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Effect of Sintering Time on Structure and Properties in CuO-doping KNN-LS-BF Piezoelectric Ceramics

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Abstract: The 0.6mol% CuO-doping 0.996($0.95Na_{0.5}K_{0.5}NbO_3$-$0.05LiSbO_3$)-$0.004FeBiO_3$ (KNN-LS-BF-CuO) piezoelectric ceramics were synthesized by a solid-state reaction technique, and the structure and piezoelectric properties dependence of sintering time in KNN-LS-BF-CuO ceramics were studied. It is found that all the samples sintered for various time are perovskite structure mixed with orthorhombic symmetry phase and tetragonal phase, but the sintering time has significant influences on the crystalline and properties. When the sintering time increases from 2 hours to 6 hours, the grain of KNN-LS-BF-CuO ceramics becomes more homogeneous and more tight-arrangement. The experimental results reveal that the longer sintering time than 4 hours is beneficial for improving partial properties, such as d_{33}, tgδ, and Q_m, but is adverse to ε_r and k_p, the KNN-LS-BF-CuO ceramics with optimum properties can be synthesized for 6 hours at 1 060 ℃.

Key words: piezoelectric ceramics; KNN-LS-BF; CuO-doping; sintering time

1 Introduction

Piezoelectric materials dominated by the lead-based ceramics have been widely used for piezoelectric actuators, sensors and transducers[1]. However, the use of lead in materials has been restricted by law in more and more countries due to its environmental pollution[2-4]. In order to adhere to recent environmental legislation, the latest research for piezoelectrics materials has been mainly focused on the lead-free piezoelectric ceramics[5-7].

Recent years, $K_{0.5}Na_{0.5}NbO_3$ (KNN)-based ceramics, which exhibit T_c values as high as 420 ℃, have been intensively investigated for the possible substitution of lead-based piezoelectric ceramics[8-10]. However, KNN-based ceramics are difficult to sinter by the conventional solid-state method, and it was found that KNN-based ceramics show a large temperature dependence of the piezoelectric properties due to multiple polymorphic phase transitions and the evaporation of Na and K sintered at high temperatures would degrade their piezoelectric properties[11,12]. The sinterability and electrical properties of KNN-based materials can be improved by many other routes, such as solid solutions with ABO_3 (A: Li, Na, K, Bi ; B: Nb, Sb, Ti, Fe)[13-17]. Excellent piezoelectric properties have been reported in the $K_{0.5}Na_{0.5}NbO_3$-$LiSbO_3$-$BiFeO_3$ systems prepared by a conventional sintering method[18,19]. Recent research has shown that sintering aids, such as V_2O_5, CuO, "hardened" the KNN-based ceramics and significantly enhanced their piezoelectric properties by decreasing the sintering temperature[20-23].

In this paper, 0.6mol% CuO-doping 0.996 ($0.95Na_{0.5}K_{0.5}NbO_3$-$0.05LiSbO_3$)-$0.004BiFeO_3$ (KNN-LS-BF) ceramics were synthesized by solid-state sintering technique, and the effects of sintering time on their structure and properties were investigated.

2 Experimental

0.6mol% CuO-doping KNN-LS (KNN-LS-BF-CuO) ceramic was synthesized by solid-state reaction method. According to stoichiometric molecular formula, the analytical-grade raw materials of K_2CO_3, Na_2CO_3, Nb_2O_5, Sb_2O_3, Li_2CO_3, Fe_2O_3, Bi_2O_3, and CuO were weighed, then, were milled with ZrO_2 balls in ethanol for 12 hours and dried, followed by calcination at 880 ℃ for 6 hours. To enhance the green strength of the powder compact, 5wt% polyvinyl alcohol (PVA) solution was added to the powder before pressing

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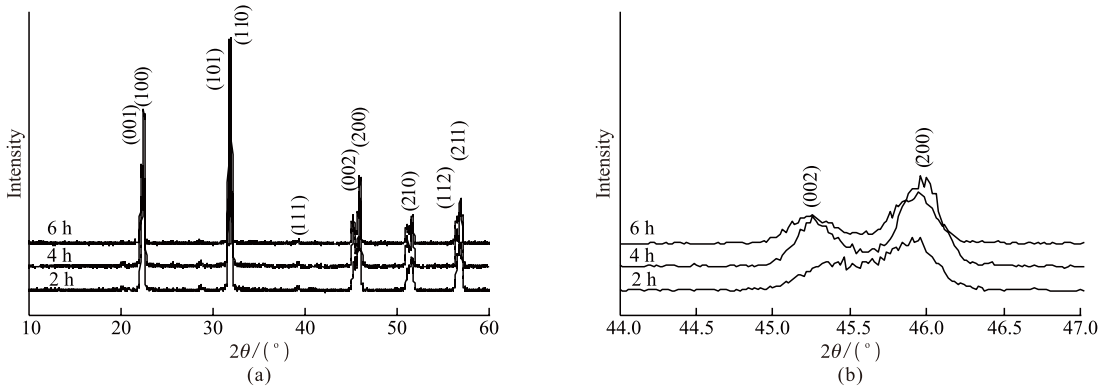

Fig.1 XRD patterns of KNN-LS-BF-CuO ceramics sintered for different time

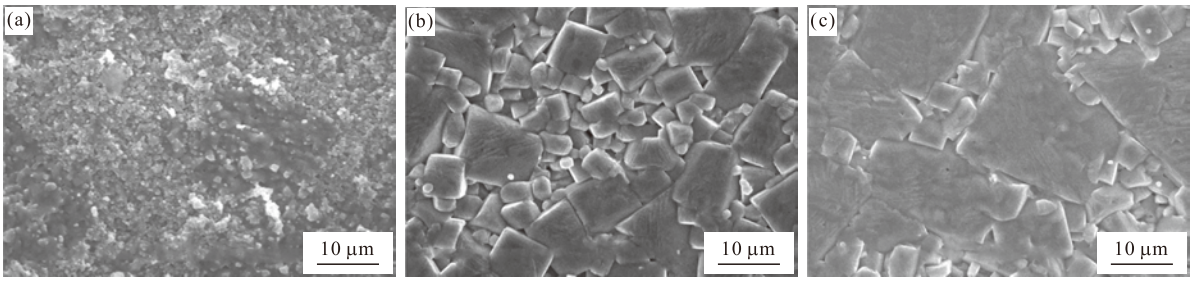

Fig.2 SEM images of KNN-LS-BF-CuO ceramics sintered for: (a) 2 hours; (b) 4 hours; (c) 6 hours

pellets of 18 mm diameter and 1.5 mm thickness under 100 MPa. The pellets were sintered at 1 060 ℃ for 4 hours. Sintered pellets were coarsely polished and silver paste electrodes were formed on both surfaces of the disk-shaped specimens. The samples were poled at 3 kV/mm for 20 minutes in the silicone oil at 80 ℃.

The crystal structure and phases of the ceramics were characterized by X-ray diffraction (XRD) with Cu-Kα radiation (AXS D8-ADVANCE, Bruker). The grain morphologies and size were observed by scanning electron microscope (SEM, JSM-5610LV, JEOL). The piezoelectric constant (d_{33}) was measured approximately 24 hours after poling by quasi-static piezoelectric d_{33} meter (ZJ-3AN). The piezoelectric and dielectric properties, such as dielectric constant (ε_r), the dielectric loss (tanδ), planar coupling coefficient (k_p), the mechanical quality factor (Q_m), were measured by impedance analyzer (4294A, Agilent).

3 Results and discussion

The room temperature X-ray diffraction (XRD) patterns for KNN-LS-BF-CuO ceramics sintered at 1 060 ℃ for different time from 2 hours to 6 hours are shown in Fig.1. As can be seen from Fig.1(a), the perovskite structure mixed with orthorhombic symmetry phase and tetragonal phase, which characterized by splitting of the (002)/(200) peaks at 2θ of 45°-46.5° in Fig.1(b). It is observed in all samples sintered for various time which indicated that the sintering time has insignificant influence on the phase structure of KNN-LS-BF-CuO. Furthermore, there is no trace of the second phase, implying that Cu ions diffuse into the KNN lattices and a solid solution forms in the ceramics. Nevertheless, the intensity of characteristic diffraction peaks in KNN-LS-BF-CuO ceramics become higher with the increase of sintering time from 2 hours to 6 hours, which means that the crystalline become better with longer sintering time. In addition, it can be seen, from Fig.1(b), that the characteristic diffraction peaks of KNN-LS-BF-CuO shift from lower angles to higher angles, which means that the crystal lattice constant of specimens is compressed.

Fig.2 is SEM images of KNN-LS-BF-CuO ceramics sintered for different time at 1 060 ℃. It can be seen that the grain is very small when the sintering time is 2 hours, which meaning inadequate grain growth because of its insufficiency of sintering time. With the increase of the sintering time, it can be seen that the grain size of KNN-LS-BF-CuO ceramics increase, but the size of grain become non-uniform, and some abnormal larger grains and holes can be observed, resulting in density performance degradation. These indicate that the appropriate sintering time is effective in improving the density of KNN-LS-BF-CuO ceramics.

The sintering time dependence of piezoelectric constant d_{33} and planar electromechanical coupling coefficient k_p of KNN-LS-BF-CuO ceramics sintered at

1060 ℃ are shown in Fig.3. With increasing sintering time, the d_{33} increase to 111 when the sintering time is below 4 hours, then, decrease with the further increase of sintering time. Like the variation trend of d_{33} value, k_p increase to a maximum values of 0.30 with the increase of sintering time from 2 hours to 4 hours, then decrease with the further increase of sintering time. The results indicated that the appropriate sintering time is beneficial for enhancing the piezoelectric properties of KNN-LS-BF-CuO ceramics due to the dense structure confirmed in Fig.2. But too long sintering time would degrade the piezoelectric properties.

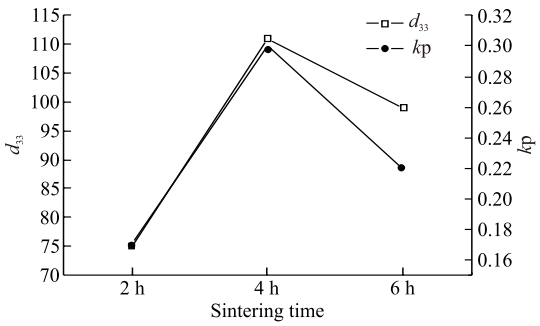

Fig.3 d_{33} and k_p of KNN-LS-BF-CuO ceramics sintered for different time

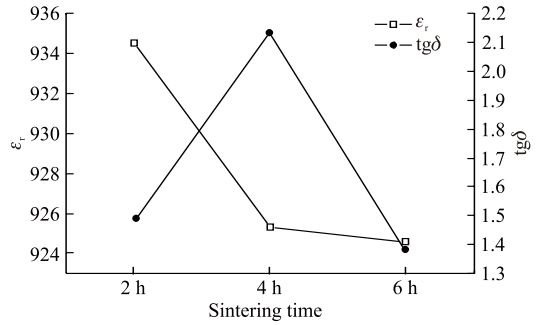

Fig.4 ε_r and tgδ of KNN-LS-BF-CuO ceramics sintered for different time

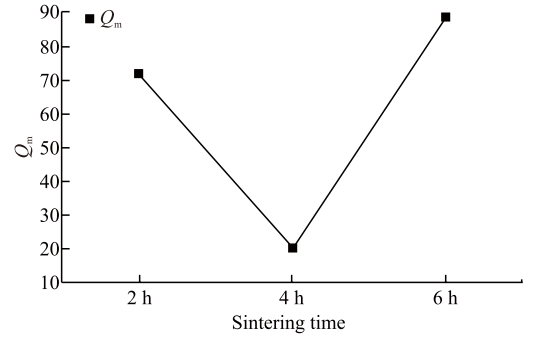

Fig.5 Q_m of KNN-LS-BF-CuO ceramics sintered for different time

The sintering time dependence of dielectric constant ε_r and dielectric loss tgδ of KNN-LS-BF-CuO ceramics sintered at 1 060 ℃ are shown in Fig.4. With the increase of sintering time from 2 hours to 6 hours, the dielectric constant ε_r decrease sharply first, then, decrease slowly when the sintering time is longer than 4 hours. Like the variation trend of piezoelectric constant d_{33} and the planar electromechanical coupling coefficient k_p, the dielectric loss tgδ increases rapidly to the a value of 2.13%, then decrease to the lowest value of 1.37% with the further increase of sintering time.

The sintering time dependence of mechanical quality factor Q_m of KNN-LS-BF-CuO ceramics sintered at 1060 ℃ is shown in Fig.5. Being contrary to the tgδ, it can be seen that the value of Q_m decreases with the increase of sintering time from 2 hours to 4 hours, then increase with the further increase of sintering time. The maximum value of 89 obtained when the sintering time is 6 hours. These results indicate that the longer sintering time more than 4 hours is beneficial for improving the dielectric loss tgδ and the mechanical quality factor Q_m, but it is adverse for enhancing piezoelectric constant d_{33}, the dielectric constant ε_r and the planar electromechanical coupling coefficient k_p. In general, the KNN-LS-BF-CuO ceramics with optimum combination properties can be synthesized for 4 hours at 1 060 ℃. When the sintering time is not enough, Cu^{2+} does not enter into the crystal lattice of KNN completely. As a “hard” additive, CuO scattered in the grain boundary bring the high mechanical quality factor Q_m. However, when the sintering is enough long, Cu^{2+} can enter into the crystal lattice of KNN completely, resulting the decrease in Q_m. With the sintering time lengthen further, CuO scattered in the grain boundary become more and more due to the limit of solid solubility, enhancing the mechanical quality factor Q_m again.

4 Conclusions

All KNN-LS-BF-CuO ceramics sintered for various time from 2 hours to 6 hours are perovskite structure mixed with orthorhombic symmetry phase and tetragonal phase. With increase of the sintering time from 2 hours to 6 hours, the grain of KNN-LS-BF-CuO ceramics becomes more homogeneous and tight-arrangement. The results revealed that the longer sintering time more than 4 hours is beneficial for improving partial properties, such as d_{33}, tgδ, and Q_m, but is adverse to ε_r and k_p. The optimum properties can be obtained in the specimen sintered for 4 hours at 1 060 ℃.

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