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Effects of CuO addition on the sinterability and electric properties in PbNb$_2$O$_6$-based ceramics

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ABSTRACT

PbNb$_2$O$_6$ (PN)-based ceramics with tungsten bronze structure are promising piezoelectric materials in high-temperature devices such as piezoelectric vibration transducers. However, the PN-based ceramics usually exhibit a low bulk density, which greatly limits their practical applications. In this work, CuO was used as the sintering aid to form a liquid-phase bridge, leading to an obvious increase of the bulk density of PN-based ceramics by 11% (from 5.25 to 5.85 g cm$^{-3}$) and the improvement of the piezoelectric constant ($d_{33}$) (from 168 to 190 pC/N) and the Curie temperature ($T_C$) from 367 to 395 °C. The positive influence of CuO on densification has been proved by SEM and fracture toughness. The XRD patterns confirmed that there was no secondary phase introduced by CuO addition. The Raman spectra revealed that part of Cu$^{2+}$ ions has probably diffused into host lattice of the PN and preferred to occupy on A-sites. These results not only demonstrate the high potential of the CuO added PN-based ceramics for high-temperature piezoelectric applications, but also reveal the corresponding structure-properties relationship as well as provide a way to improve the sinterability, $d_{33}$, and $T_C$ simultaneously.

ARTICLE INFO

Keywords:
CuO addition
PbNb$_2$O$_6$-based ceramics
Densification
Piezoelectric properties
Curie temperature

1. Introduction

Piezoelectric ceramic is an information function ceramic material that can realize the conversion of mechanical energy and electrical energy. It has important applications in high-tech fields and is a key material for manufacturing many instrument parts, such as the breathing valve of a ventilator that fights against the new coronavirus. At present, lead zirconate titanate ceramic (Pb(Zr, Ti)O$_3$, PZT) is the most extensively employed piezoelectric ceramic material for its excellent piezoelectric performance [1,2]. However, an important disadvantage of PZT ceramics is that the Curie temperature ($T_C$) is relatively low, which limits its application in high-temperature environments. Compared to the conventional PZT ceramics, PbNb$_2$O$_6$ (PN)-based piezoelectric ceramics possess a higher $T_C$ ($\approx 570$ °C) and a series of other outstanding properties such as low mechanical quality factor ($Q_m < 20$) including large anisotropy in electromechanical coupling coefficient. These characteristics make PN ceramics become a promising candidate for high-temperature devices such as wideband ultrasonic transducers and flow meters for which the traditional PZT and other piezoelectric ceramics cannot be applied. However, one of the major problems in PN-based ceramics such as commercial (Pb, Sr) Nb$_2$O$_6$ (PSN) ceramics is its low bulk density which has a negative influence on polarization. Meanwhile, it is an obvious weakness that PN-based ceramics have a small piezoelectric constant ($d_{33}$) compared with PZT ceramics.

In order to achieve densification with enhanced electrical properties, some attempts which are mainly through using various dopants have been made. As for A-site doping, Yuan et al. reported that the replacement of Sr$^{2+}$ for Pb$^{2+}$ ions is positive to reduce sintering temperature to 1240 °C, improve relative density by 1.76%, and $d_{33}$ from 66 to 73 pC/N in PN ceramics [3]. In the respect of B-site substitution, Roland et al. found that 2% Ti$^{4+}$ ions substitution on the Nb$^{5+}$ sites in Pb$_{0.95}$Sr$_{0.05}$Nb$_2$O$_6$ ceramics helps to decrease the sintering temperature by 20 °C and keep the electromechanical coefficients Q ( = 11) and $d_{33}$...
et al. reported that the substitution of Sr$^{2+}$ for Pb$^{2+}$ ions and the doping of Ta$^{5+}$ ions for Nb$^{5+}$ ions in PN ceramics is obviously beneficial to form a packed structure, and increase $d_{33}$ from 28 to 79 pC/N [5]. Other ions, such as Ba$^{2+}$, Ca$^{2+}$, Sm$^{3+}$, and Ce$^{4+}$, have been also used to increase the densification of PN ceramics [6–9]. Although these dopants can improve the density, they usually reduce the Curie temperature or piezoelectric properties, restricting the applications of PN-based piezoelectric ceramics. Based on the above results, it can be seen that PN ceramics with Sr$^{2+}$ adding have good piezoelectric properties, but the density still needs to be further improved.

In addition, it is key to choose a suitable dopant to improve density and piezoelectric performance without reducing Curie temperature. In terms of improving the densification of ceramic materials, many substances such as LiF, Li$_2$O–B$_2$O$_3$, ZnF$_2$ and BaAl$_2$Si$_2$O$_8$–Li$_2$O–MgO–ZnO–B$_2$O$_3$–SiO$_2$ glass have been made as a sintering additive [10–13]. Besides, it is well known that CuO, served as a sintering aid, can promote the densification as well as reduce the sintering temperature through forming the liquid phase. Moreover, it is reported that CuO also has an influence on piezoelectric properties by diffusing into the A site and/or B site of the crystal lattice. The addition of 0.5 wt% CuO to SrNb$_2$O$_6$ leads to a bulk density of up to 98% resulted from some Cu$^{2+}$ ions replacement at the A sites [14]. The 0.49Pb(N$_{1/3}$Ta$_{2/3}$)O$_3$-0.51Pb(Hf$_{0.3}$Ti$_{0.7}$)O$_3$ ceramics with the aid of 0.5 mol% CuO additive obtain a largest density (8.61 g cm$^{-3}$) and high $d_{33}$ (= 912 pC/N) due to the replacement of Cu$^{2+}$ ions for the high-valence ions (Nb$^{5+}$, Ti$^{4+}$) at the B sites [15]. It is also reported that the (K, Na, Li) (Nb, Ta, Sb)O$_3$ ceramics with 0.05 wt% CuO addition show a smaller coercive field owing to the replacement of Cu$^{2+}$ ions at the A sites and the improvement of $Q_m$ from 26 to 137 due to the incorporation of Cu$^{2+}$ ions into B sites [16]. However, there are little reports about CuO addition enhancing density, $d_{33}$, and $T_c$ simultaneously in PN-based ceramics.

Therefore, 0.08 wt% CuO was added to the commercial PSN ceramics for the purpose of investigating its effects on the crystallite structure, microstructure, dielectric and piezoelectric properties. Finally, the obvious increase of the bulk density of PN-based ceramics by 11% (from 5.25 to 5.85 g cm$^{-3}$) and the $d_{33}$ (from 168 to 190 pC/N) as well as the $T_c$ (from 367 to 395 °C) has been gained in this work.

2. Experimental procedure

The samples of PSN and PSN with 0.08 wt% CuO addition (abbreviated as PSN and PSN-CuO, respectively) were fabricated using a means of solid-state sintering. The commercial PSN and CuO (99.00%) powders were utilized as the original materials. The PSN powders and 0.08 wt% CuO were blended through ball-milling for 6 h, and then sintered. Afterward, the 6 wt% polyvinyl alcohol (PVA) was added as the agglomerate, then compressed into the pellets with a diameter of 13 mm and thickness of 1.5 mm through uniaxial compressed of 180 MPa. The PVA was burned out at 750 °C for 0.5 h with a heating rate of 2 °C/min. The green PSN and PSN-CuO pellets buried with the same powders were sintered for 2 h at 1300 °C and at 1280 °C, respectively. Then, the samples were processed into 10 mm in diameter and 1 mm in thickness, coated by the silver electrode which sintered at 800 °C for 10 min. Finally, the PSN and PSN-CuO ceramics were poled at 180 °C and the DC electric field of 5.6 and 6.1 kV/mm in the silicone oil bath for 30 min, respectively.

The surface morphologies were viewed through a scanning electron microscope (SEM, Hitachi, Tokyo, Japan) and the bulk density was tested by the Archimedes method. The universal testing machine (Instron-5566, USA) was used to test the fracture toughness ($K_{IC}$) with the three-point bending method and 8 samples. The $K_{IC}$ was calculated by the following formulas:

$$K_{IC} = 1.57\frac{PL}{b^{3/2}w^{1/2}}(1.93 - \frac{3.07a}{w} + 13.66\frac{a}{w})^{1/2} - 23.98(\frac{a}{w})^{3/2} + 25.22(\frac{a}{w})^4$$

Here $P$ is the largest applied force, $L$ is the length between bearing points, $a$ is the length of the crack, $b$ and $w$ are the width and thickness, respectively [17,18]. The crystal structure of all the ceramics was examined by using X-ray diffraction (XRD, D/MAX-2550V; Rigaku, Tokyo, Japan). The LCR meter (Model E4980A; Agilent, Palo Alto, CA, USA) connected to the GJW-1 high-temperature dielectric thermometry test system (Xi’an Jiao tong University Institute of Electronic Materials) was employed to test the temperature dependence of the dielectric constants and losses. The polarization-electric field (P-E) and the current-electric field (I-E) hysteresis loops were measured at about 25 °C and 1 Hz using a commercial ferroelectric system (TF Analyzer 2000, aix ACCT, Aachen, Germany). The $d_{33}$ were tested by instrument (Model ZJ-3A, Institute of Acoustics of the Chinese Academy of Sciences, Shanghai, China). The planar, thickness electromechanical coupling coefficient ($k_p$, $k_t$), as well as $Q_m$, were calculated according to the following equations (2)–(4):

$$K_{IC} = \frac{1}{k_p} = 0.395\frac{f_p}{f_a - f_p} + 0.574$$

$$k_t^2 = \frac{\pi f_c}{2 f_a} \cot\left(\frac{\pi f_c}{2 f_a}\right)$$

$$Q_m = \frac{f_c}{2(f_c - f_p)} \sqrt{\frac{Z_c}{Z_p}}$$

Here, $f_c$, $f_p$, $Z_c$, and $Z_p$ are planar resonance frequencies, anti-resonance frequency, and corresponding impedances, respectively [3,19].

3. Results and discussion

Fig. 1 shows SEM images of natural and fractured surfaces of PSN and PSN-CuO ceramics, and their corresponding grain size distributions. It is obvious that there are numerous pores on the natural and fracture surfaces of PSN ceramic, while the PSN ceramics with 0.08 wt% CuO addition exhibit better sintering behavior as characterized by markedly reduced pores and increased grain size. The bulk density of PSN-CuO ceramics is 5.85 g cm$^{-3}$, which is 11% larger than that of PSN ceramics with a density of 5.25 g cm$^{-3}$. In addition, PSN-CuO ceramics show a larger grain size of about 54 μm than that of PSN ceramics whose average grain size is about 30 μm. The improved sintering behavior of PSN-CuO ceramics can be attributed to forming the liquid phase bridge with CuO addition, which helps to accelerate mass transport, promote grain growth and particle rearrangement [15,20].

Fig. 2 shows the bending stress ($\sigma$)-bending strain ($\xi$) curves of PSN and PSN-CuO ceramics. It is obvious that PSN-CuO ceramics present smaller $\xi$ in comparison with PSN ceramics when the same $\sigma$ is applied. In addition, PSN-CuO ceramics have a larger $K_{IC}$ (= 0.60 MPa m$^{1/2}$) than that of PSN ceramics with the $K_{IC}$ of 0.33 MPa m$^{1/2}$. The increase of $K_{IC}$ which is susceptible to pores can be mainly by reason of the increased density. This result further proves the significant effect of CuO on improving the densification of PSN ceramics.

Fig. 3 shows the XRD patterns of PSN and PSN-CuO ceramics at room temperature in 2θ range of 10°–50°. It can be directly observed that the addition of CuO does not introduce a secondary phase. As is known, PN has three different crystalline phases: rhombohedral phase stable at low temperatures, tetragonal phase stable at high-temperature, and orthorhombic one transforming to tetragonal one at $T_c$ in the heating process. Among them, only the orthorhombic phase, characterized by a single (350) peak near 29° and a (131)/(311) peak
Fig. 1. SEM images of natural surfaces of (a) PSN and (b) PSN-CuO ceramics and fractured surfaces of (c) PSN and (d) PSN-CuO ceramics. And the corresponding grain size distributions of (e) PSN and (f) PSN-CuO ceramics.

Fig. 2. Bending stress-bending strain curves of PSN and PSN-CuO ceramics.

Fig. 3. XRD patterns of PSN and PSN-CuO ceramics.
splitting between 27.5–28.5°, is a ferroelectric phase and presents piezoelectric and ferroelectric properties [9]. Therefore, PSN and PSN-CuO ceramics display an orthorhombic ferroelectric phase structure.

In order to investigate the role of CuO on the structure of PSN ceramics in-depth, Raman spectra, which is highly sensitive to structural modification and has been successfully applied to the structural research of tungsten bronze structural compounds, was used to study the occupation of the Cu²⁺ ions at the lattice of PSN ceramics. Fig. 4 shows the Raman spectra of PSN and PSN-CuO ceramics. Three characteristic Raman bands, related to internal modes of the NbO₆ octahedra, are identified at around 242, 632 and 832 cm⁻¹, and classified as O–Nb–O bending vibrations, Nb–O stretching vibrations and Nb–O vibrations, respectively. In addition, the modes appearing at the low-frequency region (< 200 cm⁻¹) reflect external vibrations concerned with the movement of the A-site cations [21–23]. For PSN ceramics, from the perspective of ion chemistry, the A-sites of the crystalline structure are occupied by Pb²⁺ and Sr²⁺ ions whose radii are 1.20 Å and 1.44 Å, respectively. The radius of Cu²⁺ ions (0.73 Å) is smaller than that of Pb²⁺ and Sr²⁺ ions at A sites. So Cu²⁺ ions can dissolve into A-sites of the lattice. Furthermore, in Fig. 4c, the marked enhancement of the Raman intensity and sharpening of the mode at 76 cm⁻¹ as well as the appearance of the mode at 115 cm⁻¹ in PSN-CuO ceramics indicate that Cu²⁺ ions change the vibrations of the A-site cations compared to PSN ceramics. Therefore, it fully reveals that the A-sites of the lattice are occupied by Cu²⁺ ions in this study. From the enlarged Raman spectra around the mode at 632 cm⁻¹, as shown in Fig. 4b, it is clear that the peak narrows a little bit and shifts to the higher frequency after CuO addition, which can be ascribed to the increase of the stability of the NbO₆ octahedra, making the structure more ordered [24,25].

Fig. 5 shows the temperature dependence of dielectric constant (ε_r) and dielectric loss (tanδ) of PSN and PSN-CuO ceramics at 10 kHz. It can be seen obviously that the maximum dielectric constant (ε_m) increases from 2071 to 2797 as well as the T_c takes on a significant increase by 28 °C (from 367 to 395 °C), and tanδ reduces a bit by CuO addition. The enhancement of ε_r is mainly ascribed to the formation of a good microstructure with a substantial increase in the density and grain size [14,26]. As we all know, T_c is the transition temperature between the ferroelectric and non-ferroelectric phases, which is closely relevant to the stability of the ferroelectric one. PbNb₂O₆ has an unfilled tungsten bronze structure with many A-site vacancies. During the sintering process, some Cu²⁺ ions are likely to fill part of A-site vacancies in the crystal lattice, which is beneficial to stabilize the long-range ordered structure of the ferroelectric body, thereby improving the stability of ferroelectric phase including the transition temperature between orthorhombic ferroelectric and tetragonal non-ferroelectric phases (namely T_c) [27]. Such a consequence is consistent with the analysis of the occupation of the Cu²⁺ ions at A-sites of the lattice resulting in the increase of the stability of the NbO₆ octahedra which reflects the increase of the stability of the orthorhombic phase in Fig. 4, as well as the substitution of small Li⁺ ions in A-positions of the perovskite structural materials leading to the increased T_c [28,29]. The reduction of tanδ may be caused by reduced pores, which is in accordance with the explanation of improving density in Fig. 1. The corresponding values of these dielectric properties are listed in Table 1.

The values of piezoelectric properties such as d_{33}, Q_m, k_t, k_p and some other electrical properties such as resistivity are shown in Table 1. The resistivity of PSN-CuO ceramics increases by an order of magnitude compared with the pure PSN ceramics, which could be owing to the addition of CuO partially precipitated at the grain boundaries and partially dissolved into the crystal lattice. In addition, the Q_m, k_t, and k_p values of PSN-CuO ceramics basically unchanged compared to PSN ceramics. Besides, the d_{33} values of the PSN ceramics with CuO addition have a substantial increase from 168 to 190 pC/N. As is well known, the values of d_{33} are sensitive to grain size and polarization field strength. In this work, on the one hand, the increase of grain size caused by CuO addition leads to a decrease in the proportion of grain boundaries as shown in Fig. 1. Furthermore, the resultant “pinning effect” of grain boundaries on the ferroelectric domain and domain wall movement reduces as well according to the grain size effect [30–33]. Consequently, the enlargement of grain size makes the ferroelectric domain easier to reverse and is beneficial to domain walls motion. Therefore, the response of ferroelectric domains to polarization electric field increases. On the other hand, the polarization field strength is generally associate with porosity and resistivity. The decrease of pores and the increase of resistivity are positive to improve the polarization field strength of PSN-CuO ceramics. Therefore, the improvement of d_{33} values after CuO adding could not only attribute to the easier movement of the ferroelectric domain and domain walls but also the increase in the polarization field strength, which leads to more sufficient polarization.

4. Conclusions

In this study, the impacts of CuO adding on the sintering characteristics including the crystal structure of PSN ceramics were studied, respectively. The consequences demonstrate that CuO can affect not only the sinterability but also the crystal structure to obtain more excellent comprehensive performance. CuO serving as a sintering additive enhances the sintering behavior by forming the liquid-phase bridge with Cu²⁺ ions probably occupy the A-sites of the lattice. The PSN
ceramics with CuO addition show better electric properties, particularly gain improved $d_{33}$ (190 pC/N) and $T_C$ (395 °C). The improvement of $d_{33}$ values could be resulted from the easier movement of the ferroelectric domain and domain wall due to the enlargement of grain size, including the augment of polarization field strength owing to the enhancement of density and resistivity, which consequently makes the polarization more sufficient. The enhancement of $T_C$ may be owing to the enhanced stability of the NbO$_6$ octahedra and the orthorhombic ferroelectric phase.

Declaration of competing interest

The authors declared that they have no conflicts of interest to this work.

Acknowledgments

The authors acknowledge the financial support by the National Natural Science Foundation of China (Grant No. 51972321).


d| $d_{33}$ (pC/N) | $Q_m$ | $k_p$ | $k_l$
---|---|---|---|---
PSN | 367 | 168 | 8.7 | 0.39 | 0.47
PSN-CuO | 395 | 190 | 10.8 | 0.38 | 0.47

Table 1

Sinterability and electrical properties of PSN and PSN-CuO ceramics.

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