

Effect of LiSbO_3 on dielectric and piezoelectric properties of KNN ceramics

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K_2CO_3 , Na_2CO_3 , Li_2CO_3 , Sb_2O_3 and Nb_2O_5 were used as the starting materials, the $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_{3-x}$ mol% LiSbO_3 ($x=0.00, 0.01, 0.02, 0.03, 0.04$ and 0.05) ceramics are prepared using solid state synthesis method, and the effects of LiSbO_3 content on dielectric and piezoelectric properties of $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ ceramics are investigated. The results show that the crystal structure for $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ ceramics with different LiSbO_3 content is all perovskite structure, and the new phase structure of KNN ceramics can't be obtained when the LiSbO_3 content is $0.00 \leq x \leq 0.05$. The appropriate amount of LiSbO_3 doped KNN ceramics can refine the grain size and increase the density of the ceramics. When $x = 0.04$, the relative dielectric constant reaches 980, the dielectric loss is 0.055, and the combined effect of Li^+ and Sb^{5+} makes the KNN ceramics have better dielectric properties. Due to the more easily the domain wall rotates at the grain boundary, the $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ ceramics doped with 4 mol% LiSbO_3 shows excellent piezoelectric properties in the system of study, and the piezoelectric constant d_{33} increases sharply to the maximum value of 126 pC/N.

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1. Introduction

With the social progress and the rapid development of science and technology, the performance of ceramic materials is more and more demanding, and new ceramic materials come into being [1-3]. As one of the functional ceramic materials, piezoelectric ceramics can realize the mutual conversion between mechanical energy and electrical energy, and its typical applications include underwater transducer, ceramic transformer, piezoelectric motor, imaging equipment [4,5], etc., and many equipments in the ship involve the application of such devices. At present, lead-based piezoelectric ceramics $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) are widely used in the field of application, and lead element accounts for a large proportion (about 70%) in PZT-based piezoelectric ceramics, in addition, improper disposal of these lead-based devices will have a huge negative impact on groundwater and farmland, endangering human beings and the ecological environment [6-8]. In recent years, the need for sustainable development of human society has been increasing and the awareness of environmental protection has been gradually enhanced. Many countries have legislated to ban the use of electronic materials containing lead, the research on lead-free piezoelectric ceramics meeting the environmental requirements and practical applications has become a hot topic for researchers [9,10].

In recent years, lead-free piezoelectric ceramics have become a research hotspot of functional ceramics, especially $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN)-based lead-free piezoelectric ceramics, which is a binary system, it is a completely solid solution of anti-ferroelectrics NaNbO_3 and ferroelectrics KNbO_3 . In 2004, Saito [11] et, al studied a kind of textured KNN ceramics containing Li, Ta and Sb, and its piezoelectric coefficient d_{33} can reach 416 PC / N, which makes KNN based ceramics become a kind of hot material in the field of lead-free piezoelectric materials.

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KNN ceramics have the greatest advantage of high Curie temperature, at the same time with outstanding piezoelectric and electromechanical properties. However, KNN ceramic system also has its own defects: poor preparation technology, alkali metal elements of K and Na tend to volatile at high temperature. In order to overcome the shortcomings of KNN ceramics, researchers have improved the properties of KNN ceramics by doping modification and preparation process [12,13].

Li^+ , Ba^{2+} , Ca^{2+} and Bi^{3+} , which have similar ionic radius and electronegativity to K and Na, can be used to replace A sites. Zr^{4+} , Hf^{5+} and Ta^{5+} , which have similar ionic radius and electronegativity with Nb^{5+} , can be used to replace B sites. Some ABO_3 perovskite structures (such as CaZrO_3 , etc.) allow simultaneous substitution of A and B sites [14]. After doping substitution, due to the difference of ion radius and electronegativity, the lattice of KNN will be distorted to some extent, so that a certain small stress will be generated inside the crystal cell of KNN. The substitution of ions can not only lead to stress in the crystal cell, but also change the phase transition temperature. Therefore, the phase boundary structure of KNN ceramics can be adjusted and the piezoelectric properties of KNN ceramics can be tailored.

Sb^{5+} can partially replace the B site Nb^{5+} in ABO_3 perovskite structure. In addition, as a soft doping element, Sb^{5+} can reduce the coercivity field and cause the tripartite orthogonal phase transition to move to room temperature, and the orthogonal tetradral phase transition to room temperature, resulting in relaxation ferroelectric. In this paper, LiSbO_3 is used as dopant to improve the piezoelectric properties, and the effects of LiSbO_3 content on the crystal structure, microstructure, dielectric properties and piezoelectric properties of KNN base ceramics were studied.

2. Experimental

The general formula of the ceramics was $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ -x mol% LiSbO_3 (x=0.00, 0.01, 0.02, 0.03, 0.04 and 0.05). The samples were obtained by the two-stage method to guarantee access to a pure phase of perovskite. Reagent-grade oxide powders, K_2CO_3 , Na_2CO_3 , Li_2CO_3 , Sb_2O_3 and Nb_2O_5 , were used as the starting materials. Firstly, a powder of $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$, was obtained by sintering K_2CO_3 , Na_2CO_3 and Nb_2O_5 , at 850°C for 4 h. Secondly, the above precursor with Li_2CO_3 and Sb_2O_3 was weighed, and mixed through a polyethylene jar and agate balls milling media. The mixture was then dried at 120°C , granulated (with polyvinyl alcohol as binder), pressed into the desired form ($\Phi \times d = 12.00 \times 2.00 \text{ mm}^2$) at 10 Mpa, and then sintered at 1140°C for 3 h in the air. The sintered samples were cleaned using an ultrasonic bath, then dried. Both sides of the specimens for dielectric property measurements were screened electrode paste composing mainly of AgO, some fluxes and binders, then fired at 650°C for 10 min.

The crystal phase of the specimen was determined by X-ray diffraction (XRD, Model RIGAKU D/MAX 2500V/PC, Japan) with a 2θ range from 10° to 70° . The surface micrographs of the samples were examined by field emission scanning electron microscopy (SEM, Hitachi s4800). Room-temperature dielectric constant and dielectric loss were measured by a LCR meter (WK4225, China). The temperature dependence of dielectric constant (ϵ) and dielectric loss ($\tan\delta$) was measured using a capacitance apparatus (WK4225, China) at 1 kHz range over 25°C to 500°C . The piezoelectric coefficient d_{33} of the specimen was measured by a quasi-static piezo- d_{33} meter (ZJ-4 A, China).

3. Results and discussions

The XRD patterns of KNN ceramics doped with different content of LiSbO_3 sintered at 1140°C for 3 h are shown in Fig. 1. As can be seen from Fig. 1(a), all KNN samples with different LiSbO_3 components form a single orthogonal phase perovskite, and no second phase diffraction peak is observed, which indicates that there is no impurity in the ceramics.

Fig. 1(b) is a local magnification of the diffraction angle range from 44° to 49° . The phase structure can be judged by observing the intensity of diffraction peak, that is, the former diffraction peak is high and the latter diffraction peak is low, the sample presents the orthogonal phase structure, while the former diffraction peak is low and the latter diffraction peak is high, the sample is tetragonal phase structure. Obviously, from Fig. 1(b), it can be found that the KNN ceramics with different content of LiSbO_3 exhibit an orthogonal phase. With the increase of doping amount, the ratio of the diffraction peak strength before and after decreases gradually, and the KNN ceramics at room temperature have a trend of phase transition, the results show that the new phase structure of KNN ceramics can not be obtained when the LiSbO_3 content is $0.00 \leq x \leq 0.05$.

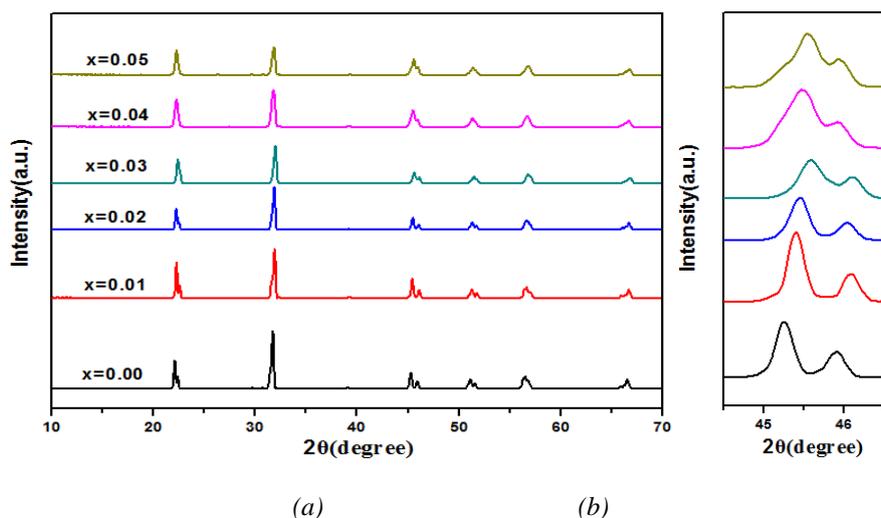


Fig. 1. XRD patterns of KNN-xLiSbO_3 ceramics.

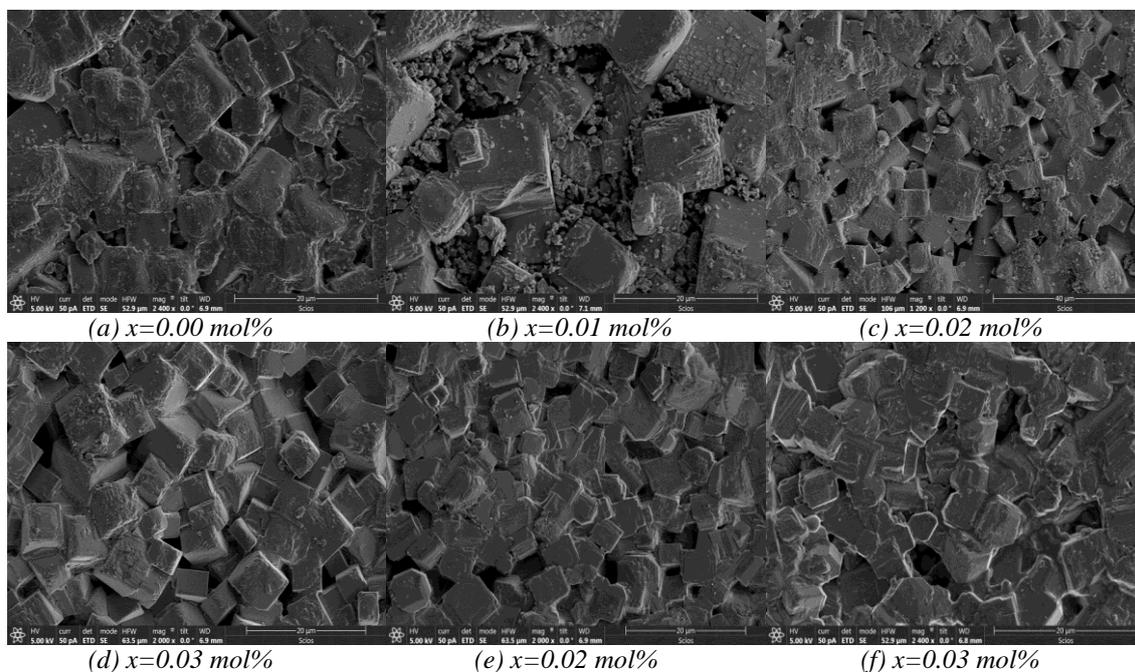


Fig. 2. SEM images of KNN-xLiSbO_3 ceramics.

The SEM images patterns of KNN ceramics doped with different content of LiSbO_3 sintered at 1140°C for 3 h are shown in Fig. 2. As can be seen from Fig. 2, in the pure KNN

ceramics, the ceramic grains are surrounded by relatively clear outline, but the size varies, and generally the large grains are surrounded by the small grains. When $x = 0.05$, the crystal grain becomes fuzzy, which indicates that the excess liquid phase in the sintering process of KNN ceramics changes into glass phase, the normal development of grains is hindered. The bulk density of ceramic samples was measured by Archimedes' principle method. The bulk density of ceramic samples were 3.91 g/cm^3 , 4.02 g/cm^3 , 4.08 g/cm^3 , 4.23 g/cm^3 and 4.30 g/cm^3 , respectively. Obviously, the bulk density of the samples increases with the increase of LiSbO_3 doping amount. Therefore, appropriate amount of LiSbO_3 doped KNN ceramics can refine the grain size and increase the density of the ceramics.

At Room temperature and at 1 kHz, the dielectric constant-doping amount and dielectric loss-doping amount of the samples are shown in Fig. 3. As can be seen from Fig. 3, the effect of LiSbO_3 dopant content on dielectric constant and dielectric loss of KNN ceramics at room temperature is significant. With the increase of the content of LiSbO_3 , the dielectric constant of KNN ceramics at room temperature first increases and then decreases, but the dielectric constant of KNN ceramics increases compared with that of pure KNN ceramics at room temperature, and the dielectric loss of KNN ceramics increases at first and then decreases. With the increasing of the LiSbO_3 content, the grains tend to be homogenized, and the substitution of Li^+ and Sb^{5+} for the ions at the A and B positions of the Perovskite structure lead to the lattice shrinkage and the increase of the density of the ceramics, thus increasing the dielectric constant. When $x = 0.04$, the relative dielectric constant reaches 980, the dielectric loss is 0.055, and the combined effect of Li^+ and Sb^{5+} makes the KNN ceramics have better dielectric properties.

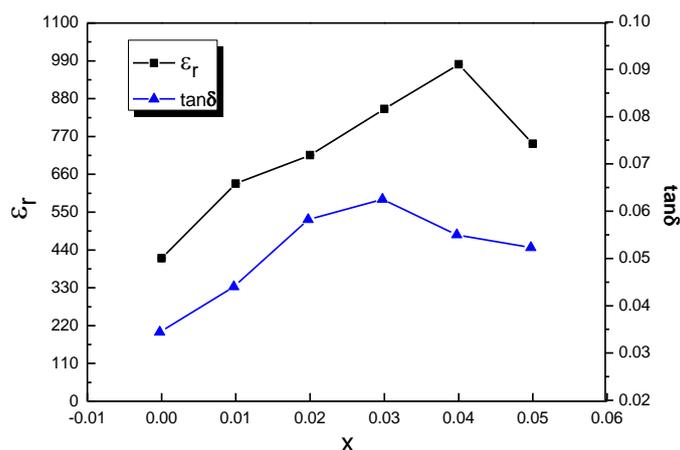


Fig. 3. Dielectric properties of KNN-xLiSbO_3 ceramics.

The dependence of dielectric constant and dielectric loss on temperature for the LiSbO_3 doped samples is shown in Fig. 4. As can be seen from Fig. 4, the samples with different doping have two abnormal dielectric peaks, which correspond to the phase structure transition of orthogonal-tetragonal phase and tetragonal-cubic phase, respectively, the orthogonal-tetragonal phase transition temperature (T_{o-t}) of pure KNN ceramics is $225 \text{ }^\circ\text{C}$, and the tetragonal-cubic phase transition temperature (T_C) is $420 \text{ }^\circ\text{C}$. T_C is called Curie temperature. With the addition of LiSbO_3 , the transformation temperature of tetragonal-cubic phase decreased gradually from $420 \text{ }^\circ\text{C}$ to $300 \text{ }^\circ\text{C}$, which was due to the decrease of the stability of KNN ceramics with the addition of LiSbO_3 , and the transition temperature of orthogonal-tetragonal phase gradually moved to room temperature. When $x = 0.04$, the dielectric peak of pure KNN ceramics is 5029, which shows excellent dielectric properties.

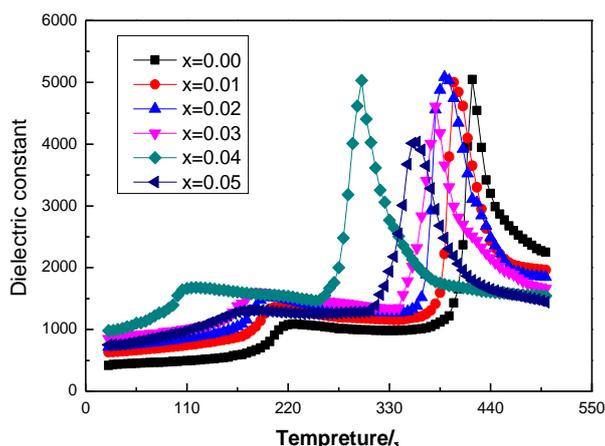


Fig. 4. The dependence of dielectric constant of KNN- x LiSbO₃ ceramics.

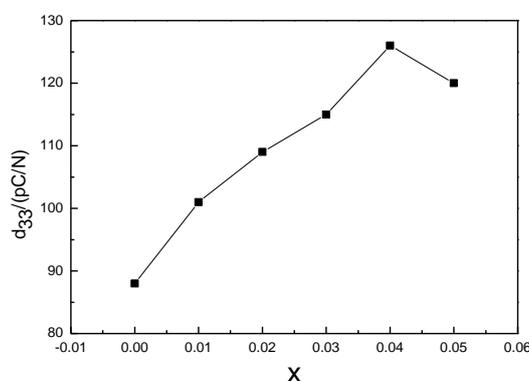


Fig. 5. Relationship between the LiSbO₃ doping amount and d_{33} .

Fig. 5 shows the relationship between the piezoelectric constant d_{33} and the LiSbO₃ doping amount. With the increase of LiSbO₃ content, the piezoelectric constant d_{33} increases first and then decreases. When $x = 0.04$, the piezoelectric constant d_{33} increases sharply to the maximum value of 126 pC/N. The addition of Li⁺ and Sb⁵⁺ leads to lattice distortion and spontaneous polarization in ceramics. Much research show that the high-voltage electric properties tend to appear on the side of tetragonal phase, that is, near the quasi-isotype phase boundary (MPB). At this point, the domain wall is more active, and the domain wall is easier to move and rotate. In addition, the higher the density, the more easily the domain wall rotates at the grain boundary, hence the ceramics doped with 4 mol% LiSbO₃ shows excellent piezoelectric properties.

4. Conclusions

(K_{0.5}Na_{0.5})NbO₃- x mol% LiSbO₃ ceramics were prepared by a solid phase reaction method using K₂CO₃, Na₂CO₃, Li₂CO₃, Sb₂O₃ and Nb₂O₅ as raw materials, and the influence of LiSbO₃ content on piezoelectric and dielectric properties were investigated. The crystal structure for KNN based ceramics with different LiSbO₃ content presents the orthogonal phase structure, and the new phase structure of KNN ceramics can't be obtained when the LiSbO₃ content is $0.00 \leq x \leq 0.05$. Owing to the substitution of Sb⁵⁺ for the ions at the B positions, thus increasing the dielectric constant, and when $x = 0.04$, the relative dielectric constant reaches 980. Due to the more easily the domain wall rotates at the grain boundary, KNN based ceramics doped with 4 mol% LiSbO₃ shows excellent piezoelectric properties in the system of study, and the piezoelectric constant d_{33} increases sharply to the maximum value of 126 pC/N.

Acknowledgements

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