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Pyroelectric Properties of Bismuth Borate BZBO Single Crystals

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Abstract: Pyroelectric properties of orthorhombic $Bi_2ZnB_2O_7$ (BZBO) crystals were investigated by using the charge integration method. The primary and the secondary pyroelectric coefficients of BZBO crystals were found to be 6.4 and −6.5 μC/(m^2·°C), respectively. The pyroelectric performance was evaluated by different figure of merits (FOMs), where BZBO crystals possessed relatively high current responsivity F_i (10.38 pm/V), and detectivity F_d (11.31 × 10^{-5}/Pa$^{1/2}$). In addition, the temperature dependent behaviours of primary pyroelectric coefficients and FOMs were studied from 15 °C to 155 °C; the pyroelectric properties were found to decrease with increases in temperature.

Keywords: oxyborate crystal; $Bi_2ZnB_2O_7$; pyroelectric properties

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1. Introduction

Oxyborate crystals are a well-known type of multifunctional crystal material, which are widely used in nonlinear, laser and piezoelectric fields [1,2]. Among oxyborate crystals, rare-earth calcium oxyborate family $ReCaO(BO_3)_3$ (ReCOB) and bismuth triborate BiB_3O_6 (BIBO) crystals have attracted considerable attention due to their optical and piezoelectric characteristics [3–9]. As the multifunctional crystals, ReCOB series crystals possess many attractive advantages not only including good thermal properties, wide transmission spectrum and high nonlinearity in nonlinear optical application, but also relatively high piezoelectric coefficients, low dielectric loss and high stability of electromechanical properties at elevated temperature in piezoelectric applications. Another important oxyborate piezoelectric crystal is BIBO; this crystal presents large effective nonlinear coefficients, high damage threshold and conversion efficiency in optical applications. Moreover, BIBO crystal possesses large piezoelectric coefficients and high temperature stability of electro-elastic properties.

In view of excellent properties of oxyborate crystals, more potential multifunctional oxyborate crystals should be explored. The $Bi_2ZnB_2O_7$ (BZBO) with an orthorhombic system is another oxyborate crystal that has been investigated by our group. The fundamental synthesis and structural determination of the BZBO compound have been reported in 2005 [10]. In addition, the BZBO crystal has been studied in terms of crystal growth and optical properties by many researchers [11–14]. Our group has carried out investigations on the electro-elastic properties and temperature dependent behaviours of BZBO crystals for piezoelectric applications [15,16]. Alongside their nonlinear optical and piezoelectric characteristics, BZBO crystals possess pyroelectric properties because of their non-centrosymmetric structure. Pyroelectric materials are used for pyroelectric sensors, which convert the non-quantified thermal flux into the output quantity, such as voltage, charge and current. Usually, the pyroelectric properties and figures of merits are investigated [17].

Reports on the pyroelectric properties of BZBO crystals are limited. In this work, pyroelectric properties of BZBO crystals were investigated. The pyroelectric coefficient p_3 was determined by using the charge integration method [18]. Different figure of merits (FOMs) including current responsivity F_i, voltage responsivity F_v and detectivity F_d

were evaluated for potential pyroelectric applications [19]. In addition, the temperature dependent behaviours of the pyroelectric and FOMs properties were studied over the temperature range of 15~155 °C.

2. Experimental Section

The pyroelectric effect is a change in polarization with temperature variation. Pyroelectricity is a first rank polar tensor property, which reflects the variation of polarization intensity caused by the temperature change. BZBO crystals belong to the orthorhombic crystallographic system, specifically the point group mm^2. According to the crystal symmetry, BZBO crystals have only one independent pyroelectric coefficient p_3. Based on the *IEEE* Piezoelectric Standard, the relationship between the crystallographic axes and the physical axes for BZBO crystals was determined. The physical *X*-, *Y*- and *Z*-axes for BZBO crystals were parallel to the crystallographic *a*-, *b*- and *c*-axes, respectively [20]. The crystallographic axes can be determined by X-ray diffraction, and the positive *Z* axis is determined by a quasi-static qiezoelectric d_{33} m. In this study, the used crystals were grown by the Kyropoulos method. The synthesized BZBO polycrystalline were melted and heated up to 800 °C for at least 24 h to ensure the uniformity of the melt. Duing the growth, the rotation speed was controlled at 15 rpm, and the cooling temperature range was within 3~4 °C. Upon completion of the growth, the BZBO crystal was pulled out and then cooled to room temparature with a rate of 5~20 °C.

For the measurement of pyroelectric coefficient p_3, the crystal cuts of 1 mm (thickness) × 8 mm (width) × 8 mm (length) were prepared for the Z square plates of BZBO crystals. The prepared samples were vacuum sputtered with 200 nm Pt film on the parallel faces. The pyroelectric properties were investigated using a pyroelectric test system consisting of a Keithley model 642 electrometer (Keithley Instruments Inc., Cleveland, OH, USA) and TF Analyzer 2000E Measurement System (aixACCT Systems GmbH, Germany).

The primary pyroelectric coefficient p_i was calculated by:

$$p_i = \frac{C_0 d_v}{AdT} \tag{1}$$

where C_0 is the capacitance of integrating capacitor (1 μF), d_v is the measured pyroelectric voltage, A is the electric area. In this work, the temperature step was controlled to be dT = 10 ± 0.5 °C, with the temperature was increasing from 15 °C to 155 °C.

The secondary pyroelectric effect is associated with a strain-induced polarization due to the thermal expansion, which can be calculated by the following equation:

$$P_{\text{sec}} = P_i^X - p_i^x = \partial_{jk} c_{jklm} d_{ilm} \tag{2}$$

where P_i^X is the unclamped pyroelectric coefficient, p_i^x is the primary pyroelectric coefficient, and α_{jk}, c_{ijlm}, d_{ilm} are the thermal expansion coefficient, elastic stiffness and piezoelectric coefficient, respectively.

Moreover, the pyroelectric performance was evaluated by figures of merit (FOMs), including current responsivity F_i, voltage responsivity F_v and detectivity F_d, as given below:

$$F_i = \frac{P_i}{C_v} \tag{3}$$

$$F_v = \frac{P_i}{C_v \varepsilon_0 \varepsilon_r} \tag{4}$$

$$F_d = \frac{P_i}{C_v \sqrt{(\varepsilon_0 \varepsilon_r \tan\delta)}} \tag{5}$$

where C_v is the volume-specific heat, ε_0 is the vacuum permittivity, ε_r is the relative dielectric permittivity, and tanδ is the dielectric loss.

3. Results and Discussion

3.1. Pyroelectric Properties of BZBO Crystals

The primary pyroelectric coefficient p_3 of BZBO crystals was determined by using the charge integration method, and the result is reported in Table 1. In addition, the secondary pyroelectric coefficient p_{sec}(Z), thermal expansion coefficients, elastic stiffness and piezoelectric coefficients of BZBO crystals are also summarized and presented in Table 1.

Table 1. Properties of $Bi_2ZnB_2O_7$(BZBO) pyroelectric crystals at 15 °C.

Pyroelectric coefficients (μC/(m^2·°C))									
Crystal	p_3	p_{sec}(Z)							
BZBO	6.4	−6.5							
TGS	60	−330							
FOMs value									
Crystal	F_i (pm/V)		F_v (m^2/°C)		F_d (10^{-5}/Pa$^{1/2}$)				
BZBO	10.38		0.06		11.31				
Thermal expansion coefficients α (10^{-6} K^{-1})									
Crystal	α_{11}	α_{22}	α_{33}						
BZBO	6.9	11.2	1.9						
Elastic stiffness constants c_{ij} (10^{10} N/m^2)									
Crystal	c_{11}	c_{12}	c_{13}	c_{22}	c_{23}	c_{33}	c_{44}	c_{55}	c_{66}
BZBO	17.0	7.4	6.3	13.1	6.9	16.4	5.8	5.8	4.9
Piezoelectric coefficient d_{ij} (10^{-12} C/N)									
Crystal	d_{15}	d_{24}	d_{31}	d_{32}	d_{33}				
BZBO	1.4	−5.5	2.5	−6.4	1.1				

Based on the charge integration method, the pyroelectric coefficient p_3 of BZBO crystals was measured to be 6.4 μC/(m^2·°C). Compared with triglycine sulfate TGS crystal, the p_3 of BZBO was about one tenth of that of TGS (60 μC/(m^2·°C)). In combination with the thermal expansion coefficients, elastic constants and piezoelectric coefficients, the secondary pyroelectric coefficient p_{sec}(Z) of BZBO crystals was evaluated. The p_{sec}(Z) value was found to be in the order of −6.5 μC/(m^2·°C), nearly one-fiftieth of that of TGS. The lower pyroelectric coefficient indicated that the BZBO crystal was beneficial for the charge type pyroelectric sensors with wide temperature ranges.

In addition, as shown in Table 1, the FOMs were calculated (Equations (3)–(5)) to evaluate the pyroelectric performance of BZBO crystals. It was found that the F_i value of BZBO crystals was 10.38 pm/V, similar with the PVDF (11 pm/V) [21]. Particularly, the detectivity value F_d of BZBO crystals was high, and was found to be 11.31 × 10^{-5}/Pa$^{1/2}$, which was similar to that of $LiTaO_3$ crystals (12.6 × 10^{-5}/Pa$^{1/2}$) [19], higher than that of ReCOB crystals (7.6~11.5 × 10^{-5}/Pa$^{1/2}$) [22], and about twice as much as that of TGS crystals [23]. The high responsivity and detectivity of BZBO crystals are desirable for sensor applications.

3.2. Temperature Dependence of Pyroelectric Properties

For further investigation of pyroelectric properties, the temperature dependent behaviours of pyroelectric properties for BZBO crystals were studied from 15 °C to 155 °C. Figure 1 presented the variation of pyroelectric coefficient p_3 as a function of temperature for BZBO crystals, and the small insets showed the schematic of the Z crystal cut. To obtain a reasonable average value, the values were measured three times. It was observed that the pyroelectric coefficient p_3 decreased with increasing temperature. The coefficient p_3 was 6.41 μC/(m^2·°C) at 15 °C and 2.89 μC/(m^2·°C) at 155 °C, respectively. The pyroelectric coefficient p_3 showed small temperature dependent pyroelectric behaviour from 15 °C to 85 °C, and the variation was 18%.

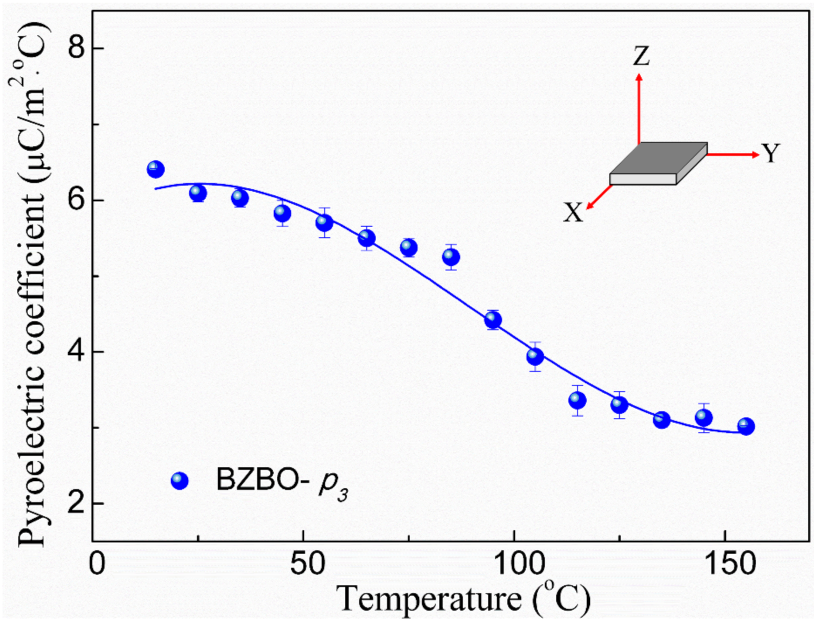

Figure 1. Temperature dependence of pyroelectric coefficient p_3 for BZBO crystals.

To evaluate the pyroelectric performance of BZBO crystals, the dielectric and thermal expansion behaviours, as a function of temperature, were investigated over the temperature range of 15 °C to 155 °C, and the result is presented in Figure 2. It was observed that the relative dielectric constant, dielectric loss and specific heat of BZBO crystals increased with increasing temperature, exhibiting a positive variation. According to the computational equation, we can infer that the FOMs value should be decreased with increases in temperature.

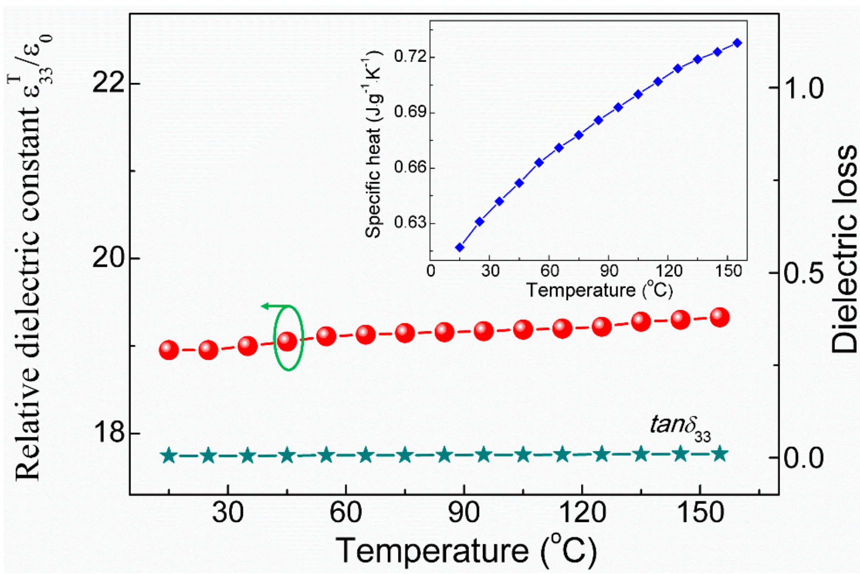

Figure 2. Temperature dependence of relative dielectric constant, dielectric loss and specific heat for BZBO crystals.

Based on the dielectric and thermal expansion properties of BZBO crystals, the temperature dependence of the FOMs value was investigated over the temperature range of 15~155 °C, including current responsivity F_i and detectivity F_d, and the result is shown in

Figure 3. The F_i and F_d were decreased when the temperature increased, where the F_i was 10.38 pm/V at 15 °C and 4.14 pm/V at 155 °C. The detectivety F_d was 11.31 × $10^{-5}/Pa^{1/2}$ at 15 °C and decreased to 3.20 × $10^{-5}/Pa^{1/2}$ when the temperature was at 155 °C.

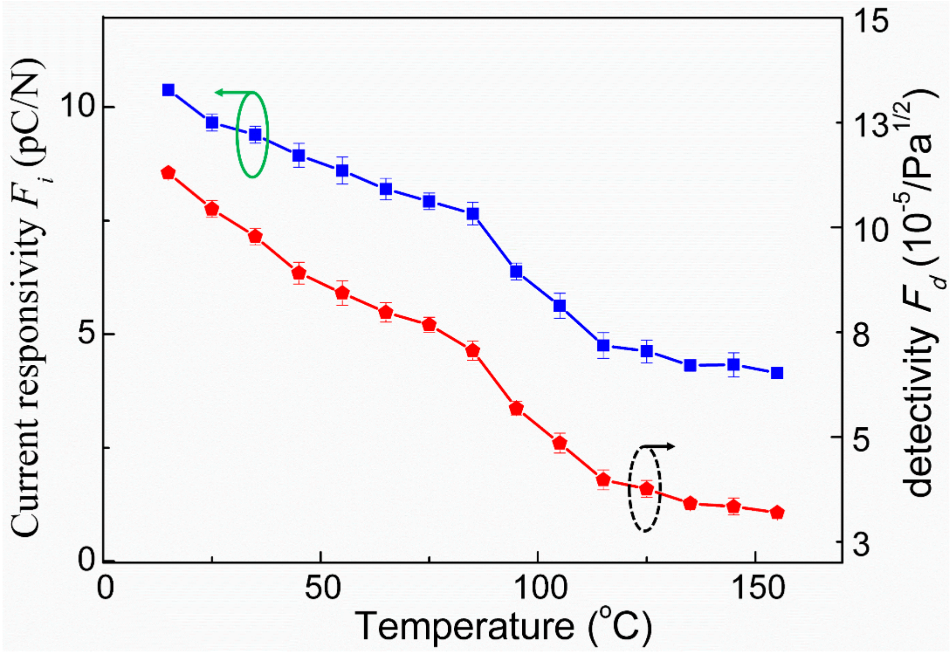

Figure 3. Variation of FOMs as a function of temperature for BZBO crystals.

In view of the good pyroelectric performance of BZBO crystals, the orientation dependence of the pyroelectric coefficient was discussed in accordance with coordinate rotation. Figure 4 presented the variation of the pyroelectric coefficient p_i with the rotation angle around the *X*-axis. It can be observed that when the angles were 0°, 90°, 180°, 270° and 360°, the p_i reached the maximum, being on the order of 6.41 μC/(m^2·°C).

Based on the results, the pyroelectric coefficient p_3 of BZBO crystals was low and stable at the measured temperature range, which makes BZBO a promising candidate for pyroelectric sensors wide temperature ranges.

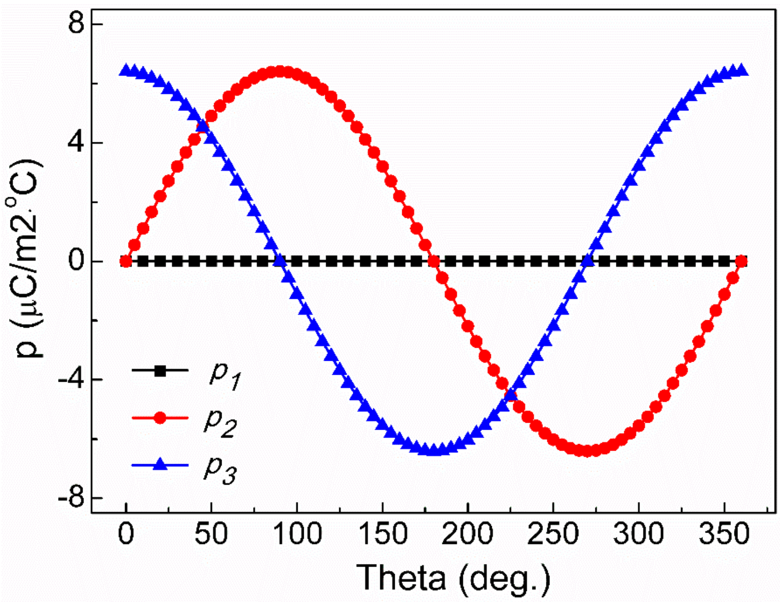

Figure 4. Orientation dependence of p_i for BZBO crystals.

4. Conclusions

In this work, pyroelectric properties of orthorhombic BZBO crystals were studied. The primary and the secondary pyroelectric coefficients of BZBO crystals were on the order of 6.4 and −6.5 μC/(m^2·°C), respectively. Of particular interest, the BZBO crystals possessed relatively high current responsivity F_i and detectivity F_d, with the values of 10.38 pm/V and 11.31 × 10^{-5}/Pa$^{1/2}$. Moreover, the temperature dependent behaviours were studied from 5 °C to 155 °C, where the primary pyroelectric coefficients and FOMs were decreasing with increases in temperature. These, together with the reported pyroelectric properties, make BZBO crystals a promising candidate for pyroelectric sensor applications.

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