

EFFECT OF HOLDING TIME DURING SINTERING ON DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF 0.96KNN-0.04 LiSbO₃ CERAMICS

R. WANG^{a,*}, Y. LI^b, Y. TIAN^b, Z. LI^c

^a*Marine Engineering Department, Tianjin Maritime College, Tianjin 300350, China*

^b*Analysis and Testing Research Centre, North China University of Science and Technology, Tangshan 063210, China*

^c*Chemical College, Shijiazhuang University, Shijiazhuang 050035, China*

K₂CO₃, Na₂CO₃, Li₂CO₃, Sb₂O₃ and Nb₂O₅ were used as the starting materials, the 0.96(Na_{0.5}K_{0.5})NbO₃-0.04LiSbO₃ ceramics are prepared using solid state synthesis method, and effects of holding time during sintering on dielectric and piezoelectric properties of 0.96KNN-0.04 LiSbO₃ ceramics are investigated. The crystal structure was detected using X-ray diffraction characterization, and the micrographs were observed by field emission scanning electron microscopy. The results show that the crystal structure for 0.96KNN-0.04 LiSbO₃ ceramics with different holding time is all perovskite structure, with the extension of holding time, the proportion of the two diffraction peaks decreases gradually, and presents the trend of gradually merging into a single peak. With the extension of the holding time, the relative dielectric constant increases first and then decreases, reaching the maximum value of 1015 at 5 h. With the increase of holding time, the Curie temperature T_c moves to high temperature, T_c rises from 295 °C to 350 °C, at the same time, the dielectric constant at Curie point reaches 4869 when the holding time is 5 h. Afterwards, the piezoelectric constant increases first and then decreases with the increase of holding time, and the holding time is 5 h, $d_{33} = 147$ pC/N, reaching the maximum value. So the dielectric and piezoelectric properties of 0.96KNN-0.04 LiSbO₃ ceramics are optimized when the holding time is 5 h.

(Received December 4, 2019; Accepted March 23, 2020)

Keywords: Ceramics, Dielectric properties, Piezoelectric, Holding time

1. Introduction

Piezoelectric material is a kind of functional material which can realize the mutual conversion of electrical energy and mechanical energy. It is widely used in the fields of electronic information, medical equipment, industrial automation and so on. its typical applications include sensors, actuators, ultrasonic motors, imaging equipment [1-4], etc., and many equipments in the ship involve the application of such devices. Since the discovery of PbZr_{1-x}Ti_xO₃ (PZT) ceramics in 1950s, the research of piezoelectric ceramics has entered a new chapter because of its excellent piezoelectric properties. However, PZT ceramics contain lead and lead compounds, which does great harm to human body and environment. Therefore, the researchers are trying to explore a

* Corresponding author: lylll2004@aliyun.com

lead-free piezoelectric material [5-8] with good piezoelectric properties to replace lead-based piezoelectric ceramics.

In recent years, potassium sodium niobate $\{(KNa)NbO_3, KNN\}$ ceramics have been widely concerned and made great achievements because of its high piezoelectric constant, Curie temperature and environmental protection [9-11]. Potassium sodium niobate ceramics have perovskite (ABO_3) structure, which can be substituted by ion doping at A or B position to realize the phase transition temperature shift and build polycrystalline phase boundary at room temperature. Due to the coexistence of multiphase in ceramics, the spontaneous polarization direction increases, and the piezoelectric properties will be significantly improved. The construction of phase boundary is the key to replace PZT ceramics with KNN based piezoelectric ceramics. Due to the high volatility of basic elements at high temperature, it is difficult for pure KNN ceramics to achieve good densification by ordinary sintering methods. Due to the high temperature sintering of ceramics, it is difficult to control the stoichiometric ratio, so it can not perform extremely well in performance [12]. In recent decades, through improving the preparation process and adjusting the Na / K ratio to 48 / 52, the piezoelectric constant d_{33} of KNN ceramics can reach about 160 pC/N [13]. Although this performance has been greatly improved, there is still a big gap between this and PZT ceramics. In 2004, Saito [14] et, al reported a kind of textured KNN based lead-free piezoelectric ceramics containing Li, Ta and Sb, and its piezoelectric constant d_{33} can reach 416 PC / N, which makes KNN based ceramics become the key research direction in the field of lead-free piezoelectric materials.

Sb element and Nb element are in the same period, they have similar electronic arrangement outside the core, electronegativity and ion radius. Sb^{5+} ion can partially replace the position of Nb^{5+} in B-site in the perovskite structure of ABO_3 , and Li^+ ion can replace the position of K^+ and Na^+ in A-site, so as to change the phase structure of KNN based piezoelectric ceramics and adjust its electrical properties [2,15,16]. In this paper, $LiSbO_3$ is used as dopant to improve the piezoelectric properties, and the effects of holding time on the crystal structure, microstructure, dielectric properties and piezoelectric properties of KNN base ceramics were studied.

2. Experimental

The general formula of the materials studied was $0.96(Na_{0.5}K_{0.5})NbO_3-0.04LiSbO_3$. The samples were prepared by the two-stage method to acquire 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. At first, a powder of $0.96(Na_{0.5}K_{0.5})NbO_3$, was prepared by calcination of K_2CO_3 , Na_2CO_3 and Nb_2O_5 , at $850^\circ C$ for 4 h. Secondly, the above precursor with Li_2CO_3 and Sb_2O_3 was weighed and mixed through use of a polyethylene jar and agate balls milling media. The mixture was then dried at $120^\circ C$, 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 $1140^\circ C$ for 2 h, 3 h, 4 h, 5 h and 6 h, in the air, respectively. 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 $650^\circ C$ for 10 minutes.

The crystal structure of the samples was detected using X-ray diffraction (XRD, Model RIGAKU D/MAX 2500V/PC, Japan) characterization with a 2θ range from 10° to 70° . The

micrographs of the samples were observed by field emission scanning electron microscopy (SEM, Hitachi s4800). Room-temperature dielectric constant and dielectric loss were measured using an LCR meter (Model YY 281 automatic LCR Meter 4225). The temperature dependence of the dielectric constant (ϵ) and the dielectric loss ($\tan\delta$) was measured using a capacitance apparatus (Model YY 281 automatic LCR Meter 4225) at 1 kHz in a temperature range over 25 °C to 500 °C. The piezoelectric constant d_{33} of 0.96(Na_{0.5}K_{0.5})NbO₃-0.04LiSbO₃ ceramics was measured by a quasi-static piezo- d_{33} meter (ZJ-4 A, China) after the sample was placed for 24 h.

3. Results and discussions

0.96(Na_{0.5}K_{0.5})NbO₃-0.04LiSbO₃ ceramics were prepared at the sintering temperature of 1140 °C for 2 h, 3 h, 4 h, 5 h and 6 h, respectively. Their XRD patterns are shown in Fig.1 (a). It can be seen from Fig. 1 (a) that the 0.96(Na_{0.5}K_{0.5})NbO₃-0.04LiSbO₃ ceramics with different holding time are all perovskite structure, when the holding time is 5 h, the diffraction peak is the strongest, which indicates that prolonging the holding time can promote the development of ceramic grains. When the holding time is further increased to 6 h, because the holding time is too long, the alkali metal ions K⁺ and Na⁺ are partially volatilized, which results in the formation of the second phase impurities, indicating that the dopants LiSbO₃ and KNN ceramics can not form a continuous solid solution. Fig. 1 (b) is the diffraction pattern near 45 °, it can be seen that the holding time is 2 h, KNN ceramics is a single orthogonal phase, with the extension of holding time, the proportion of the two diffraction peaks decreases gradually, and presents the trend of gradually merging into a single peak, that is, the transformation from orthorhombic phase to tetragonal phase is characterized by coexistence of orthorhombic phase and tetragonal phase [17].

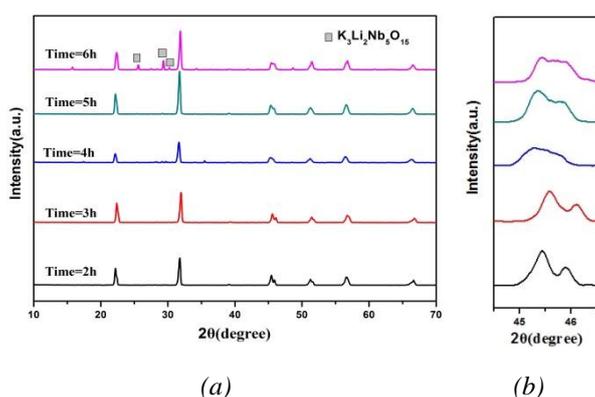


Fig. 1. XRD patterns of 0.96KNN-0.04LiSbO₃ ceramics with different holding time.

Fig. 2 is the surface image of KNN ceramics sintered at 1140 °C for 2 h, 3 h, 4 h, 5 h and 6 h, respectively. According to Fig.2 (a), the holding time is 2 h, the grain size is large, and the porosity is also large. With the extension of the holding time, the grains gradually develop completely, the grains gradually become uniform, the cavities decrease, and the compactness increases. When the holding time is 5 h, the uniformity of grains increases obviously, the large-size

grains decrease and the grains become uniform, as shown in Fig.2 (d). In the process of grain growth, the growth and merging of grain boundaries play an important role. The low energy grain boundaries are relatively stable, and the high energy grain boundaries will merge rapidly and lead to grain growth, which makes the distribution of grain size uneven. Through liquid-phase mixing, the raw materials dissolved in water can be evenly distributed in the solution, which makes the raw materials more uniform, reduces the anisotropy of grain boundary energy, and in the process of solid-phase sintering, the grains will grow rapidly, thus improving the degree of grain uniformity. In Fig2. (e), the density of crystal particles is relatively high, but there are obvious large particles, indicating that the long holding time causes lattice changes, resulting in the generation of second phase impurities. It is consistent with the results in Fig. 1.

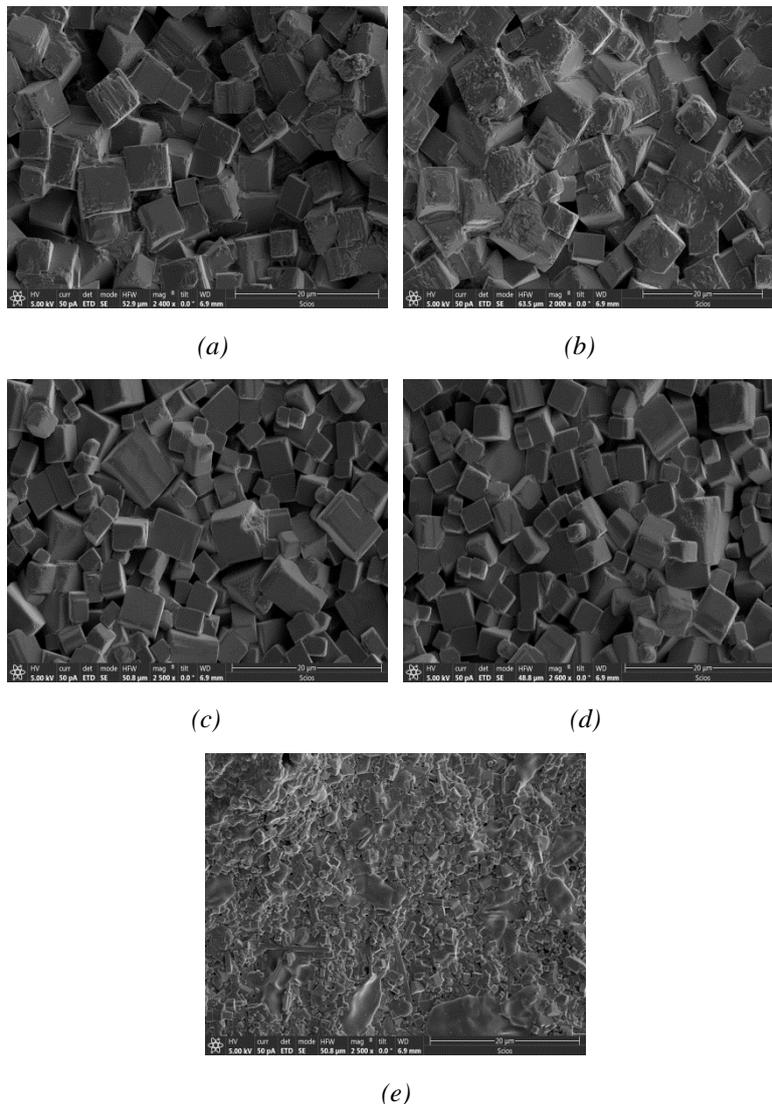


Fig. 2. SEM micrographs of the surface of $0.96\text{KNN}-0.04\text{LiSbO}_3$ ceramics with different holding time: (a) 2 h; (b) 3 h; (c) 4 h; (d) 5 h; (e) 6 h

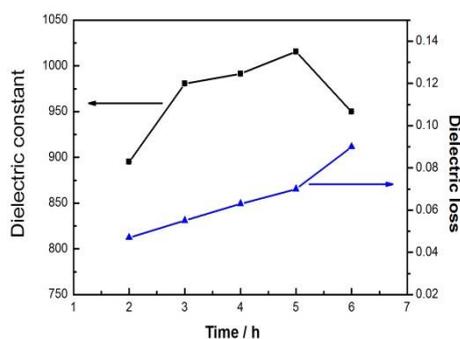


Fig. 3. Dielectric constants and dielectric loss of 0.96KNN-0.04LiSbO₃ ceramics with different holding time.

Fig. 3 shows the change of dielectric constant and dielectric loss of ceramic samples with various holding time. It can be seen from the figure that the dielectric constant is 895 when the holding time is 2 h. With the extension of the holding time, the relative dielectric constant increases first and then decreases, reaching the maximum value of 1015 at 5 h, which is attribute to the increase of holding time, the fuller solid-state reaction, the more uniform grain growth and the higher density of ceramics. With the increase of holding time, the dielectric constant decreased to 921, because the holding time was too long, the alkali metal ions volatilized, the solid-phase reaction was not sufficient, then the dielectric properties decreased [18]. In addition, the dielectric loss increases with the prolongation of holding time, and increases sharply when it is more than 5 h. At the end of sintering, some isolated and closed pores are still on the grain boundary, the elimination of pores or gaps can only be achieved by the way of grain boundary diffusion and space point diffusion. The pores can be eliminated by prolonging the holding time properly. However, if the holding time is too long, it may cause secondary recrystallization, the pores will not be able to diffuse through the interface and fall into the grains. These pores can hardly be eliminated, so the dense sinter can not be obtained. It is reflected in the performance that the dielectric loss increases and the dielectric constant decreases, which is consistent with our results.

The dielectric temperature spectrum of ceramic samples at different holding times is shown in Fig. 4. It can be seen from Fig. 4 that with the increase of holding time, the Curie temperature T_c moves to high temperature, T_c rises from 295 °C to 350 °C. It can be seen that the Curie temperature can be increased by prolonging holding time, in the mean the dielectric constant at Curie point increases first and then decreases. When the holding time is 5 h, the dielectric constant at Curie point reaches 4869, and the dielectric constant at Curie point decreases with the holding time continues to increase to 6 h, which may be due to that the generation of hetero phase weakened the dielectric properties when the holding time increases continuously.

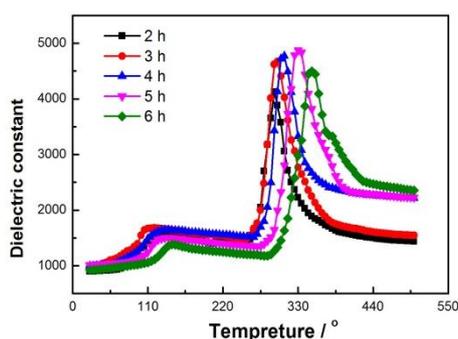


Fig. 4. Temperature dependence of dielectric constants of 0.96KNN-0.04LiSbO₃ ceramics with different holding time.

The samples with different holding time were polarized and placed for 24 h. The piezoelectric constant d_{33} was measured by a quasi-static piezo- d_{33} meter. Fig. 5 shows the change of piezoelectric constant d_{33} of KNN ceramic sample with holding time. It can be seen from the figure that the piezoelectric constant increases first and then decreases with the increase of holding time for 2 h, $d_{33} = 105$ pC/N, and the holding time is 5 h, $d_{33} = 147$ pC/N, reaching the maximum value. At this time, the homogeneity of ceramic grains is good, which is conducive to the elimination of internal stress, weakens the confinement of grain boundaries on the domain, and makes the migration of domain walls easier, so the piezoelectric properties are improved. When the holding time continues to increase for 6 h, the piezoelectric constant decreases, because the holding time is too long, the alkali metal ions are easy to volatilize at high temperature, and the oxygen vacancy in the lattice appears, which can nail the domain and reduce the piezoelectric properties.

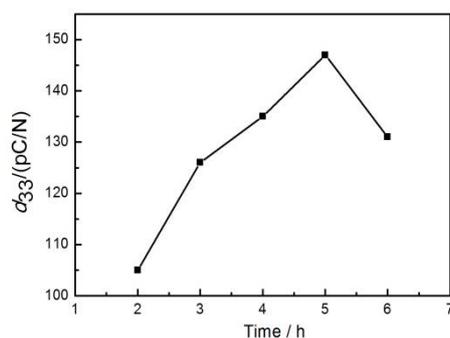


Fig. 5. Piezoelectric constant d_{33} of dielectric constants of 0.96KNN-0.04LiSbO₃ ceramics with different holding time.

4. Conclusions

0.96KNN-0.04LiSbO₃ ceramics were prepared by a solid phase reaction method using K₂CO₃, Na₂CO₃, Li₂CO₃, Sb₂O₃ and Nb₂O₅ as raw materials, and the influence of the holding time on piezoelectric and dielectric properties were investigated. The crystal structure was detected using X-ray diffraction characterization, and the micrographs were observed by field emission

scanning electron microscopy. The XRD results show that the Crystalline phase for 0.96KNN-0.04 LiSbO₃ ceramics with different holding time is all perovskite structure, with the extension of holding time, the proportion of the two diffraction peaks decreases gradually, and presents the trend of gradually merging into a single peak. Due to the increase of holding time, the fuller solid-state reaction, the more uniform grain growth and the higher density of ceramics, the dielectric constant increases to 1015 at 5 h. When the holding time is 5 h, the dielectric constant at Curie point reaches 4869, and the dielectric constant at Curie point decreases with the holding time continues to increase to 6 h, which can result from the generation of hetero phase. Afterwards, the piezoelectric constant increases first and then decreases with the increase of holding time, and the holding time is 5 h, $d_{33} = 147$ pC/N, reaching the maximum value.

Acknowledgements

This work was supported partially by the National Natural Science Foundation of China (Grant No. 51502075).

References

- [1] T. L. Zhao, C. L. Fei, X. Y. Dai et al., *Journal of Alloys and Compounds* **806**, 11 (2019).
- [2] J. L. Zhang, X. Sun, W. B. Su, et al, *Scripta Materialia* **176**, 108 (2020).
- [3] H. Jia, X. K. Hu, J. G. Chen, *Journal of the European Ceramic Society* **39**, 2348 (2019).
- [4] L. Wang, J. J. Ding, Z. D. Jiang et al., *Sensors and Actuators A: Physical* **295**, 629 (2019).
- [5] A. R. M. Siddique, S. Mahmud, B. V. Heyst, *Energy Conversion and Management* **106**, 728 (2015).
- [6] Z. H. Zhao, Y. J. Dai, F. Huang, *Sustainable Materials and Technologies* **20**, e00092 (2019).
- [7] S. A. Khan, F. Akram, J. Bae et al., *Solid State Sciences* **98**, 106040 (2019).
- [8] P. Li, Y. Huan, W. W. Yang et al., *Acta Materialia* **165**, 486 (2019).
- [9] Y. Huan, T. Wei, Z. X. Wang et al., *Journal of the European Ceramic Society* **39**, 1002 (2019).
- [10] B. H. Liu, P. Li, B. Shen et al., *Ceramics International* **43**, 8004 (2017).
- [11] J. Du, G. Z. Zang, X. J. Yi et al., *Materials Letters* **70**, 23 (2012).
- [12] J. F. Li, K. Wang, F. Y. Zhu et al., *Journal of the American Ceramic Society* **96**, 12715 (2013).
- [13] Y. J. Dai, X. W. Zhang et al., *Applied Physics Letters* **94**, 4141 (2009).
- [14] Y. Saito, H. Takao, T. Tani et al., *Nature* **432**, 84 (2004).
- [15] W. Z. Yao, J. L. Zhang, C. M. Zhou et al., *Journal of the European Ceramic Society*, in press.
- [16] E. Shafiee, M. D. Chermahini, A. Doostmohammadi et al., *Ceramics International* **45**, 22203 (2019).
- [17] Z. Q. Fu, J. Yang, P. Lu et al., *Ceramics International* **43**, 12893 (2017).
- [18] R. Nadar Nandini, M. Krishna, A. V. Suresh et al., *Materials Science and Engineering B* **231**, 40 (2018).