

Structure and Physical Properties of ZnO-Doped KNLN Lead-Free Piezoelectric Ceramics

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Abstract: The ZnO-doped $0.96(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3-0.04\text{LiNbO}_3$ (KNLN) piezoelectric ceramics were prepared by conventional ceramics process, using oxides and carbonates mixture, sintered in the solid state at 1050°C . Effect of ZnO on structure and dielectric, ferroelectric, piezoelectric properties of KNLN ceramics were studied. The experimental results showed that the ZnO-doped KNLN ceramics have the pure perovskite structure with orthorhombic symmetry at $x \leq 0.5$ wt.% ZnO. The ZnO addition significantly improved the electrical properties of KNLN ceramics. At ZnO content of 0.5 wt.%, the electrical properties of ceramics are the best: $k_p=0.35$, $k_t=0.45$, $d_{31}=52\text{pC/N}$, $Q_m=33$, $P_f=8.0 \mu\text{C/cm}^2$.

Keywords: Lead-Free Piezoceramics, Crystal Structure, ZnO Addition, Dielectric

1. Introduction

Over the last half century, the piezoelectric ceramic systems have been manufactured and mainly used by basing on the lead zirconate titanate (PZT). [1-3] However, they contain a large amounts of toxic lead, the toxicity of lead oxide and its high vapor pressure during processing leading to environmental pollution and affect human health. [4, 5] In recent years, many countries have required all new electronic products to be lead-free for the environmental protection and human health. [6, 7] Therefore, it is necessary to develop lead-free piezoelectric ceramics with excellent ferroelectric, piezoelectric properties for replacing the lead-based ceramics in different devices. [8]

In general, a lot of various lead-free piezoceramic systems with perovskite structure have been studied [9-12], among which $(\text{K},\text{Na})\text{NbO}_3$ (KNN)-based ceramic systems have attracted much attention due to their strong ferroelectricity, high Curie temperature (about 420°C) and the minimization of toxicity, thereby it has become one of the most promising candidates to substitute for Pb-based ceramics. [13-18] However, it is very difficult to obtain dense KNN ceramics and good electrical properties using ordinary sintering process due to the high volatility of alkaline elements. [19] Compositional modification is an effective way to enhance

the ferroelectric and piezoelectric properties of these ceramics by combining KNN with other compounds to form KNN-based new solid solutions, such as KNN-LiNbO₃ [1], KNN-LiTaO₃ [2], KNN-LiSbO₃ [3]. According to the above reports, the combination of KNN with the dopants will appear the morphotropic phase boundary (MPB) between orthorhombic and tetragonal ferroelectric phase and increases the electrical properties of the KNN based ceramics, similar to that observed in the PZT system. Among the KNN-based solid solutions above mentioned, because of high costs of Ta and toxicity of Sb, the studies often focus on solid solution $(\text{Na},\text{K})\text{NbO}_3\text{-LiNbO}_3$ (KNLN). [14, 20-22]

In addition, to further improve the physical properties of the KNN based ceramics, some works showed that the addition of ZnO could improve the ferroelectric and piezoelectric properties of the KNLN ceramics due to the "softening" effect induced by Zn^{2+} . [22-24]

By using the conventional solid-state reaction method for synthesizing piezoelectric ceramics, we have been fabricated successfully the $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-x\text{LiNbO}_3$ ($x=0-0.08$) lead-free piezoelectric ceramic system and the effect of LiNbO₃ on the density, structure and dielectric properties of ceramic system was studied. [25] From the results of structural analysis, we have determined morphotropic phase boundary of $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-x\text{LiNbO}_3$ ceramic system with x was approximately ~ 0.04 . The tetragonal-

orthorhombic transition point (T_{O-T}) and the Curie temperature (T_C) of the ceramics shifted to the lower and higher temperatures, respectively, when LiNbO_3 content increased. However, at $x \sim 0.04$, the T_{O-T} temperature was high (196°C). Therefore, the electrical properties of the ceramics are not good at room temperature.

In this paper, the different amounts of ZnO was added to $0.96(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-0.04\text{LiNbO}_3$ ceramics with hopes to improve the electrical characteristics of ceramics. The purpose of the paper is study effect of ZnO content on the structure and dielectric, piezoelectric properties of $0.96(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-0.04\text{LiNbO}_3$ lead free ceramics.

2. Experimental Procedure

The general formula of the studied material was $0.96(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3-0.04\text{LiNbO}_3 + x \text{ wt.}\% \text{ ZnO}$ (KNLN-xZnO), where x is 0, 0.1, 0.3, 0.5, 0.7 and are denoted by M0, M1, M3, M5, M7, respectively. Reagent grade oxide powders (purity $\geq 99\%$) of K_2CO_3 , Na_2CO_3 , Li_2CO_3 , Nb_2O_5 , ZnO were used as starting materials. Before being weighed, the K_2CO_3 and Na_2CO_3 powders were dried in an oven at 200°C for 2 h to minimize the effect of moisture. Mixed powder was milled using the Retsch PM 400/2 (Germany) planetary high energy ball mill for 20h with the ZrO_2 balls in ethanol, reversing mode with speed of 350 rpm, in order to obtain an appropriate distribution of the particle size, the small particle size will improve the reactivity of the powders [29]. Two calcinations at temperature 850°C for 2 h were then performed to obtain compositionally homogeneous powders and the single phase formation [30]. Thereafter the calcined, powders were ball milled again for 16h to create a more uniform distribution of powders and the reaction occurs completely [30]. The ground materials were pressed into disk 12 mm in diameter and 1.5 mm in thick under 100 MPa. In order to limit the evaporation of alkaline elements, these pellets were covered by the powders with the same composition and then were sintered in a sealed alumina crucible at the temperature of 1050°C for 2 h

The crystal structure of the sintered samples were examined by X-ray diffraction with $\text{CuK}\alpha$ radiation, $\lambda = 0.15406\text{nm}$ (XRD, D8 ADVANCE-Bruker). The grain morphology of the samples was examined by scanning electron microscopy (Novanano SEM 450-Fei). The densities of samples were measured by Archimedes method. The ceramic samples were poled in a silicone oil bath at 80°C by applying dc field of 30kV/cm for 20min then cooling under the same electric field. They were aged for 24 h prior to testing.

The piezoelectric properties were determined from the resonance and antiresonance frequency by using an Impedance Analyzer HP 1493A and RLC HIOKI 3532. The dielectric constant at room temperature is calculated by measuring the capacitance C of samples using RLC HIOKI 3532 at frequency of 1kHz. Temperature dependence of dielectric properties was determined using RLC HIOKI 3532 with automatic programming; temperature of the samples was measured using Digital Multimeter 7562. The ferroelectric

property was measured by Sawyer-Tower method [3].

3. Results and Discussion

3.1. Effect of ZnO Addition on the Structure and Microstructure of KNLN-xZnO Ceramics

Figure 1(a) shows the density of the KNLN-xZnO ceramic samples sintered at 1050°C as a function of the ZnO content. The undoped KNLN ceramics shows low density, 4.03g/cm^3 . With increasing of ZnO content, the density initially increases strongly and reach the maximum value of 4.34g/cm^3 at 0.5wt.% ZnO, then decrease. These results are consistent with microstructure of fracture surfaces of the samples as shown in figures 1(b)-1(f).

As shown in Figure 1(b), the microstructure of the pure KNLN sample ($x=0$) consisted of irregular large and small grains, the discrete distributions, porous. However, the microstructure of samples becomes denser and more uniform as the ZnO content increases from 0.1 to 0.5 wt.% (Figure. 1(c)-(e)). A homogeneous microstructure developed for the sample with 0.5wt.% added (Figure. 2(e)). Figure 1(f) shows that further increasing ZnO content to 0.7wt.% gives rise to some porous. According to research results of F. Rubio-Marcos [29], the decrease of density at high values of x ($x = 0.7\text{wt.}\%$) may be attributed to the formation of the secondary phase $\text{K}_3\text{LiNb}_6\text{O}_{17}$ (Figure 2(a), the XRD patterns of KNLN-xZnO ceramics). Such with the 0.5wt.% ZnO added ceramics, the highly dense and homogeneous microstructure was obtained.

Figure 2(a) shows the XRD patterns at room temperature with the 2θ range from 20 to 80° of KNLN-xZnO ceramic samples sintered at 1050°C . It can be seen that all samples with x from 0 to 0.5 exhibit single phase structure of orthorhombic perovskite ABO_3 type (the corresponding XRD patterns can be indexed by Ref. [31]), which is characterized by the double peaks (220) and (020) [26], without any secondary phases. However, when $x > 0.5$, a small amount of secondary phase lithium potassium niobium oxide, $\text{K}_3\text{LiNb}_6\text{O}_{17}$ (JCPDS036-0533) with the tetragonal tungsten bronze structure was detected. [27] The appearance of second phase may be due to slight changes in stoichiometric ratio resulting from highly volatile alkaline elements during sintering process. [28] Figure 2(b) shows the enlarged XRD patterns of the ceramics in the ranges of 2θ from 44 to 47° . It can be seen that the diffraction peaks shift to higher diffraction angles with increasing the ZnO content, suggesting that the crystal lattice volume has decreased with ZnO substitution. As known, the ionic radius of Zn^{2+} (0.74\AA) is smaller than those of A-site ions ($\text{K}^+ : 1.33\text{\AA}$, $\text{Na}^+ : 0.97\text{\AA}$) for the KNLN-xZnO ceramics. [22] It showed that Zn^{2+} ions have entered the A-sites of the perovskite unit cell and replaced the K^+ , Na^+ ions. Rubio-Marcos et al. found that the lattice volume of $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})(\text{Nb}_{0.86}\text{Ta}_{0.10}\text{Sb}_{0.04})\text{O}_3$ decreases with increasing concentration of ZnO dopant due to the incorporation of Zn^{2+} cations into the perovskite structure [29]

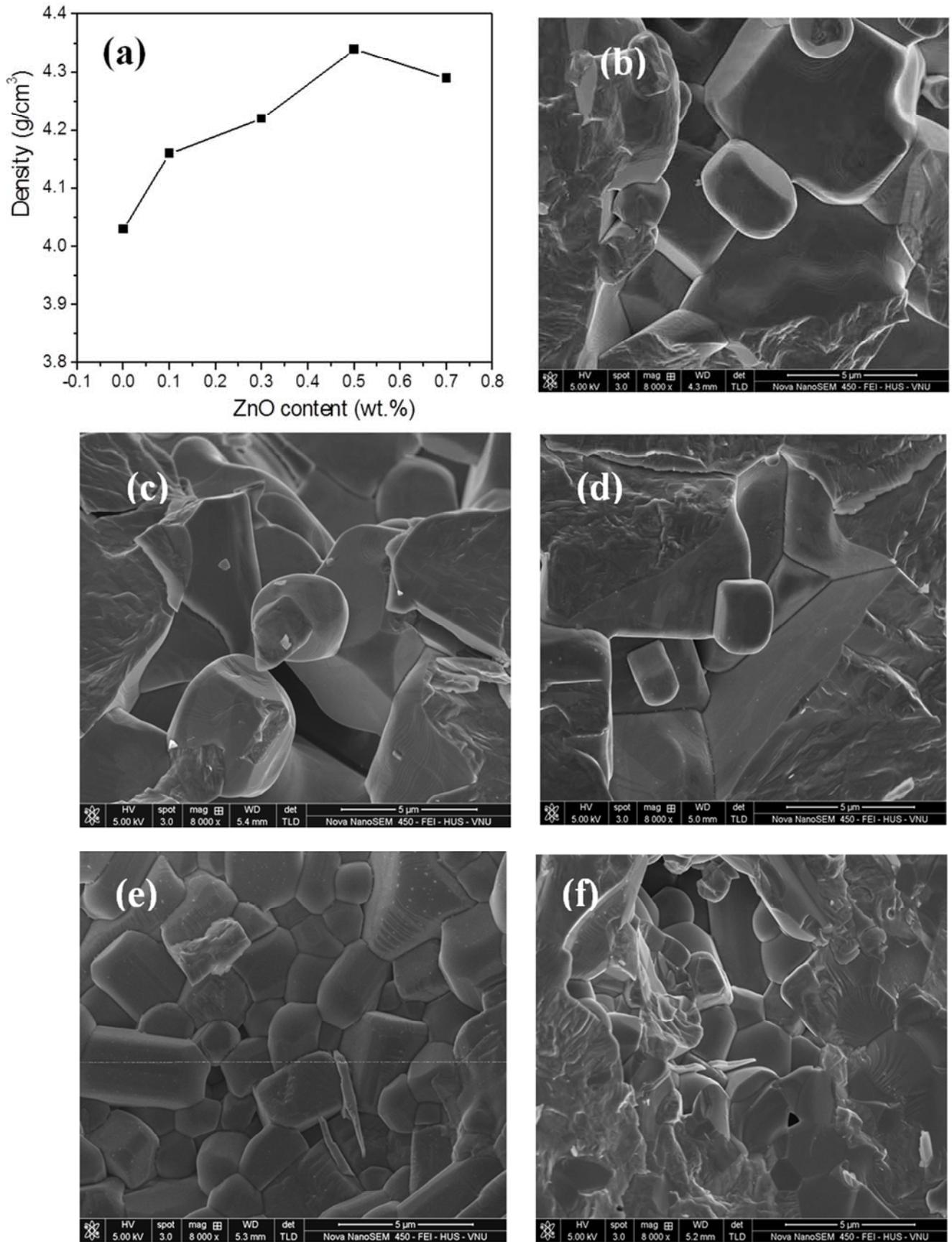


Figure 1. The ZnO content dependence of the density of KNLN ceramics measured at room temperature and the SEM micrographs of KNLN-xZnO ceramics with $x=0$ (b), $x=0.1$ (c), $x=0.3$ (d), $x=0.5$ (e) and $x=0.7$ (f).

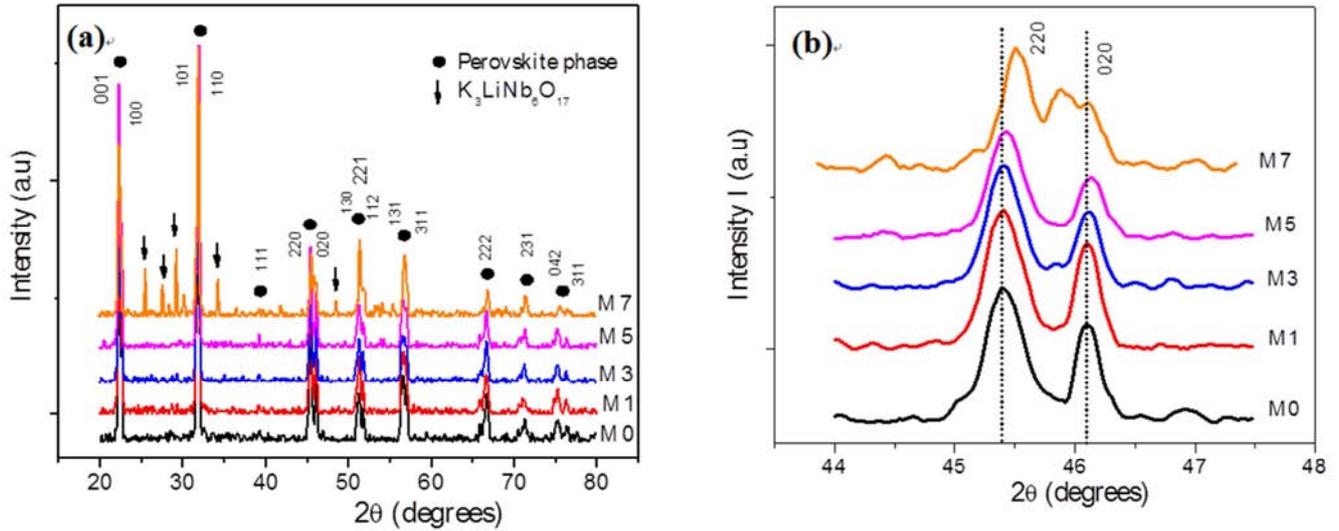


Figure 2. XRD patterns of the KNLN-xZnO ceramics (a) and enlarged region for (220)/(020) peaks of the diffraction patterns (b).

3.2. Effect of ZnO Addition on Physical Properties of KNLN-xZnO Ceramics

The change of ZnO content also significantly affect the dielectric, ferroelectric and piezoelectric properties of KNLN-xZnO ceramics.

Figure 3 shows the room temperature dielectric constant ϵ and dielectric loss $\text{tg}\delta$ was measured at 1kHz frequency of KNLN-xZnO ceramics as function of the ZnO contents. The dielectric constant ϵ increases with the ZnO content increases and reaches highest value (666) at $x=0.5$. However, when $x > 0.5$, the dielectric constant ϵ decreased. This is related to density and microstructure of ceramics. The variation trend of dielectric loss tangent with the ZnO contents is inverse to that of the measured dielectric constant, the minimum value of dielectric loss is 0.06 were obtained at $x=0.5$ wt.% ZnO

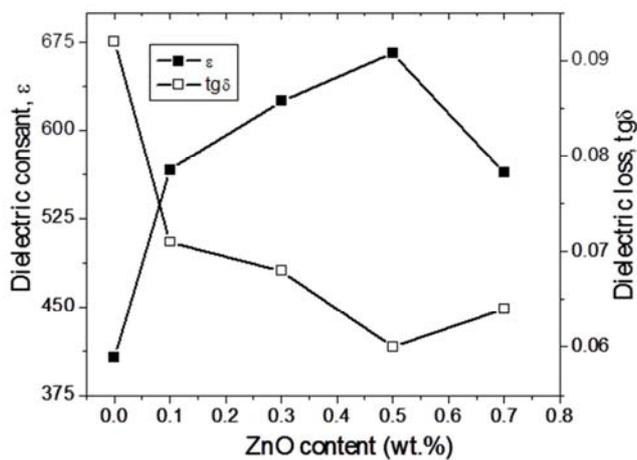


Figure 3. Room-temperature dielectric constant ϵ and dielectric loss $\text{tg}\delta$ of ceramics with different amounts of ZnO.

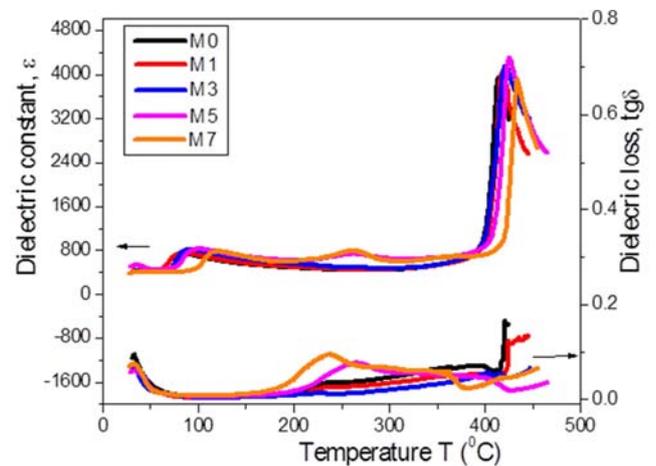


Figure 4. Temperature dependence of dielectric constant ϵ and dielectric loss $\text{tg}\delta$ of the KNLN-xZnO ceramic samples sintered at 1050°C.

Figure 4 shows temperature dependence of dielectric constant ϵ and dielectric loss $\text{tg}\delta$ was measured at 10kHz frequency from room temperature to about 460°C of KNLN-xZnO ceramics sintered at 1050°C. As seen in Figure 4, all the dielectric peaks for KNLN-xZnO ceramics are still sharp, indicating that the ceramics are a normal ferroelectric [3]. Moreover, two transitional points corresponding to the orthorhombic-tetragonal ferroelectric phase transition temperature (T_{O-T}) and ferroelectric-paraelectric phase transition temperature (T_C) are observed during the measured temperature range.[22] Figure 5 shows the T_{O-T} temperature and Curie temperature T_C of KNLN-xZnO ceramics change as a function of ZnO content. With the addition of ZnO, the Curie temperature T_C of ceramics increased from 414°C to 434°C, in contrast to the situation found with ZnO doped $\text{Li}_{0.06}(\text{Na}_{0.535}\text{K}_{0.48})_{0.94}\text{NbO}_3$ ceramics. [22] This result is consistent with the change of the unit cell size indicating that the A-site replacement of Zn^{2+} increases T_C . The phase transition temperature T_{O-T} increases from 83°C to 120°C with the ZnO content. These shifts in the T_{O-T} suggested the

presence of a phase polymorphism. [30] These results are consistent with the work of F.Rubio-Marcos [29]

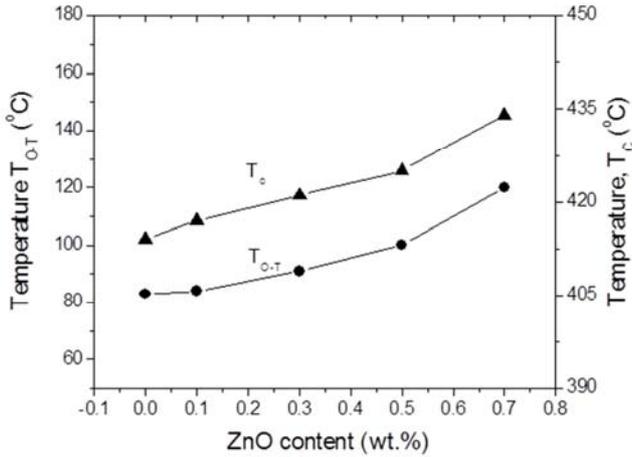


Figure 5. The orthorhombic-tetragonal phase transition temperature (T_{O-T}) and Curie temperature (T_c) of KNLN- x ZnO ceramics as a function of ZnO content.

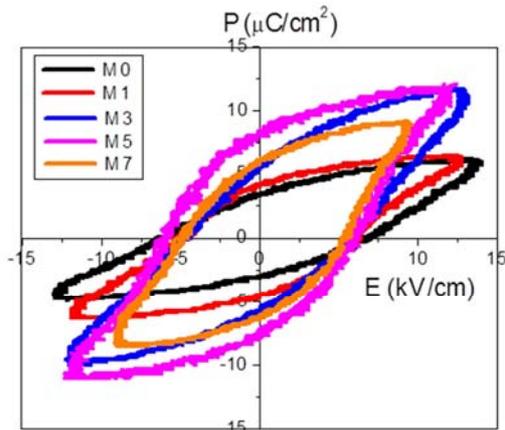


Figure 6. Hysteresis loops of KNLN- x ZnO ceramic samples measured at room temperature.

Figure 6 shows the shape of ferroelectric hysteresis loops of the KNLN- x ZnO samples measured at room temperature. From the shape of these loops, the remanent polarization P_r and the coercive field E_c of ceramics were determined, as

shown in Figure 7. With increasing of ZnO content, a sharp increases in P_r was observed for samples until $x=0.5$, reaches the highest value ($8.0\mu\text{C}/\text{cm}^2$) at this content, and then decreases; while the coercive field E_c steadily decreased from 6.83 to 5.32kV/cm. These results are in good agreement with the studied dielectric properties at room temperature of the ceramic samples and relating to the softening effect in the properties of the ceramics due to A-site replacement of Zn^{2+} ions which provokes the cationic vacancies formation [29]

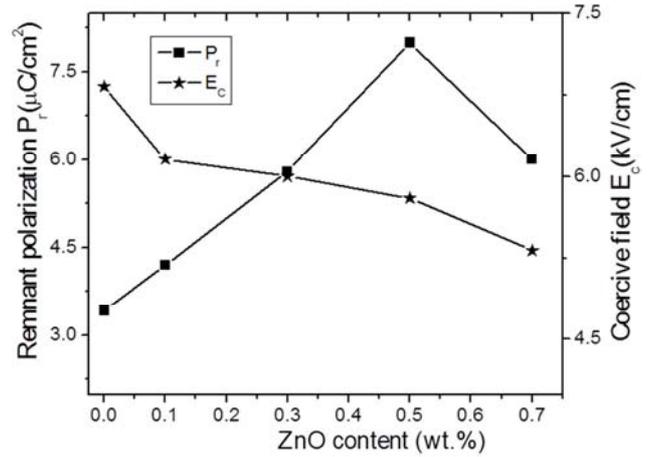


Figure 7. The remnant polarization (P_r) and coercive field (E_c) of KNLN- x ZnO ceramics as a function of the ZnO content.

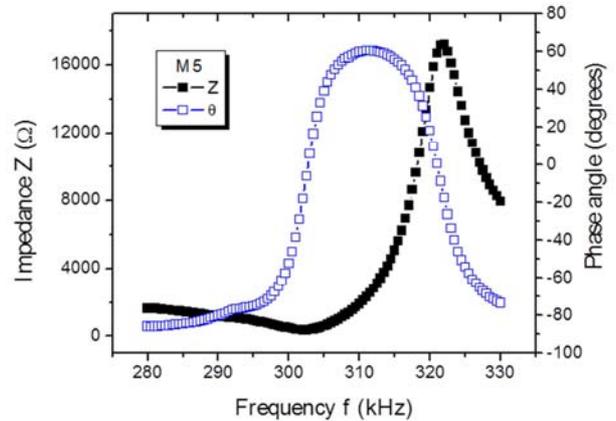


Figure 8. Spectrum of radial resonance of KNLN-0.5wt.% ZnO ceramic sample sintered at 1050°C.

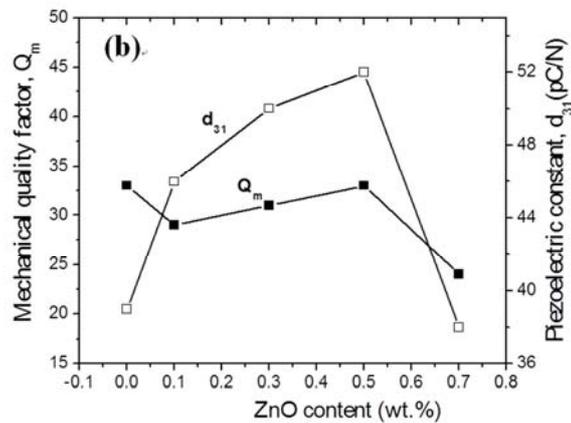
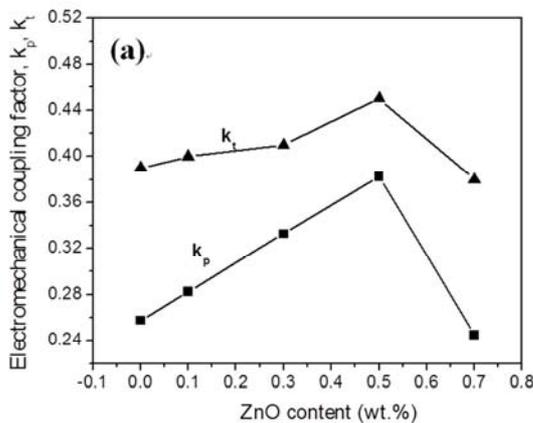


Figure 9. The ZnO content dependence of the values k_p , k_t (a) and d_{31} , Q_m (b) of KNLN- x ZnO ceramics.

To determine piezoelectric properties of ceramics, resonant vibration spectra of samples were measured at room temperature (Figure 8). From these resonant spectra, piezoelectric parameters of samples were determined. Figure 9(a) and (b) show the electromechanical coupling factors (k_p , k_t), the piezoelectric constant (d_{31}), mechanical quality factor Q_m change as a function of the ZnO content. When the amount of ZnO is ≤ 0.5 wt.%, the values of k_p , k_t , d_{31} are rapidly increased with increasing content of ZnO, while the mechanical quality factor Q_m is lightly changes. The largest values for k_p of 0.35, k_t of 0.45, d_{31} of 52 pC/N reached at $x=0.5$. These are probably related to the softening characteristic in the properties of the ceramics induced by Zn^{2+} ions, which leads to the improvement of the electrical properties of KNLN-xZnO ceramics.

4. Conclusions

The effect of ZnO addition on the structure, microstructure and dielectric, ferroelectric properties of $0.96(K_{0.5}Na_{0.5})NbO_3-0.04LiNbO_3$ ceramics was investigated. The addition of ZnO caused an increase in the density and dielectric constant at room temperature. All samples have perovskite phase structure, without any secondary phases at $x \leq 0.5$. With increasing ZnO, the T_{O-T} and T_C temperatures of the ceramics was shifted to higher temperature. The ZnO additive significantly improved the electrical properties of KNLN-xZnO ceramics, at the ZnO content of 0.5 wt.%, dielectric, ferroelectric, piezoelectric properties of ceramics are best.

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