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Research Article

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Fabrication and performance of PNN-PZT piezoelectric ceramics obtained by low-temperature sintering

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Abstract: The $Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_xTi_{1-x})O_3$ (PNN-PZT) piezoelectric ceramics with CuO and $LiBiO_2$ doping were successfully fabricated by the low-temperature solid-state reaction to effectively restrain the PbO volatilization. The microstructure and electrical properties of the PNN-PZT ceramics were characterized. The experimental results reveal that the PNN-PZT ceramics are composed of a pure perovskite structure in which the rhombohedral and tetragonal phases coexist. Meanwhile, the good electric properties, including low dielectric loss, outstanding diffusion phase transition and palpable dielectric relaxation, are exhibited in PNN-PZT ceramics with 0.2 wt.% CuO and 1 wt.% $LiBiO_2$ addition. This piezoceramic composition possibly provides a reference for the application of multi-layer piezoelectric actuators.

Keywords: piezoelectric ceramics; low-temperature sintering; electric properties; dielectric relaxation

1 Introduction

With the rapid development of the electronic information technology, the electronic components widely applied in various devices, such as transformers, reproducers and filters, trend to be smaller, lighter and cheaper [1–3]. As the most popular lead-based piezoelectric ceramic, The PNN-PZT system with excellent piezoelectric constant, high electromechanical coupling factor and eminent permittivity are widely used both in military and civilian applications [4, 5]. As is known, the sintering temperature of PNN-PZT ceramic is about 1200 ~ 1300°C [6]. The strong volatilization of lead oxide beyond 960°C in the conventional solid-state reaction can deteriorate the electrical properties of samples [7]. Moreover, the lead is one of heavy metals which are extremely harmful for human health [8]. Additionally, the PbO volatilization in the cofire of PNN-PZT ceramic and Ag-Pd electrode can substantially improve the crack formation in the multi-layer piezoelectric actuators. Currently, the most common approach to slow the volatilization of PbO is sintering in a hermetic atmosphere and adding an excessive amount of PbO, however this problem is not solved efficiently. Thereby, the adjustable sintering temperature (below 960°C), which can postpone availably the volatilization of PbO and promote the energy saving, has aroused the extensive concerns [9–11].

The research on the low-temperature sintering of piezoelectric ceramics has been developed for decades [12]. Generally, there are two methods to reduce the sintering temperature. One is refining effectively the particle size of powders. The ceramic powders prepared by sol-gel methods or hydrothermal process possess superfine particle sizes and high surface energy, which can indeed reduce the sintering temperature [13]. Besides, the another one is adding tiny amounts of efficacious sintering aids, such as V_2O_5, SiO_2, *etc*, which is an economic and efficient approach to reducing the sintering temperature. The sintering aids are conducive to forming low-melting-point glass phases during the solid reaction. The glass phase formed in the grain boundary accelerates the rate of atomic migration, which is contribute to fast growth of grains. The studies showed that moderate B_2O_3 and CuO doped (Ba, Ca)(Ti, Sn)O_3 can reduce the sintering temperature from 1250°C to 1200°C. Furthermore, the introduction of a tiny amount of

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low-melting frit (B_2O_3-Bi_2O_3-CdO) can reduce the sintering temperature even to 960°C.

Commonly, the electrical properties of piezoelectric ceramics could be deteriorated when the sintering temperature reduced improperly [14, 15]. Therefore, on the basis of ensuring that Ag layer is not melted (~960°C), obtaining high-performance piezoelectric ceramic materials is a key scientific problem to be solved urgently in the development of piezoelectric actuators. As is known, the PNN-PZT ceramic is a typical "soft material", which exhibits a relatively low sintering-temperature and excellent electrical properties. Introduction of CuO and Bi_2O_3 into the PNN-PZT ceramics as the sintering aids can reduce effectively the sintering temperature [16–18]. Therefore in this notion, a series of PNN-PZT ceramics doped by various amounts of CuO and $LiBiO_2$ as sintering aids to achieve a novel electric properties via low-temperature sintering. Thereinto, the $LiBiO_2$ can be synthesized by $Li_2CO_3 + Bi_2O_3 = 2LiBiO_2 + CO_2$. The effect of varying contents of sintering aids on the microstructure and electrical performances were carefully investigated. The related research results will provide a potential candidate for the multi-layer piezoelectric actuators.

2 Material and experimental procedures

2.1 Piezoceramic preparation

The 0.3 $Pb(Ni_{1/3}Nb_{2/3})O_3$-0.7 $Pb(Zr0._{41}Ti_{0.59})O_3$+$x$ wt.% CuO+y wt.% $LiBiO_2$+1 wt.% Pb_3O_4 (x = 0.1, 0.2, 0.3, y = 1, 2) piezoelectric ceramics were fabricated by traditional solid-state reaction technique. The Pb_3O_4, ZrO_2, TiO_2, Nb_2O_5, NiO, CuO, Bi_2O_3 and Li_2CO_3 powders with a purity of more than 99.9% were used as the raw materials. The powders were weighed by an electronic balance of 0.1mg (AL204), and then blended with alcohol by ball-milling in a nylon jar for 12 h at 300 rpm. Subsequently, the mixed powders were dried and calcined at 900°C for 2h. After addition of CuO, Li_2CO_3 and Bi_2O_3, the pre-sintered powders were ball-milled again with alcohol and dried. Hereafter, these powders mixed with 5 wt.% PVA as binder were pressed under 12 MPa into a planchette whose size is Φ10 mm×1 mm. Besides, the ceramics were sintered at 960°C in air for 2 h. And then the sintered samples were printed on both sides with sliver electrodes at 850°C. Finally, the samples for piezoelectric measurements were poled at 70°C in silicone oil by applying a DC electric field of 3 kV·mm^{-1} for 20 min.

2.2 Piezoceramic characterization

The phase composition of samples was measured by a X'pert-PRO X-ray diffractometer (XRD). The microstructure was observed by a Supra-40 scanning electron microscopy (SEM, Germany). The piezoelectric constant (d_{33}) was tested at room temperature using a quasi-static piezo-d_{33} meter (ZJ-3A, China), in which at least 10 times were conducted to obtain the average value. The dielectric properties were characterized using an LCR meter (Agilent, E4980A), connected to a computer-controlled temperature chamber, by measuring at 10 kHz.

3 Results

3.1 Phase identification of PNN-PZT ceramics

Figure 1 shows the XRD patterns of PNN-PZT+ x CuO+ y $LiBiO_2$ ceramics with various amounts of CuO, Li_2CO_3 and Bi_2O_3 addition. Clearly, all the specimens exhibit a single perovskite structure (ABO_3). No intermediate phases, such as pyrochlore or Zr and Ti-rich phases, was found, indicating that CuO and $LiBiO_2$ could have solved completely into the perovskite solid solution, rather than concentrated in the grain boundaries. Meanwhile, the peak around 45^o has been split into two ones: the right one (R) is (002) and the left (T) is (200) preferred orientation, indicating the coexistence of the rhombohedral (R) and the tetragonal phase (T) in PNN-PZT piezoelectric ceramics. It has been reported that the interface between R and T phases is perfectly lo-

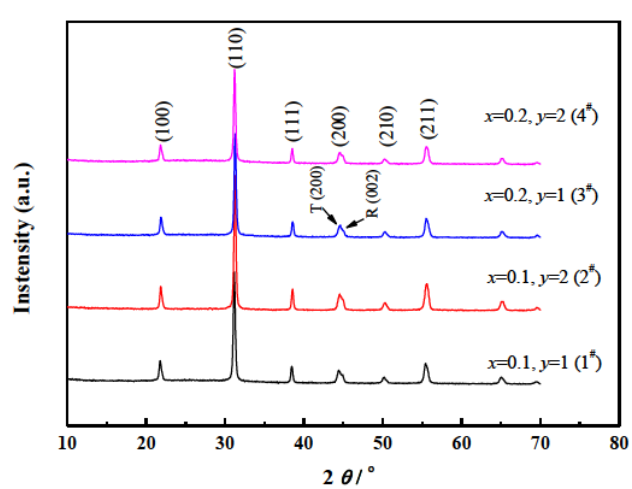

Figure 1: X-ray diffraction patterns of PNN-PZT + $x$wt.% CuO + ywt.% $LiBiO_2$ + 1wt.% Pb_3O_4 ceramics with different amounts of CuO, Li_2CO_3 and Bi_2O_3.

cated in morphotropic phase boundary (MPB), possessing the excellent piezoelectric properties [19, 20].

3.2 Microstructure of PNN-PZT ceramics

Figure 2(a) ~ (d) shows the microstructure of PNN-PZT-*x*CuO-*y*$LiBiO_2$ piezoelectric ceramics. It is suggested that the grains are relatively small and many pores exist while the sintering aids short supplied. However, with the increase of sintering aids, the grains grow gradually and the density and homogeneity of ceramics get better, particularly in the PNN-PZT- 0.1% CuO- 2% $LiBiO_2$ ceramic. It demonstrates that moderate CuO and $LiBiO_2$ additions could enhance the grain growth and increase the densification. Nevertheless, as the dopant successively increases, the CuO and $LiBiO_2$ will aggregate at the grain boundary and cannot dissolve completely into crystal lattices as shown in Figure 2 (c), causing that the overall electric performance gets worse.

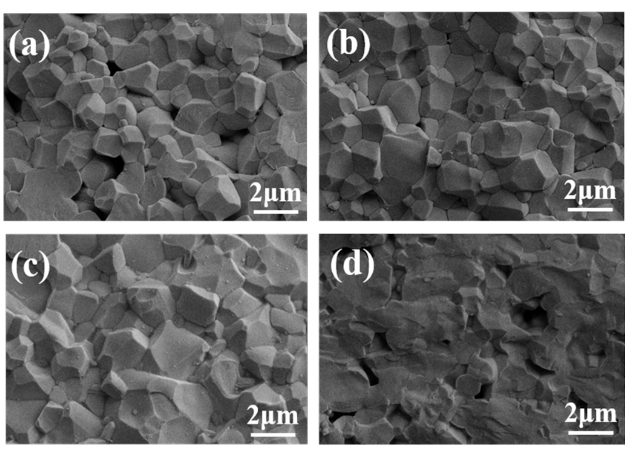

Figure 2: Microstructures of PNN-PZT-xCuO-y$LiBiO_2$ ceramics. (a) x = 0.1, y = 1; (b) x = 0.1, y = 2; (c) x = 0.2, y = 1; (d) x = 0.2, y = 2.

3.3 Electric properties of PNN-PZT ceramics

Table 1 shows the electrical properties of PNN-PZT+xCuO +y$LiBiO_2$ ceramics. As is seen from Table 1, the changes of k_p and d_{33} possess the same tendency and reach the maximum values when $x = 0.2$, $y = 1$. They are 608 pC·N^{-1} and 0.65 respectively. Meanwhile, the relative permittivity (ϵ_r) reaches 3843 and the loss (tan δ) is approximately equal to 2.19%. That means, the upper density, good homogeneity and few second phases (in the sample 3[#]) are significantly helpful for improving the electric properties of ceramics.

Table 1: Electric properties of PNN-PZT ceramics.

Composition	k_p	d_{33} (pC·N^{-1})	tan δ (%)	ϵ_r
x = 0.1, y = 1	0.51	490	2.34	3228
x = 0.1, y = 2	0.54	551	2.62	3789
x = 0.2, y = 1	0.65	608	2.19	3843
x = 0.2, y = 2	0.48	470	2.51	3277
x = 0.3, y = 1	0.43	440	2.74	3412
x = 0.3, y = 2	0.41	410	2.71	3220

3.4 Dielectric properties at various temperatures of PNN-PZT ceramics

Figure 3 shows the temperature dependence of dielectric constant and loss of PNN-PZT ceramics with different contents of CuO and $LiBiO_2$ measured at 100 kHz. As can be

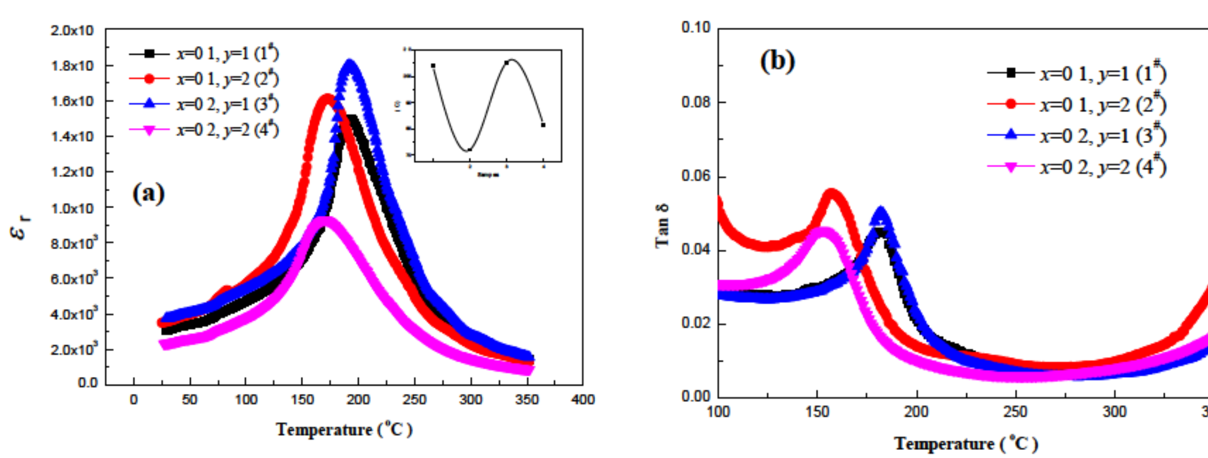

Figure 3: Temperature dependence of (a) ϵ_r and (b) tan δ of PNN-PZT ceramics with different contents of CuO and $LiBiO_2$ measured at 100 kHz.

seen from Figure 3 (a), the phase-transition peaks of ferroelectric and paraelectric are observed in all ceramics, which corresponds to the Curie temperature (T_c). Obviously, the T_c reduced with the increasing of $LiBiO_2$ contents. However, the content of CuO is helpful for the increasing of T_c and the reduction of tan δ. The ceramic with 0.2 wt.% CuO and 1wt.% $LiBiO_2$ possesses the highest T_c of 191.6°C, and the lowest loss of 2.19%, respectively.

3.5 Relaxation behavior of PNN-PZT ceramics

Figure 4 shows the relationship between inverse dielectric constant and temperature of PNN-PZT+x CuO+y $LiBiO_2$ ceramics at 10 kHz. The permittivity of the ferroelectric materials calculated according to the Curie-Weiss law when the temperature is beyond T_c, as shown in Eq. (1) [12]:

$$\epsilon = \frac{C}{T - T_{cw}} \qquad (1)$$

where T_{cw} represents the Curie-Weiss temperature and C is the Curie-Weiss constant. The deviation degree of Curie transition can be described in Eq. (2) [12]:

$$\Delta T_m = T_B - T_m \qquad (2)$$

where ΔT_m is the deviation, T_B is the initial temperature that the dielectric materials obey the Curie-Weiss law, and T_m refers to the temperature corresponding to the maximum of permittivity. It can be seen from Figure 4 that PNN-PZT ceramic belongs to a typical relaxor ferroelectric. The ceramics with fewer $LiBiO_2$ contents exhibits a higher ΔT_m than that of ceramic with 2 wt.% $LiBiO_2$ additions. Hence, the appropriate addition of $LiBiO_2$ can lower the sintering temperature, thus enhancing the relaxation behavior of piezoelectric ceramics.

The plots of $\ln(1/\epsilon_r - 1/\epsilon_m)/\ln(T - T_m)$ for PNN-PZT+x CuO+y $LiBiO_2$ ceramics measured at 100 kHz are shown in Figure 5. The dispersion coefficient γ can be obtained by linear fitting of Eq. 2. The ceramic will be a normal ferroelectric when γ is equal to 1, but will transform into imperfect relaxor ferroelectric when γ is ranged from 1 to 2.

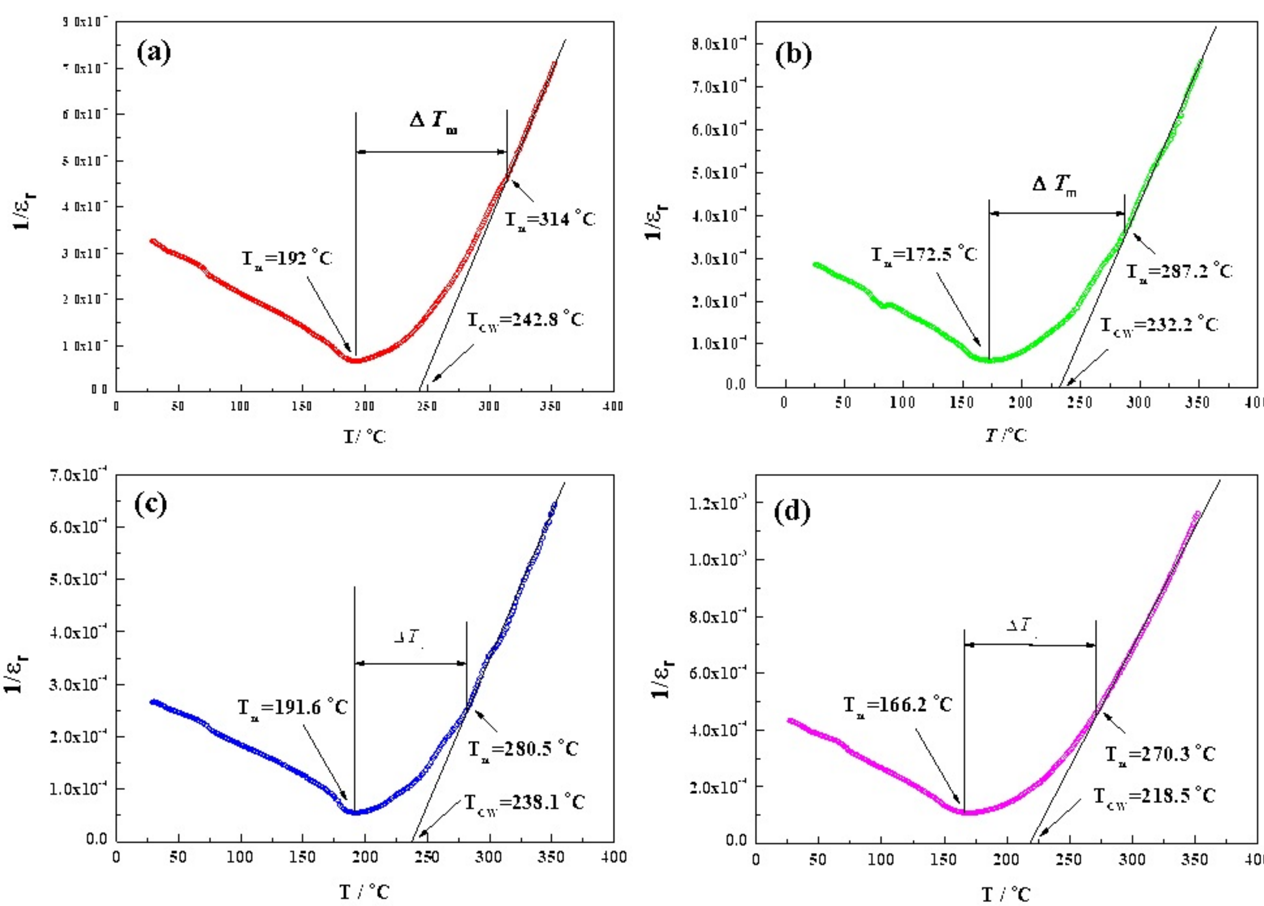

Figure 4: Inverse permittivity as a function of temperature for ceramics at 100 kHz (a) x = 0.1, y = 1; (b) x = 0.1, y = 2; (c) x = 0.2, y = 1; (d) x = 0.2, y = 2.

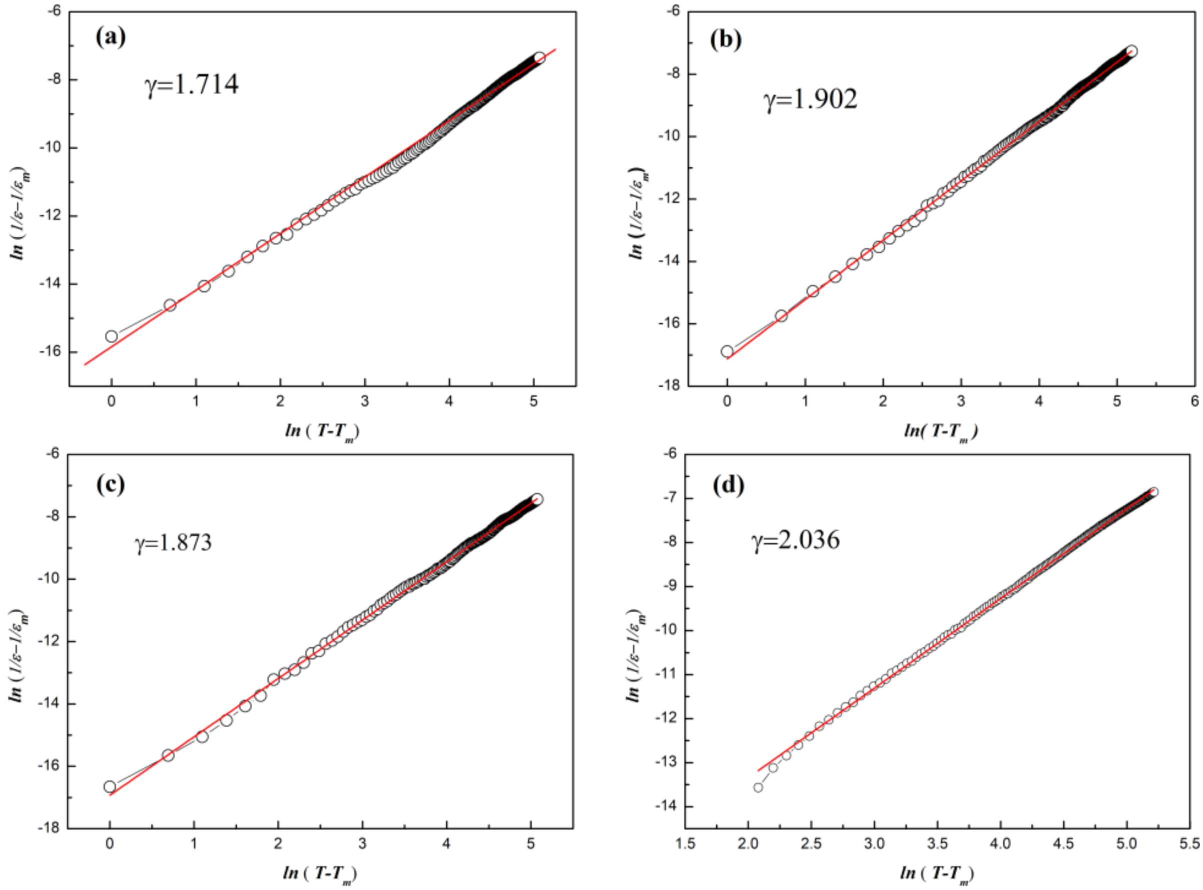

Figure 5: Plot of $\ln(1/\epsilon r - 1/\epsilon m)/\ \ln(T - Tm)$ for ceramics at 100 kHz (a) x = 0.1, y = 1; (b) x = 0.1, y = 2; (c) x = 0.2, y = 1; (d) x = 0.2, y = 2.

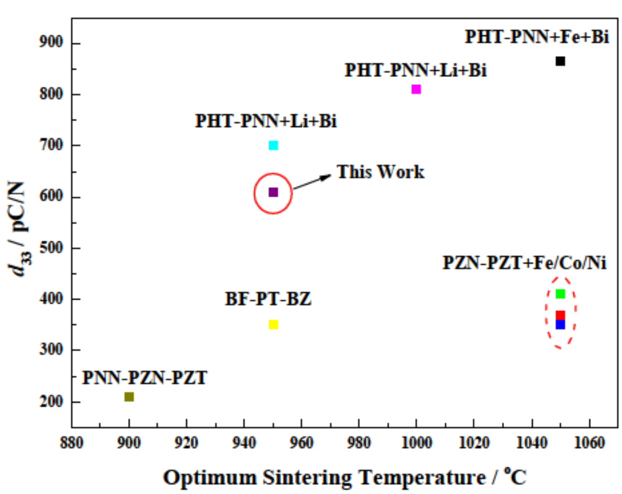

Figure 6: Piezoelectric properties of lead-based ceramics fabricated by low-temperature sintering [21–23].

When $\gamma = 2$, the ceramic will become a relaxor ferroelectric with diffuse phase transition. It is observed from Figure 5 that the γ increases firstly with the increase of $LiBiO_2$ concentration, especially for the PNN-PZT ceramic modified with 1wt.%CuO and 2wt.%$LiBiO_2$, the γ is approach to 2.036 at 100 Hz, which means that the PNN-PZT ceramic modified with 1wt.%CuO and 2wt.%$LiBiO_2$ is an excellent relaxor ferroelectric.

4 Discussion

Universally, the improvement of dielectric constant (d_{33}) is closely related to the formation of Pb-ion vacancies to effectively promote the domain rotation. The extensive additions of $Bi3^{+}$ introduced into the ceramics substitute for the Pb-sites, also result in many Pb^{2+} vacancies to keep the electrical neutrality. In this study, the adjustable amounts of sintering aids were dissolved into the perovskite solid solution, further leading to the increase of d33. However, the excessive additions of sintering aids could segregate in the grain boundaries to pin the domain rotation, further decreasing the value of d33. Besides, the LiBiO2 and CuO added to the PNN-PZT ceramics are much beneficial for achieving a dense and uniform microstructure, which was also helpful to obtain a prominent d_{33} improvement.

To comprehensively evaluate the piezoelectric properties of the PNN-PZT ceramics with CuO and LiBiO2 additions, the d_{33} and sintering temperature of conventional lead-based ceramics have been listed in Figure 6. As is seen, the PHT-PNN ceramics with various sintering aids possess excellent piezoelectric properties while sintered at 950, 1000 and 1050°C. However, a large amount of precious Hf elements were contained in the PHT-PNN ceramics, seriously limiting their industrial applications. Hereinto, the d33 of the ceramic achieved in this work shows the high value among the low-temperature sintering piezoceramics ever reported in the literature.

5 Conclusions

1. A series of 0.3 $Pb(Ni_{1/3}Nb_{2/3})O_3$-0.7 $Pb(Zr0._{41}Ti_{0.59})O_3$ + *x* wt.% CuO + *y* wt.% $LiBiO_2$ piezoelectric ceramics with a pure perovskite structure were successfully achieved by the low-temperature solid-state reaction.
2. The CuO and $LiBiO_2$ are suitable sintering aids for improving effectively the electric performance of piezoelectric ceramics. The rhombohedral and tetragonal phase are coexisted in PNN-PZT sample when x = 0.2 and y = 1, in which showed outstanding electric properties in the MPB. The d_{33}, k_p, ϵ_r, tan δ and T_c are 608 pC·N^{-1}, 0.65, 3843, 2.19% and 191.6°C respectively.
3. The diffusion phase transition and the dielectric relaxation characteristics associated with Curie temperature can be found in this series, especially when x = 0.2 and y = 2, the sample shows the lowest T_c, the maximum of diffusion phase transition and dielectric relaxation behavior.

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