, microwave synthesis, CaZrO$_3$-modifing, phase transition, piezoelectric propertiess*

## I. Introduction

Within the field of piezoelectric materials, Pb(Zr,Ti)O$_3$ (PZT) has been widely utilized in piezoelectric actuator and sensor applications due to its excellent electrical properties. However, the high toxicity of the lead, which constitutes for more than 60 wt.% in PZT-based materials, leads to the substantial environmental pollution during their processing and recycling [1]. Therefore, tremendous efforts have been devoted to developing lead free piezoelectric materials [2,3]. In recent years, K$_{0.5}$Na$_{0.5}$NbO$_3$ (KNN)-based ceramics have drawn a great deal of attention because of their high Curie temperature ($T_C$ > 400 °C), large electromechanical coupling coefficient, appropriate dielectric constant and environmental friendliness. The KNN-based ceramics are considered to be one of the most promising alternative materials to replace the lead-based ceramics. However, the piezoelectricity of KNN lead-free piezoelectric material is still inferior to that of lead-based material. Generally, the $d_{33}$ of the PZT series is higher than 400 pC/N, while the $d_{33}$ of the pure KNN base material is only 80 pC/N [4–6].

It is reported that the piezoelectricity of KNN can be greatly improved by the formation of multiphase coexistence [7,8]. Doping is commonly used, such as doping with Li$^+$ and Ag$^+$ into A site, or Sb$^{5+}$ and Ta$^{5+}$ which can act as the B site adulteration. In addition, when the ABO$_3$ perovskite structure (such as LiSbO$_3$, LiTaO$_3$, Bi$_{0.5}$Li$_{0.5}$TiO$_3$, Ba(Zr$_{0.52}$Ti$_{0.48}$)TiO$_3$) is introduced in KNN, the orthogonal tetragonal (O-T) coexistence near room temperature can be obtained. Formation of

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polymorphic phase transition (PPT) can increase the piezoelectric constant $d_{33}$ to 150–300 pC/N [9–12]. Zhang *et al.* [13] reported that when $0.04 \leq x \leq 0.06$ in $(1-x)[(K_{0.50}Na_{0.50})_{0.97}Li_{0.03}Nb_{0.97}Sb_{0.03}O_3]$-$x$BaZrO$_3$ ceramics, the rhombohedral and orthogonal (R-O) coexisting phases can be constructed with the $d_{33}$ = 235 pC/N. As it is well known, KNN is an orthorhombic ferroelectric at room temperature. Ca$^{2+}$ ion and Ba$^{2+}$ ion belong to the same main group and have similar arrangement of extranuclear electron. Therefore, the addition of CaZrO$_3$ compound into KNN is also expected to effectively adjust the phase structure of KNN ceramics, as BaZrO$_3$ did, so as to obtain excellent piezoelectric properties.

In order to improve the piezoelectric properties, it has been reported that another effective method is to improve the synthesis process and obtain nanoscale powders, thereby improving the sintering activity of ceramics [14,15]. At present, KNN ceramic powders can be synthesized by a variety of methods, such as solid-state reaction [16], sol-gel [17,18], etc. The KNN ceramic powders synthesized by the traditional solid state method have the disadvantages of low purity, large particle size (usually in micron grade), serious agglomeration and so on. The melting points of the alkali elements are close to the normal synthesis temperature (850 °C) by solid method, which leads to the volatilization of K and Na elements, resulting in a large number of vacancies in the perovskite structure which deteriorates the ceramics properties.

Over the past few decades, microwave processing has emerged as a new method for synthesis or sintering various ceramic materials, which shows significant advantages over conventional sintering. In microwave processing, energy is directly transferred to the material through the interaction of electromagnetic waves with molecules leading to heating. Moreover, a smaller grain size can be obtained with microwave processing due to higher heating rate and shorter sintering cycles [19–21]. Lead-piezoelectric ceramics synthesized by microwave methods have been reported in literature, but they mainly focused on the structure and electrical

behaviour [22]. Particular research on microwave synthesis of KNN based powders has been rarely reported so far.

In this paper, a new potassium sodium niobate $x$CaZrO$_3$-(1-$x$)(K$_{0.48}$Na$_{0.48}$Li$_{0.04}$)(Nb$_{0.95}$Sb$_{0.05}$)O$_3$ (abbreviated as CZ-KNLNS) with $0 \leq x \leq 0.06$ ($x$ denotes the molar ratio of CaZrO$_3$) is designed to develop lead-free ceramics. The CZ-KNLNS powders are synthesized by microwave heating. The effects of microwave heating on the morphology of synthesized powders are studied. The effects of CaZrO$_3$ content on the phase structure, microstructure and piezoelectric properties of the CZ-KNLNS ceramics are also investigated.

## II. Experimental

$x$CaZrO$_3$-(1-$x$)(K$_{0.48}$Na$_{0.48}$Li$_{0.04}$)(Nb$_{0.95}$Sb$_{0.05}$)O$_3$ ($x$ = 0, 0.02, 0.03, 0.04, 0.06) powders were synthesized using microwave heating. Chemically pure Na$_2$CO$_3$ (99.9%), K$_2$CO$_3$ (99.9%), CaO (99.99%), Li$_2$CO$_3$ (98%), Nb$_2$O$_5$ (99.5%), Sb$_2$O$_5$ (99%) and ZrO$_2$ (99.99%) were commercially available. All the raw materials were dried separately in an oven at 120 °C for 24 h prior to weighing. Each raw material was weighed accurately according to the chemical formula. The starting materials were blended by planetary ball milling (QM-3SP2) in plastic bottle with zirconia balls for 12 h. The medium was ethanol and the ball-to-powder ratio was chosen to be 10:1. The homogenized raw mixture was dried at 120 °C for 24 h, and then directly heated in a microwave chamber with a resonant mode of TE666 free of aided heater (WXD20S-07, China Nanjing Shanle Microwave Co. limited). The microwave frequency was 2450 MHz with maximum input power of 10 kW. The microwave heating system was based on our previous work and schematically illustrated in Fig. 1. The changes in reflected power versus temperature were detected. Temperature was monitored by using an infrared radiation thermometer (OI-T6I2-B-1-type, GOIDSUN, USA) through a hole in the top of insulation on the surface of the samples. The average heating rate was well-controlled at ~15 °C/min by adjusting the input power. Based on the previous experiments, the microwave synthesis technology parameters were selected as 650 °C for 10 min.

The synthesized powders were pressed into disks with a diameter of 12.0 mm and a thickness of 2.0 mm using a uniaxial press of 10 MPa. All the specimens were sintered in air at 1120 °C for 4 h with 5 °C/min heating and cooling rates using the conventional solid-state method. The sintered ceramics were carefully polished, silver electrodes were plated on both sides of the pellets with Ag paste and then fired at 550 °C for 30 min as the electrodes. A poling process was then conducted under a DC electric field of 4 kV/mm for 30 min at 120 °C in silicone oil bath.

The phase structure of different samples was identified by X-ray diffraction (XRD, Rigaku Ultima IV)
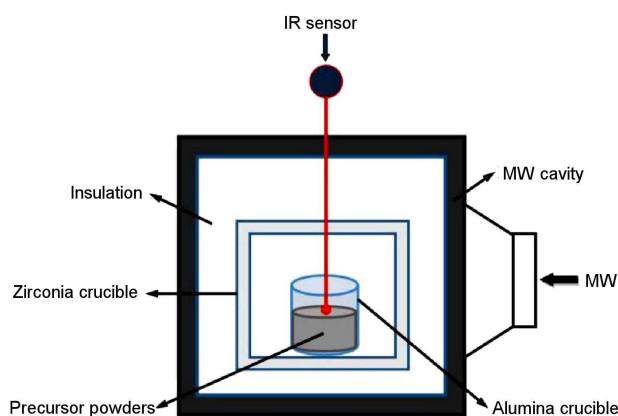
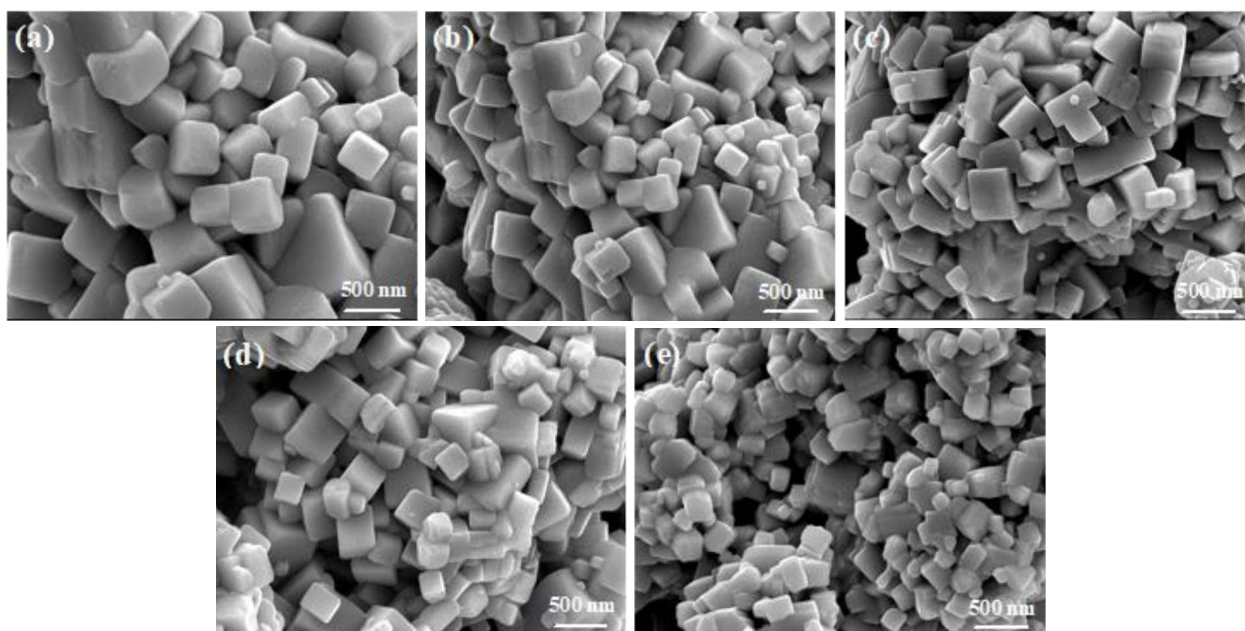**Figure 1. Schematic diagram of microwave calcination system**

**Figure 2. SEM images of CZ-KNLNS powders with different CaZrO$_3$ content *x*: a) 0, b) 0.02, c) 0.03, d) 0.04, and e) 0.06**

using Cu K$\alpha$ radiation ($\lambda$ = 0.15418 nm). FTIR spectroscopy was carried out from 400 to 3750 cm$^{-1}$, using KBr pellets containing 1 wt.% of sample in KBr. The morphologies of the obtained particles and ceramics were observed by the FE-SEM (JSM-7001F, Tokyo, Japan). The particle size and size distribution of the samples were measured by a laser diffraction instrument (Malvern Zetasizer Nano ZS90; England). The planar electromechanical coupling factor $K_p$ was determined by the resonance and anti-resonance method using an impedance analyser (Agilent 4294A; Agilent Inc, USA). The quasistatic piezoelectric constant ($d_{33}$) was measured using a piezo-$d_{33}$ meter (ZJ-6A; Institute of Acoustics, Chinese Academy of Sciences, Beijing, China).

## III. Results and discussion

### 3.1. Structure of CZ-KNLNS powders

The SEM images of the CZ-KNLNS powders synthesized by microwave heating with different CaZrO$_3$ content (0, 0.02, 0.03, 0.04 and 0.06) are shown in Fig. 2. The typical perovskite structure of regular cubic morphology of the powders can be clearly seen in Fig. 2, indicating that the CZ-KNLNS powders can be rapidly synthesized at low temperature of 650 °C for 10 min under microwave heating, which is about 200 °C lower than that prepared by solid-state reaction. If compared with the existing literature reports, it needs 120 min to synthesize potassium sodium niobate-based powders by traditional solid state method [23], while the time required for microwave synthesis of CZ-KNLNS powder can be shortened to only 10 min.

It is most likely that a more uniform temperature field will be obtained between the precursor powders under the microwave heating, which makes a great contribu-

tion to promote the reaction between the ions in the calcination process and to decrease the calcination temperature [24–26]. It has a positive effect on improving the sintering properties of the powders and the electrical properties of the final CZ-KNLNS piezoelectric ceramics [27].

Figure 3 shows the particle size distribution of the CZ-KNLNS powders with different CaZrO$_3$ content. As can be seen from the figure, the size of all particles is between 300–600 nm. With the increase of the amount of CaZrO$_3$, the average particle size decreases. Among them, the average particle size of the powders with 0.02 mol of CaZrO$_3$ is approximately 550 nm. When the CaZrO$_3$ quantity is 0.06 mol, the particle size distribution of the synthesized powders is wider, about 200–400 nm. It is concluded that CaZrO$_3$-addition suppresses the growth of particles, which is consistent with the conclusions reported in the literature [28].
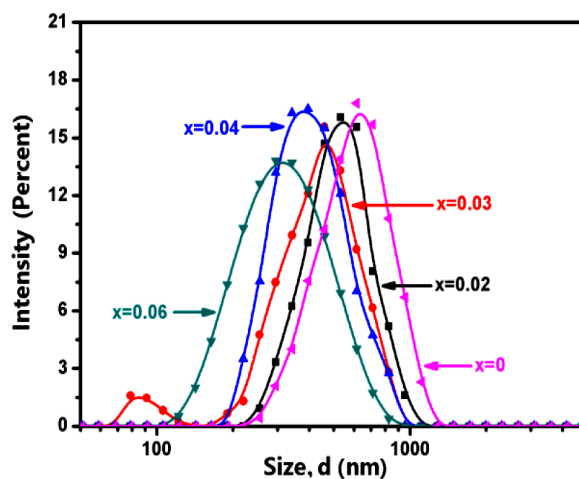


**Figure 3. Comparison analysis of *x*CZ-(1-*x*)KNLNS particles size distribution profiles after the microwave heating**
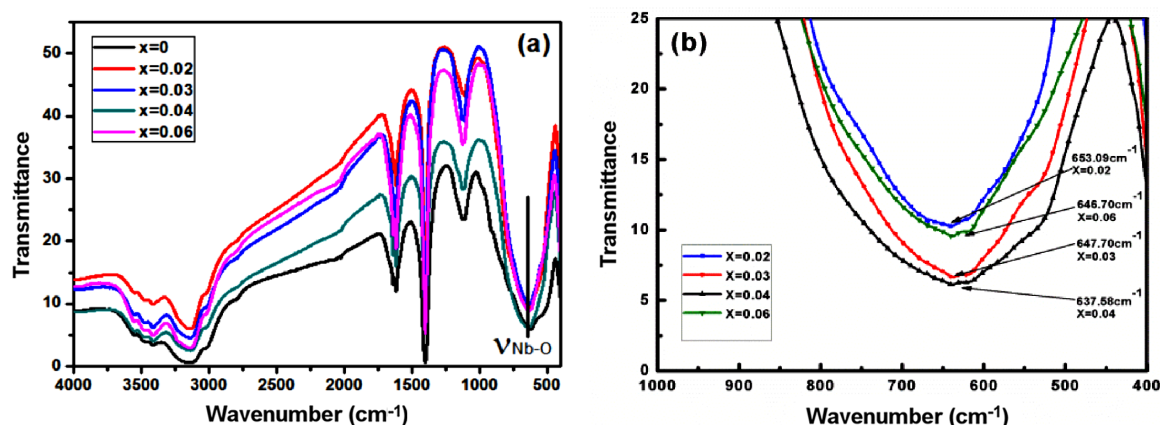
**Figure 4. FTIR spectra of calcined CZ-KNLNS powders with different CaZrO₃ content (a) and partial enlargement of Nb–O absorption peak with different CaZrO₃ content**

Figure 4a portrays the FT-IR spectroscopic studies of the CZ-KNLNS powders with different $CaZrO_3$ content. For all particles, an IR band of around $3400 \, cm^{-1}$ is assigned to O–H asymmetric stretching ($v_3$), and it relates to the moisture content. The characteristic peaks at around $1385 \, cm^{-1}$ can be assigned to $CO_2$. Another broad FTIR band is detected at a low wavenumber between $600 \, cm^{-1}$ and $1000 \, cm^{-1}$ without any specific peaks. It is known as characteristic peak related to the Nb–O octahedral vibrations and it is a sign of the formation of perovskite structure [29,30]. Figure 4b shows the partial amplification of Nb–O characteristic peak. When the $CaZrO_3$ amount is 0.02, 0.03, 0.04, and 0.06, the wavenumber of Nb–O bond is $653.09 \, cm^{-1}$, $647.70 \, cm^{-1}$, $637.58 \, cm^{-1}$, $646.69 \, cm^{-1}$, respectively, presenting a tendency to decline at first and then increase. This can be explained by analysing the radius and valence states of $K^+$, $Nb^{5+}$ and doped elements $Ca^{2+}$, $Zr^{4+}$. When the $CaZrO_3$ amount is less than 0.04, $Zr^{4+}$ enters the $ABO_3$ perovskite structure to replace the $Nb^{5+}$. The ionic radius of $Zr^{4+}$ ($0.74 \, Å$) is larger than that of $Nb^{5+}$ ($0.69 \, Å$), and this causes the increase of cell volume and length of the Nb–O bond. On the other hand, because the valence of $Zr^{4+}$ is lower than that of $Nb^{5+}$, the Coulomb forces between $Zr^{4+}$ and $O^{2-}$ are lower than that of $Nb^{5+}$ and $O_2$, resulting in a decrease in bond energy, so the wavenumber of the Nb–O bond absorption peak is reduced. When the $CaZrO_3$ amount $x$ is higher than 0.04, $Ca^{2+}$ ($0.99 \, Å$) enters into the $ABO_3$ perovskite structure and replaces the $K^+$ ($1.33 \, Å$) in A place. This results in the decrease of unit cell volume and Nb–O bond length, and thereby increasing the bond energy. When the $CaZrO_3$ amount is $0.04 \leq x \leq 0.6$, the number of absorption peaks of Nb–O bond reaches the minimum.

When CZ-KNLNS powders are synthesized by microwave heating, the ultra-high frequency electromagnetic wave enters inside the medium and directly acts on it. The interior molecules of the powders resonate with the change of microwave field so microwaves increase the heating efficiency by concentrating the heating process within the material rather than on the surface. Microwave electromagnetic energy can make particles vibrate at high speed, promote ion activation and achieve the activation energy required for synthetic reactions at lower temperature, resulting in an increase in diffusion coefficient and the rate of chemical reactions.

In the first step, raw materials $Na_2CO_3$ and $K_2CO_3$ absorb microwave heating and decompose to form $CO_2$ gas. Equations 1 and 2 illustrate the decomposition process of $Na_2CO_3$ and $K_2CO_3$:

$$Na_2CO_3 \longrightarrow 2Na^+ + O^{2-} + CO_2(g) \qquad (1)$$

$$K_2CO_3 \longrightarrow 2K^+ + O^{2-} + CO_2(g) \qquad (2)$$
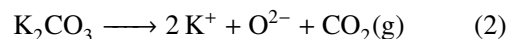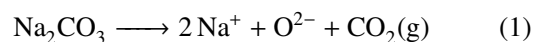
The formed $CO_2$ gas could be ionized in the high frequency microwave field. Microwave plasma effect is stimulated, prompting $Na^+$, $K^+$ ions to form solid solution. The raw $Nb_2O_5$ material is relatively stable and ($Na^+$, $K^+$) solid solution diffuses into $Nb_2O_5$ to induce the interface reaction [31]. At the same time, CaO, $Li_2CO_3$, $Sb_2O_5$ and $ZrO_2$ react with $Na^+$, $K^+$ ions and $Nb_2O_5$ under microwave irradiation, and finally form the CZ-KNLNS particles.

In addition, there is a microwave "non-thermal effect" phenomenon in the process of synthesis of powders. The non-thermal effect can promote the material diffusion, reduce the activation energy, and speed up the reaction process, which would produce a local activation and purification of the particles to achieve low-temperature, fast and efficient synthesized process. Our experimental results indicated that the microwave thermal effect can accelerate the process of synthesis. Thus, the CZ-KNLNS powders could be obtained at a relatively low temperature and short time of $650 \, °C$ and 10 min, respectively. In comparison, the synthesis of potassium niobate sodium-based powders by conventional solid phase method needs to be insulated at $850 \, °C$ for 120 min [23]. The obtained CZ-KNLNS powders have cubic structure with average particle size of 300–700 nm. Moreover, the synthesized powders have good dispersibility and uniform particle size, which is benefi-
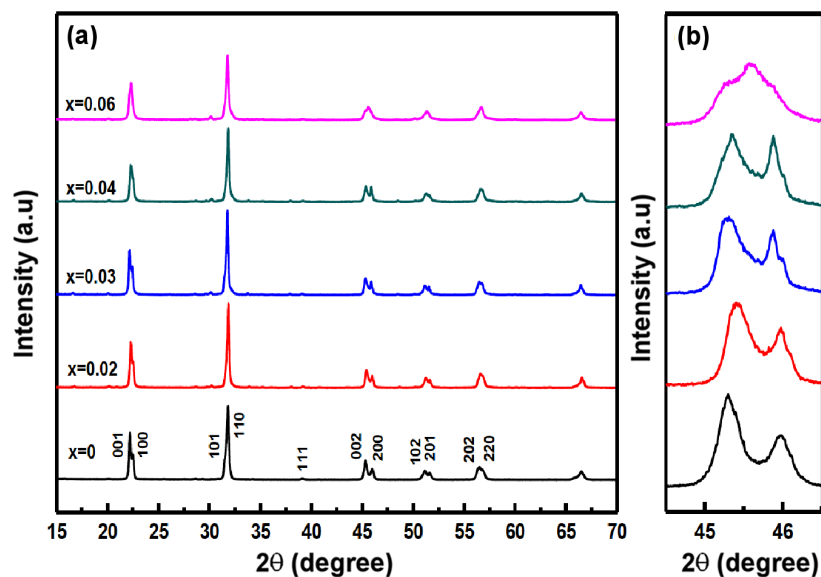
**Figure 5. XRD patterns of CZ-KNLNS sintered ceramics (a) and expanded XRD patterns in the 2θ range of 44.5–46.5°**

cial for improving the sintering activity of the ceramics, thereby improving the electrical properties of the piezoelectric ceramic materials [27].

### 3.2. Structure of CZ-KNLNS ceramics

Figure 5 demonstrates the XRD patterns of the CZ-KNLNS ceramics ($x$ = 0, 0.02, 0.03, 0.04, 0.06). As can be seen, all the peaks can be indexed and they are typical of perovskite structures. Diffraction peaks of other impurities are not observed, indicating that $Li^+$, $Sb^{5+}$, $Ca^{2+}$, $Zr^{4+}$ have been completely dissolved in the KNLNS lattice during the microwave calcination stage. The characteristics of the KNLNS based ceramic crystal structures can be quantitatively identified from the relative intensities of the 002 and 200 peaks ($I_{002}/I_{200}$) in the 2θ range of 44–47° [32,33]. As displayed in partially magnified view in Fig. 5b, when $x \leq 0.3$ the characteristic XRD peak around 45° splits obviously, showing two 002 and 200 reflections. Its peak intensity ratio ($I_{002}/I_{200}$) is close to 2/1, which is the characteristics of orthorhombic (O) phase [32,33]. For the samples with $x = 0.06$, two peaks are merged into a single peak, a characteristic of rhombohedral (R) phase. Therefore, for the composition around $x = 0.04$, the 002 peak and the 200 peak are very close, and the peak intensity ratio ($I_{002}/I_{200}$) gradually decreases with the increase of $x$, indicating that the amount orthorhombic phase is gradually reduced, while rhombohedral phase is gradually increased. This region can be considered as the coexistence zone of orthorhombic-rhombohedral (O-R) phase.

The ionic radii of $(Na_{0.5}K_{0.5})^+$, $Ca^{2+}$, $Nb^{5+}$, and $Zr^{4+}$ are $r_{(Na_{0.5}K_{0.5})^+} = 1.52\,\text{Å}$, $r_{Ca^{2+}} = 0.99\,\text{Å}$, $r_{Nb^{5+}} = 0.64\,\text{Å}$, and $r_{Zr^{4+}} = 0.72\,\text{Å}$, respectively. When $CaZrO_3$ is introduced into KNLNS, $(K_{0.48}Na_{0.48}Li_{0.04})$ is substituted by $Ca^{2+}$, and $Nb^{5+}$ is substituted by $Zr^{4+}$. The A site of KNLNS ceramic lattice is replaced by the doping ion with a smaller ion radius, and the B site is replaced by a larger ion. This causes the average A-site ionic radius to decrease and the average B-site ionic radius to increase, inducing the formation of the R phase in the KNLNS near room temperature. Multi-phase coexistence is considered as one of the major contributing factors for those excellent properties in KNLNS based ceramics [34]. An explanation for these effects may be the low free energy barrier that occurs at the phase boundary, which is beneficial to the transformation and polarization of domains in ceramics and improvement of piezoelectric properties.

The microstructures of the sintered CZ-KNLNS ceramics with different $CaZrO_3$ content $x = 0$, 0.02, 0.03, 0.04, and 0.06 are illustrated in Fig. 6. Dense microstructures were observed, matching the high relative densities, which were estimated from the dimensions and masses of the samples to be higher than 90% for all the samples. The $CaZrO_3$ addition has an evident influence on the grain size of the CZ-KNLNS ceramics. As shown in Fig.6, with the increase of $x$, the grain size tends to gradually decrease. It is clear from the Fig. 6a that the pure KNLNS ceramic sample ($x = 0$) exhibits a coarse morphology with an average grain size of approximately $2\,\mu m$. The grain size of the specimens decreases from approximately $2\,\mu m$ for $x = 0$ to a grain size of around $1\,\mu m$ for $x = 0.03$. Moreover, for $x = 0.04$ in Fig. 6d, the grain size becomes smaller and the grain boundaries are indistinguishable while a dense ceramic section appears. The decrease in grain size may be due to the accumulation of $CaZrO_3$ at the grain boundaries, thereby inhibiting grain growth. For $x = 0.06$, the microstructure of the CZ-KNLNS ceramics with a high $CaZrO_3$ content is inhomogeneous and a much smaller grain size with a crude surface is observed (Fig. 6e). Large and small grains are mixed, showing a bimodal structure.

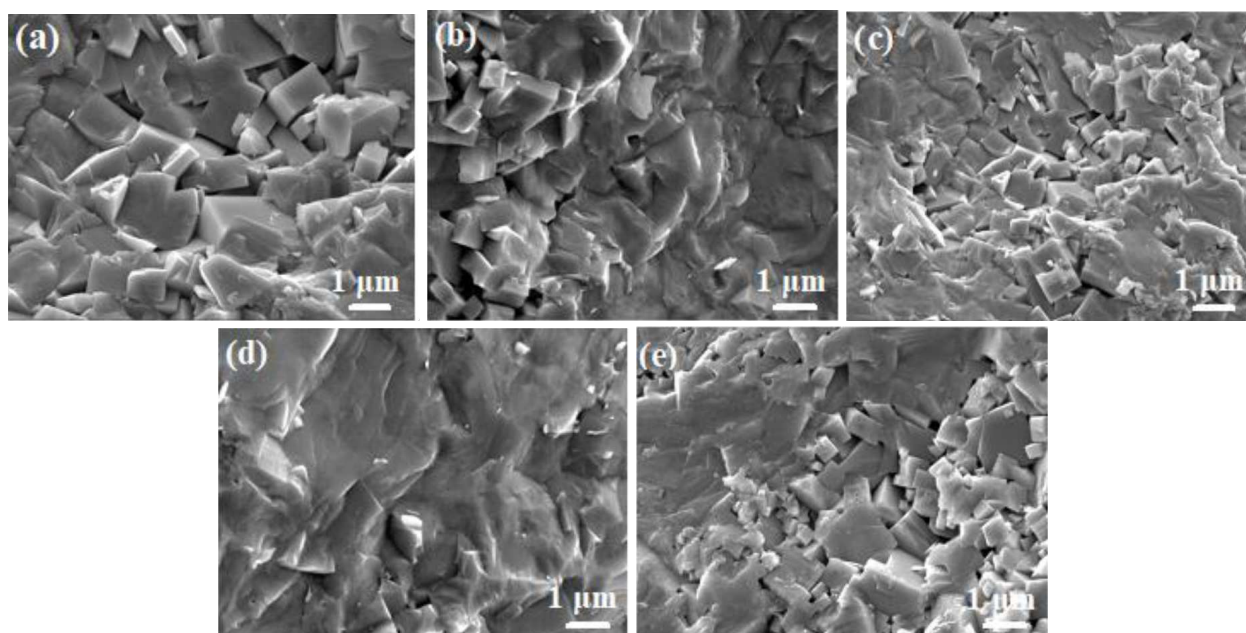Excess amount of $Ca^{2+}$ and $Zr^{4+}$ cannot enter the KNLNS lattice and they assemble at grain boundaries,

**Figure 6. SEM images of CZ-KNLNS ceramics sintered at 1120 °C for 4 h with different CaZrO₃ content *x*: a) 0, b) 0.02, c) 0.03, d) 0.04, and e) 0.06**
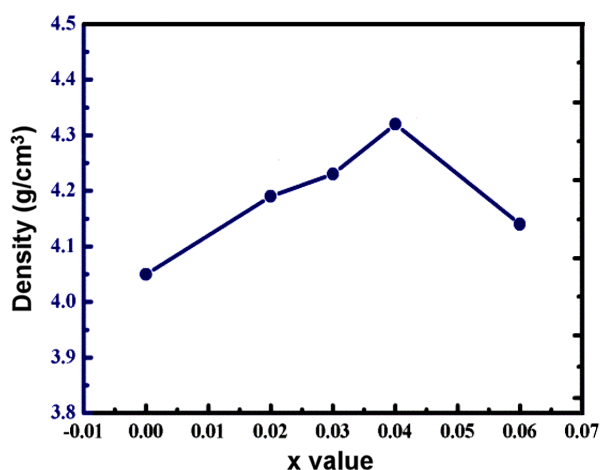


**Figure 7. Density of the CZ-KNLNS ceramics as a function of CaZrO₃ content**

hindering the grain boundary movement. This might be due to the changed ratio of the two phases as indicated in the diffraction patterns, which could result in the orientation difficulties and therefore account for the degradation of the electrical properties for higher doping levels. Similar cases of grain size reduction due to the doping have been reported in previous paper [35].

Figure 7 shows the bulk densities of the CZ-KNLNS ceramics. It can be seen that with the increase in CaZrO₃ content the bulk density of the samples gradually increases from 4.05 g/cm³ and reaches maximum of 4.32 g/cm³ at $x = 0.04$. However, the density decreases to 4.14 g/cm³ when $x = 0.06$. At room temperature, the theoretical density of CaZrO₃ is 4.78 g/cm³, which is higher than the theoretical density of KNN 4.5 g/cm³. During sintering of the ceramics, CaZrO₃ can be melted with other components to produce liquid phase, there-

fore, the introduction of a small amount of CaZrO₃ is beneficial to the improvement of ceramic density. However, excess CaZrO₃ resulted in an uneven grain size and increased pores in the sample (Fig. 6e), resulting in the decreased density.

### 3.3. Piezoelectric properties of CZ-KNLNS

Figure 8 shows the piezoelectric constant ($d_{33}$) and the plane electromechanical coupling coefficient ($K_p$) of specimens sintered under optimum conditions of 1120 °C for 4 h as a function of CaZrO₃ content. The CaZrO₃ content has a great impact on the piezoelectric parameters. Figure 8 shows that the CZ-KNLNS ceramics exhibits a high piezoelectric constant ($d_{33}$ = 201.2 pC/N) at $x = 0.04$. The variation trend of the electromechanical coupling coefficient is almost the same as that of piezoelectric constant $d_{33}$. With the increase in CaZrO₃ content, the plane electromechanical cou-
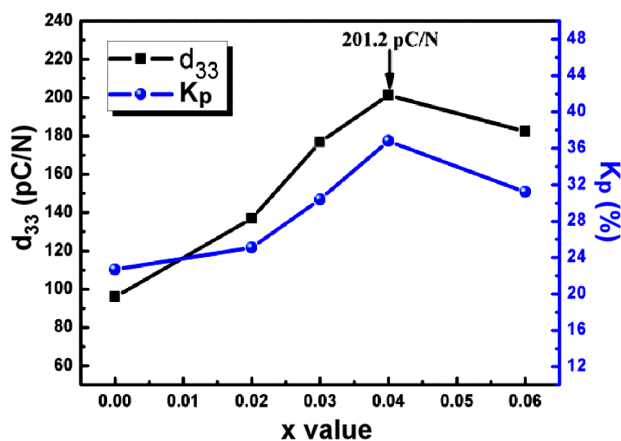


**Figure 8. $d_{33}$ and $K_p$ of the CZ-KNLNS ceramics as a function of *x* value**

pling coefficient initially increases, reaches the maximum value ($K_p = 36.8\%$) at $x = 0.04$ and subsequently decreases. According to the XRD analysis of the CZ-KNLNS ceramics in Fig. 5, at $x = 0.04$ the phase structure of the ceramics is coexistence of the rhombohedral phase and the orthorhombic phase. Compared with the single-phase structure, the electric domain of the multiphase coexisting structure is more easily flipped under the action of polarized electric field, thereby improving the piezoelectricity of the material [34,35]. It is also attributed to a dense homogeneous microstructure and steady domain configuration at $x = 0.04$, thus improving the piezoelectric properties. Furthermore, the improved piezoelectric properties of the ceramics observed in this work may be due to the high activity of the CZ-KNLNS powders obtained by microwave process.

## IV. Conclusions

Well-crystallized lead-free $x$CaZrO$_3$-(1-$x$)(K$_{0.48}$Na$_{0.48}$Li$_{0.04}$)(Nb$_{0.95}$Sb$_{0.05}$)O$_3$ (where $x = 0$, 0.02, 0.03, 0.04 and 0.06) powders were successfully synthesized by using microwave heating followed by conventional solid state sintering. The CZ-KNLNS powders, obtained at a relatively low temperature and short time of 650 °C and 10 min, have cubic structure with an average particle size of 300–700 nm. It is found that the phase constitution and domain configuration of the CZ-KNLNS ceramics can be tailored by changing the content of CaZrO$_3$. Piezoelectric properties (both $d_{33}$ and $K_p$) of the CZ-KNLNS ceramics first increased and then decreased as $x$ increased, simultaneously reaching a peak value for the ceramics with the orthorhombic-rhombohedral (O-R) phase coexistence boundaries. The CZ-KNLNS ceramics sintered at 1120 °C for 4 h with $x = 0.04$ had excellent piezoelectric properties of $d_{33} = 201.2$ pC/N and $K_p = 36.8\%$.

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