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Pyroelectric properties of 91.5$Na_{0.5}Bi_{0.5}TiO_3$–8.5$K_{0.5}Bi_{0.5}TiO_3$ lead-free single crystal

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The dielectric and pyroelectric performances of 91.5$Na_{0.5}Bi_{0.5}TiO_3$–8.5$K_{0.5}Bi_{0.5}TiO_3$ lead-free single crystal were investigated. The depolarization temperature of the crystal is about 153 °C. Among the <001>, <110>, and <111> crystallographic orientations, the <111>-oriented crystal possesses the highest pyroelectric coefficient and the largest figures of merit, and the values of p, F_v, and F_d are 5.63×10^{-4} C/m$^2\cdot$K, 0.06 m^2/C, and 21.5 μPa$^{-1/2}$ for the <111>-oriented crystal at room temperature. The F_d and F_v exhibit weak frequency dependence in the range of 100–300 Hz. With the increase of the temperature, the value of p increases, while the value of F_v decreases from 18 °C to 103 °C.

Keywords: Lead-free; single crystal; pyroelectric properties; dielectric properties.

1. Introduction

At present, lead zirconate titanate (PZT) family-based materials are the most practical pyroelectric and piezoelectric materials due to their outstanding electrical properties. However, the content of lead is as high as 60%. Serious lead pollution has become a key problem restricting the development of electrical materials industry. In recent years, with the improvement of people's health and environmental awareness, the investigation of lead-free materials has rapidly become a research hotspot. For example, $Bi_{0.5}Na_{0.5}TiO_3$-based, $K_{0.5}Na_{0.5}NbO_3$-based, and $Ba(Ti_{0.8}Zr_{0.2})O_3$–$(Ba_{0.7}Ca_{0.3})TiO_3$-based lead-free materials are widely investigated.[1–9] Among these lead-free materials, lead-free single crystal materials, such as $Bi_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$–$Bi_{0.5}K_{0.5}TiO_3$, and $K_{0.5}Na_{0.5}NbO_3$ single crystals,[3–5] have attracted more attention because of their outstanding electrical properties. For these lead-free single crystal materials, there are more studies on the dielectric, ferroelectric, and piezoelectric properties, but their pyroelectric properties have been less studied.

In this paper, orientation dependences of pyroelectric and dielectric properties along with the temperature dependences of 91.5$Na_{0.5}Bi_{0.5}TiO_3$–8.5$K_{0.5}Bi_{0.5}TiO_3$ (91.5NBT–8.5KBT) lead-free single crystal were investigated in detail.

2. Experimental Procedure

The 91.5NBT–8.5KBT single crystal was grown by the top-seeded solution growth (TSSG) method. The chemical materials of Na_2CO_3, Bi_2O_3, TiO_2, and K_2CO_3 with purities of 99.90% were used as the raw materials. The details of the growth process were similar to those of the $Na_{0.5}Bi_{0.5}TiO_3$–$Na_{0.5}Bi_{0.5}TiO_3$ single crystal growth.[4] X-ray powder diffraction (XRPD) measurement was carried out to check the lattice structure. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used to measure the concentration of K. The <001>-, <110>-, and <111>-direction crystal wafers were cut into 3 × 3 × 0.5-mm^3 size for specific heat per unit mass, pyroelectric, and dielectric properties characterization. The silver electrodes were fired on both sides at 800 °C after these crystal wafers were polished with Al_2O_3 powders. These samples were poled under a DC electric field of 3 kV/mm for 15 min in silicon oil. The pyroelectric coefficient was measured by a dynamic technique

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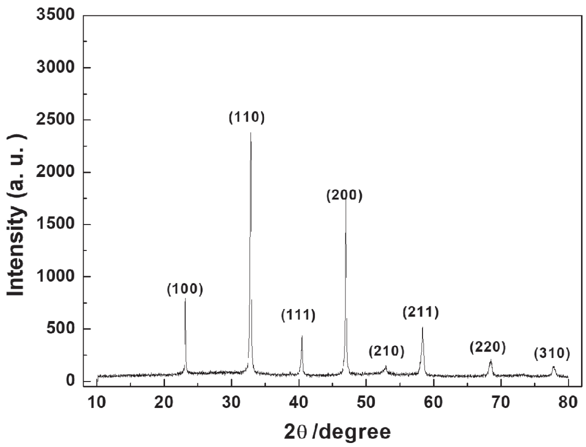

Fig. 1. XRPD patterns of 91.5NBT–8.5KBT single crystal.

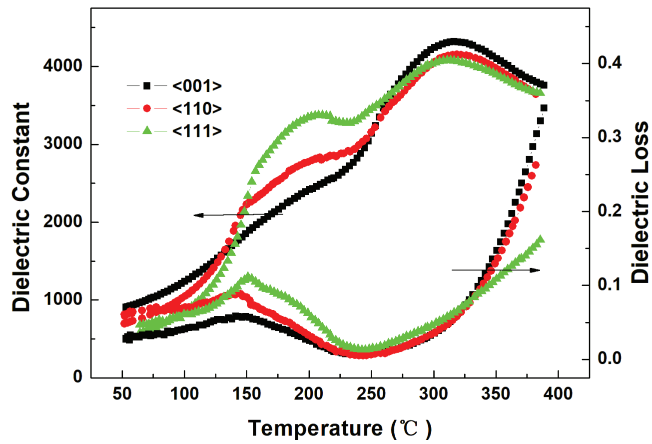

Fig. 2. Temperature dependences of dielectric constant and loss at 1 kHz for the 91.5NBT–8.5KBT crystal.

using sinusoidal temperature change with an amplitude of 0.25 °C at a frequency of 45 mHz.[10]

3. Results and Discussion

3.1. *Crystal structure*

The concentration of K-ion in the as-grown single crystal is 8.5 at.%, measured by ICP-AES. The XRPD patterns are shown in Fig. 1. All the diffraction reflections exhibit sharp and symmetric single diffraction peaks with rhombohedral symmetry (pseudocubic phase). So the as-grown crystal exists in pure rhombohedral perovskite structure. The unit-cell parameters are $a = b = c = 3.8949$ Å and $\alpha = \beta = \gamma = 90.037$ Å, which are calculated based on the XRPD data.

3.2. *Dielectric properties*

The temperature dependences of dielectric constant and dielectric loss for <001>-, <110>-, and <111>-oriented poled 91.5NBT–8.5KBT crystals are shown in Fig. 2, which were measured at 1 kHz. The (T_m, ε_m) values for <001>-, <110>-, and <111>-oriented poled crystals are (318 °C, 4868), (319 °C, 2909), and (317 °C, 1348), respectively. The T_m is almost independent of crystal orientations. However, the difference of ε_m for the three crystallographic orientation crystals is large, which indicates the crystal shows obvious anisotropy. There are two distinct dielectric anomalies in the $\varepsilon(T)$ curves, which are related to two phase transitions. According to Refs. 11 and 12, the maximum permittivity peak at about 318 °C relates to the *Pnma* orthorhombic–tetragonal phase transition, while a small hump at about 153 °C relates to the rhombohedral–*Pnma* orthorhombic phase transition. The depolarization temperature (T_d) of 91.5NBT–8.5KBT crystal is about 153 °C, which is higher than that (~120 °C) of Mn:94.6NBT–5.4BT crystal.[7] Compared with Mn:94.6NBT–5.4BT crystal, 91.5NBT–8.5KBT crystal owns wider operation temperatures in practical application. The depolarization mechanism has been discussed in detail in the previously published literature.[13]

Figure 3 shows the frequency dependences of dielectric constant and loss for 91.5NBT–8.5KBT crystal at room temperature. At 100 Hz, dielectric constant and loss are 690 and 0.020, 534 and 0.022, and 350 and 0.026 for <001>-, <110>-, and <111>-oriented 91.5NBT–8.5KBT crystals at 18 °C, which are listed in Table 1. The dielectric constant and loss show frequency dependence in the range of 100–800 Hz, and remain invariable in the range of 800–5000 Hz. The as-grown crystal exhibits relatively larger dielectric loss, which can be attributed to the presence of a space charge conduction mechanism. The space charge may result from bismuth V_{Bi}''' and oxygen $V_o^{\cdot\cdot}$ vacancies, due to Bi_2O_3 volatility during crystal growth.[3]

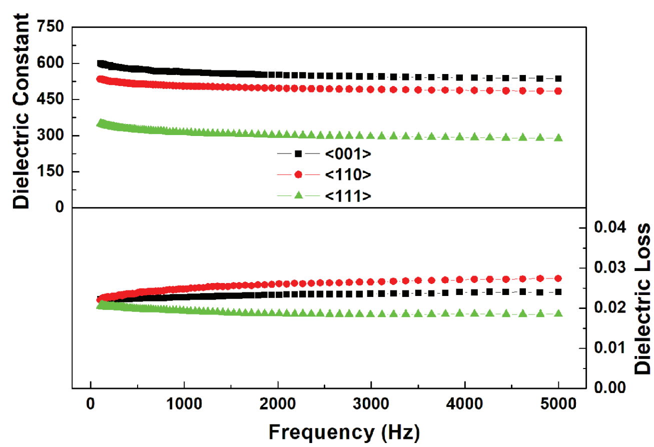

Fig. 3. Frequency dependences of dielectric constant and loss for the 91.5NBT–8.5KBT crystal at room temperature.

Table 1. Pyroelectric and dielectric parameters of poled 91.5NBT–8.5KBT single crystal and other lead-free materials at room temperature.

Material	Type	T_c (°C)	T_d (°C)	p (μC/m$^2\cdot$K)	ε_r (@100 Hz)	tanθ (@100 Hz)	F_i (pm/V)	F_v (m^2/C)	F_d ($\times 10^{-6}$ Pa$^{-1/2}$)	Source
91.5NBT–8.5KBT <001>	Crystal	318	153	302	690	0.020	96.8	0.020	8.8	This work
91.5NBT–8.5KBT <110>	Crystal	319	153	504	534	0.022	161.5	0.040	18.7	This work
91.5NBT–8.5KBT <111>	Crystal	317	153	563	350	0.026	180.4	0.080	21.5	This work
Mn:94.6NBT–5.4BT <111>	Crystal	280	120	588	279	0.019	203.5	0.080	29.8	Ref. 7
PZT	Ceramic	315	—	350	471	0.005	109	0.026	24	Ref. 18
$[Bi_{0.5}(Na_{0.95}K_{0.05})_{0.05}]_{0.95}$–$Ba_{0.05}TiO_3$	Ceramic	—	—	325	853	0.028	194.6	0.026	13.4	Ref. 19

3.3. *Pyroelectric properties at room temperature*

Infrared detector made by pyroelectric material has many advantages, such as wide wavelength response, no requirement for cooling, high temperature stability, and high sensitivity. The pyroelectric coefficient (p) and figures of merits (FOMs) are important parameters for selecting the materials for pyroelectric applications. The FOMs include current responsivity $F_i = p/C_v$, voltage responsivity $F_v = p/(C_v\varepsilon_0\varepsilon_r)$, and detectivity $F_d = p/[C_v(\varepsilon_0\varepsilon_r\tan\theta)^{1/2}]$, where C_v, ε_0, ε_r, and tanθ are volume specific heat, permittivity of free space, dielectric constant, and dielectric loss, respectively.

The values of pyroelectric coefficient at 18 °C are listed in Table 1. The pyroelectric coefficients are 3.02×10^{-4}, 5.04×10^{-4}, and 5.63×10^{-4} C/m$^2\cdot$K for <001>-, <110>-, and <111>- oriented crystals. Similar to dielectric constant and loss, pyroelectric coefficient also shows obvious anisotropy. The <111>- oriented crystal possesses the highest p and the lowest ε_r. The value of p for <111>- oriented crystal is larger than those of the widely used pyroelectric materials such as $LiTaO_3$ crystal (2.3×10^{-4} C/m$^2\cdot$K) and similar-composition Mn:82NBT–18KBT thick-film materials (3.8×10^{-4} C/m$^2\cdot$K).[14,15] Some literature works reported high pyroelectric coefficients for lead-free pyroelectric materials, such as $0.94(Bi_{0.5}Na_{0.5})TiO_3$– $0.06Ba(Ti_{0.75}Zr_{0.25})O_3$ ceramic (27.20×10^{-4} C/m$^2\cdot$K)[16] and Li-doped $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ ceramic (8.6×10^{-4} C/m$^2\cdot$K).[17] However, low phase transition temperature (near room temperature) limits the practical application for these materials. The pyroelectric parameters of conventional pyroelectric material, representative lead-free single crystal, and similar-composition ceramics, such as PZT ceramic, Mn:NBT–KBT single crystal, and $[Bi_{0.5}(Na_{0.95}K_{0.05})_{0.05}]_{0.95}$–$Ba_{0.05}TiO_3$ ceramics, are listed in Table 1 as a comparison.[18,7,19]

The dependency on the crystal orientation for pyroelectric properties can be considered as relating to the differences of spontaneous polarization direction and domain configuration.[20] The 91.5NBT–8.5KBT crystal is rhombohedral structure at room temperature, with spontaneous polarization along the <111>- direction. After poled along the polar axis, the <111>- oriented crystal approaches closely the monodomain state and presents a largest remnant polarization, which results in the largest pyroelectric coefficient. The FOMs are calculated based on the above experimental results. The volume specific heat (C_v) is calculated to be 3.12×10^6 J/m$^3\cdot$K on the basis of the specific heat per unit mass (C_p). These parameters are summarized in Table 1. At 18°C, F_i values are 96.8, 161.5, and 180.4 pm/V, F_v values are 0.02, 0.04, and 0.08 m^2/C, and F_d values are 8.8, 18.7, and 21.5 μPa$^{1/2}$ for the <001>-, <110>-, and <111>- oriented 91.5NBT–8.5KBT crystals, respectively. Among the three crystallographic orientations, F_v and F_d of <111>- oriented crystals own the largest values, which are attributed to the largest pyroelectric coefficient and the lowest dielectric constant caused by domain configuration.[20]

3.4. *The influence of temperature and frequency on pyroelectric properties*

In this work, the temperature and frequency dependences of pyroelectric properties of <001>-, <110>-, and <111>- oriented 91.5 NBT–8.5 KBT crystals were investigated. The p, F_d, and F_v were measured from 18 °C to 103 °C with the steps of $\Delta T = 5$ °C, which are shown in Fig. 4. From 18 °C to 103 °C, the pyroelectric coefficients increase by 10.6%, 9.9%, and 10.7% for the <001>-, <110>-, and <111>-oriented crystals, showing relatively high thermal stability. With the increase of the temperature, it can be seen from Fig. 4 that the F_v values gradually decrease, while the F_d values decrease at first, then increase at about 28 °C, and finally, decrease again at 48 °C. The variations of the F_v and F_d values can be attributed to the variations of dielectric constant and loss values with the increase of temperature, which may be related to the structural phase transition.

Instead of operating under various temperatures, the pyroelectric detectors made of pyroelectric materials need to operate under various frequencies. The frequency dependences of pyroelectric properties of 91.5NBT–8.5KBT crystal were also investigated. The frequency dependences of F_d and F_v for <001>-, <110>-, and <111>- oriented 91.5NBT–8.5KBT crystals are shown in Fig. 5. For the three crystallographic

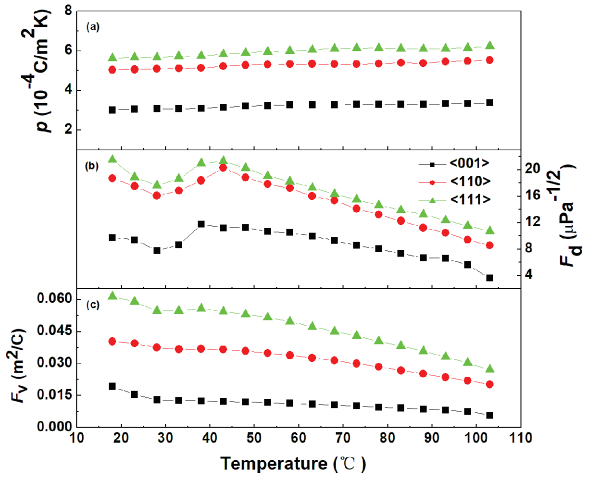

Fig. 4. Temperature dependences of p, F_d, and F_v for the <001>-, <110>-, and <111>-oriented crystals.

orientations of crystals, the F_d and F_v values slightly increase with the increase of the frequency from 100 Hz to 300 Hz, then remain invariable in the range of 300–4000 Hz.

4. Conclusions

In summary, the dielectric and pyroelectric properties of 91.5NBT–8.5KBT single crystal were investigated. The as-grown crystal exhibits obvious anisotropy. For the <111> orientation crystal, the value of ε_r is the lowest, while the values of p, F_d, and F_v are the largest among the three crystallographic orientations of crystals. The F_d and F_v exhibit weak frequency dependence in the range of 100–300 Hz. The pyroelectric coefficient increases with the increase of temperature from 18 °C to 103 °C, while the F_d and F_v values decrease in general from 18 °C to 103 °C. If the dielectric loss of the as-grown crystal can be reduced, its pyroelectric properties will be optimized. So, further work on decreasing the dielectric loss deserves more attention.

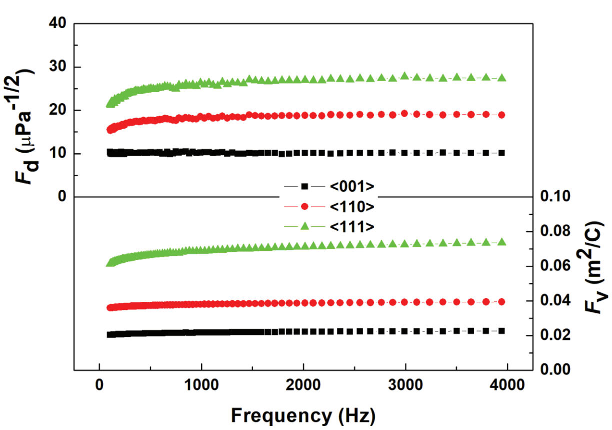

Fig. 5. Frequency dependences of figures of merit F_d and F_v for the <001>-, <110>-, and <111>-oriented crystals at room temperature.

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