Crystal growth, structure and thermal properties of noncentrosymmetric single crystals PrCa4O(BO3)3+

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Abstract
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Keywords
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Crystal growth, structure and thermal properties of noncentrosymmetric single crystals PrCa$_4$O(BO$_3$)$_3$†

Fapeng Yu,$^a$ Shujun Zhang,$^{a,b}$ Xiufeng Cheng,$^a$ Xiulan Duan,$^a$ Tingfeng Ma$^c$ and Xian Zhao$^{a,a}$

Noncentrosymmetric praseodymium calcium oxyborate single crystals, PrCa$_4$O(BO$_3$)$_3$ (PrCOB), were grown by the Czochralski technique. The monoclinic unit cell parameters were found to be $a = 8.177$ Å, $b = 16.157$ Å, $c = 3.629$ Å and $Z = 2$ with space group $Cm$. Crystal density was measured using the Archimedes method, being on the order of 3.47 g cm$^{-3}$. Thermal properties of PrCOB were investigated, where the specific heat was found to be 0.63 J g$^{-1}$ K$^{-1}$ at room temperature, increasing to 0.85 J g$^{-1}$ K$^{-1}$ at 700 °C. The thermal expansion coefficients were measured to be $\alpha_1 = 7.99$, $\alpha_2 = 4.90$ and $\alpha_3 = 9.46$ (10$^{-6}$/°C), respectively. In addition, thermal diffusivity $\lambda_2$ and thermal conductivity $\kappa_2$ as a function of temperature were studied, where $\lambda_2$ was observed to decrease from 0.89 to 0.58 mm$^2$ s$^{-1}$, while $\kappa_2$ was found to maintain the same value, being $\sim 1.90$ W m$^{-1}$ K$^{-1}$ over the temperature range of 20–700 °C.

**Motivation**

Rare-earth calcium oxyborate crystals ReCa$_4$O(BO$_3$)$_3$ (Re = rare earth element, abbreviated as ReCOB) with monoclinic phase in space group $Cm$, are multifunctional materials. These crystals possess the merits of none phase transformation, chemical stable and easy to polish. Moreover, due to their noncentrosymmetric structure characteristics, extensive studies have been carried out for nonlinear optical applications, such as second- and third-harmonic generation, and laser frequency-doubling devices in the last two decades.$^{1-7}$

To date, several kinds of ReCOB crystals (Re = Er, Y, Gd, Sm, Nd and La) grown by the Czochralski (Cz) pulling technique have been reported.$^{3-7}$ Other ReCOB crystals, e.g. YbCOB, TbCOB and EuCOB etc., are very difficult to grow using traditional Cz method, due to the noncongruent melting or narrow congruent melting region. Recently, electro-elastic properties of ReCOB type crystals, including YCOB, GdCOB, NdCOB and LaCOB, have been extensively investigated.$^{8-15}$ Among these crystals, NdCOB crystals were reported to possess a relatively high surface acoustic wave (SAW) coupling factor ($k^2 = 0.8\%$) and low linear temperature coefficient of delay (TCD) (close to zero),$^{16}$ while YCOB crystals were observed to show high stability of electromechanical properties at elevated temperatures,$^{14,15}$ and explored for high temperature accelerometer applications.$^{17-19}$ In previous reports, it has been revealed that the piezoelectric coefficient $d_{33}$ and electromechanical coupling factor $k_{33}$ increase with increasing rare-earth ionic radius, the relationship between crystal structure and piezoelectric properties was established, where the distortions of Re–O and Ca–O octahedra in ReCOB crystals were believed to account for the enhancement of piezoelectric coefficient $d_{33}$. However, among ReCOB crystals, reports on the growth and structure of PrCOB crystals are very limited.$^{20,22}$ In addition, high temperature thermal properties of PrCOB crystal have not been reported yet, which are important for high temperature (piezoelectric) device design.

In this work, Cz growth of PrCOB crystals was studied and the crystal structure was analyzed. Furthermore, thermal properties, including the specific heat, thermal diffusivity and thermal conductivity of PrCOB crystals at room temperature and elevated temperatures were measured and compared with its analogues, for potential high temperature applications.

**Growth of PrCOB single crystals**

Starting materials for PrCOB crystal growth were high purity (99.99%) CaCO$_3$, Pr$_6$O$_{11}$ and H$_3$BO$_3$ powders. They were weighed according to the nominal composition. Considering the evaporation of B$_2$O$_3$ during the growth process, an excess of H$_3$BO$_3$ (1.0%-1.5%) was added to the starting components, which was found to benefit the crystal growth. The starting materials were fully mixed, and then pressed into tablets and calcined at 1000 °C for 10 h, to decompose H$_3$BO$_3$ and CaCO$_3$. 

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† CCDC reference number 917976. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ee00024a
which the habitual faces (PrCOB single crystals pulled along the thermal stress and to avoid cracks in the grown crystals. Cracks and inclusions can be obtained. After thermal profile modification (thermal gradient and melt may also give rise to the inclusions in the grown crystals. In addition, the inhomogeneous supercooling of the melt. In addition, the inhomogeneous thermal gradient distribution, leading to the improper thermal gradient, distribution, leading to the supercooling of the melt. In addition, the inhomogeneous melt may also give rise to the inclusions in the grown crystals. After thermal profile modification (thermal gradient and growth speed), high quality single crystals (Fig. 1(b)) free of cracks and inclusions can be obtained.

Fig. 1(a) and (b) present the photographs of as-grown PrCOB single crystals pulled along the <010> direction, in which the habitual faces (−201) and (101) can be observed. Fig. 1(a) shows the PrCOB crystal with inclusions, induced by the improper thermal gradient distribution, leading to the supercooling of the melt. In addition, the inhomogeneous melt may also give rise to the inclusions in the grown crystals. After thermal profile modification (thermal gradient and growth speed), high quality single crystals (Fig. 1(b)) free of cracks and inclusions can be obtained.

Experimental

Phase identification of the as-grown PrCOB crystals were performed by X-ray powder diffraction (XRPD) with a D8 Advance diffractometer (Bruker AXS, Advanced X-ray Solutions) using Cu Kα radiation (λ = 1.5406 Å) and graphite monochromator, at room temperature over a 2θ range of 10° to 60°. The crystal structure was determined using a Bruker APEX2 CCD area-detector diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å).

The crystal density was obtained by two methods. The theoretical density, ρ₂θ, was calculated using the lattice parameters determined from a four circle X-ray diffractometer, following equation: ρ₂θ = M/[absin(βN_A)], where M is the molar weight of the crystal, N_A is Avogadro’s constant, Z is the number of molecules in one unit cell, which is two for PrCOB crystal, a, b and c are the lattice parameters obtained by the X-ray diffraction. For comparison, the experimental density, ρ_exp, was determined by the Archimedes method.

Thermal expansion behavior of PrCOB crystal was measured in the temperature range of 25 to 500 °C using a thermal dilatometer (Diamond TMA, Perkin-Elmer) with a heating rate of 5 °C min⁻¹. Specific heat was measured by differential scanning calorimeter using a simultaneous thermal analyzer (Diamond DSC, Perkin-Elmer) in the temperature range between 20 to 300 °C, at a constant heating rate of 5 °C min⁻¹. The values of the specific heat were calculated by the supplied software (Perkin-Elmer Co.). The thermal diffusion coefficient and thermal conductivity of PrCOB crystal were measured using a Netzsch Nanoflash model LFA 457 apparatus along the crystallographic b axis (physical Y axis), by the laser pulse method in the temperature range of 20 to 700 °C. During the measurement, square wafers [4.00 × 4.00 × 1.20 mm³ (X × Y × Z)] were coated with graphite on opposite faces, the front surface of the wafer was heated by a laser pulse (the laser voltage was 1826 V and pulse width was 0.5 ns), and the temperature rise versus time on the opposite surface was measured using an InSb IR detector. The thermal diffusion coefficients and thermal conductivity values were then calculated using the analytical software provided (Netzsch Co.).

Results and discussions

Crystal structure

Crystal phase of PrCOB single crystals were determined by XRPD, results are shown in Fig. 2, where strong diffraction peaks were observed for (220), (150), (−201), (240), (060) and (170) planes, with diffraction angles (2θ) being 24.778°, 29.787°, 30.091°, 31.418°, 33.244° and 40.643°, respectively. Compared to XRPD patterns of ReCOB single crystals, PrCOB was found to show similar diffraction peaks as YCOB, GdCOB and NdCOB etc. Based on XRPD and the four-circle diffractometer measurement, PrCOB was found to possess space group Cm (Z = 2), with cell parameters a = 8.177 Å, b = 16.157 Å, c = 3.629 Å and β = 101.40°, slightly higher than NdCOB (PCPDF Card 04-009-2919: a = 8.145 Å, b = 16.06 Å, c = 3.607 Å and β = 101.37°), though the rare-earth ionic radius for Nd³⁺ and Pr³⁺ are very close (rNd³⁺ = 0.983 Å and rPr³⁺ = 0.990 Å (ref. 23)).
The structure building unit was considered to consist of five oxygen octahedra linked to three borate groups (as shown in Fig. 3(A)). In the structure unit, there is one distorted octahedron around the Pr atom, two different distorted octahedral positions for Ca atoms, which can be categorized as a Pr-O octahedron and Ca(1)-O and Ca(2)-O octahedra. The average bond length of the Pr–O octahedron was calculated and found to be shorter than the Ca(2)–O octahedron, but longer than those of Ca(1)–O octahedron. In addition, there are two kinds of boron site, B(1) and B(2), observed in the PrCOB structure. The boron atoms in the octahedron were found to range from 1.3712 to 1.3976 Å, with the standard deviation being on the order of 1.12%.

Crystal density

Based on the crystal structure data ($a = 8.177 \, \text{Å}$, $b = 16.157 \, \text{Å}$, $c = 3.629 \, \text{Å}$ and $\beta = 101.40^\circ$), theoretical crystal density was calculated to be $\rho_t = 3.49 \, \text{g cm}^{-3}$. For comparison, crystal density was measured using Archimedes method, the average experimental density was obtained and found to be $\rho_e = 3.47 \, \text{g cm}^{-3}$, slightly lower than the theoretical calculated value.

Thermal expansion

For crystals with a monoclinic phase, there are four independent thermal expansion coefficients ($x_{11}$, $x_{22}$, $x_{33}$, and $z_{13}$). In the principal coordinate system, the $[x_{ij}]$ tensor is diagonal, among which, $x_{11}$, $x_{22}$, $x_{33}$ can be obtained by measuring the thermal expansion along physical $X$, $Y$, $Z$ axes, according to the IEEE standard on piezoelectricity,$^{24}$ while for $z_{13}$, rotated cut crystal can be used, which has been discussed in previous work (the $z_{13}$ value is small (<1.0 ppm °C$^{-1}$), so it is neglectable).$^{25}$ Fig. 4 gives the thermal expansion curves along physical $X$, $Y$ and $Z$ axes as a function of temperature for PrCOB. After calculation, the thermal expansion coefficients were determined to be $x_{11} = 7.99$, $x_{22} = 4.90$ and $x_{33} = 9.46 \times 10^{-5}$ °C$^{-1}$, respectively. In addition, the variation of crystal density as a function of temperature was calculated based on the thermal expansion, and temperature coefficients of crystal density were obtained, where the first ($T_{p}^{(1)}$), second ($T_{p}^{(2)}$) and third ($T_{p}^{(3)}$) order of temperature coefficient were found to be $T_{p}^{(1)} = -1.61 \times 10^{-5}$ °C, $T_{p}^{(2)} = -2.60 \times 10^{-8}$ °C$^2$ and $T_{p}^{(3)} = 4.77 \times 10^{-11}$ °C$^3$, respectively.

Specific heat

The specific heat of the crystalline solids was generally described by the Debye lattice theory in terms of the harmonic frequency spectrum. However, due to the complex structure of the PrCOB crystal, it is hard to explain the measured specific heat with the predictions of the lattice theory. The dependence of specific heat ($C_p$) of PrCOB with temperature is shown in Fig. 5, from which, it can be seen that the PrCOB crystal has a specific heat value of 0.63 J g$^{-1}$ °C$^{-1}$ at 20 °C, that increases linearly with increasing temperature. For comparison, the specific heat as a function of temperature for the ErCOB crystal was also measured and given in the inset of Fig. 5, where the...
specific heat at room temperature was found to be 0.71 J g⁻¹ °C⁻¹, slightly higher than that of PrCOB, but similar to that of YCOB (0.73 J g⁻¹ °C⁻¹). Table 1 lists the specific heat values for various ReCOB crystals, at room temperature and 300 °C.

Thermal diffusivity and thermal conductivity

Thermal diffusivity (λ) and thermal conductivity (κ) are anisotropic and can be expressed by a second order tensor, similar to the thermal expansion coefficients. The thermal conductivity κ can be obtained by measuring the specific heat $C_p$ and thermal diffusivity $\lambda$, according to equation below,

$$\kappa = \lambda \rho C_p$$

In this work, thermal conductivity (κ) and thermal diffusivity (λ) of PrCOB crystals were measured along the crystallographic axis b. Fig. 6 shows the variation of thermal conductivity and thermal diffusivity of PrCOB crystals in the temperature range of 20–700 °C. In addition, the related specific heats at elevated temperatures obtained by laser pulsed method are also presented. It was found that the specific heat was slightly increased with increasing temperature, this is consistent with that obtained by differential scanning calorimeter, where the room temperature specific heat was determined to be $\sim$0.63 J g⁻¹ °C⁻¹. In contrast to the specific heat, the thermal diffusivity $\lambda$ was found to decrease with increasing temperature, with values being on the order of 0.89 mm² s⁻¹ and 0.58 mm² s⁻¹ at room temperature and 700 °C, respectively. Of particular importance is that the thermal conductivity $\kappa$ of PrCOB crystal was found to maintain the same value, being on the order of $\sim$1.90 W m⁻¹ °C⁻¹ over the studied temperature range.

For better understanding the thermal behavior, YCOB and ErCOB single crystals were also investigated for comparison. The specific heat, thermal diffusivity and thermal conductivity were measured from 20 to 700 °C, results are shown in Fig 7. It can be observed that the specific heat of YCOB crystal increased with increasing temperature, ranging from 0.73 to 1.13 J g⁻¹ °C⁻¹, while the thermal diffusivity $\lambda$ firstly decreased with increasing temperature, exhibiting a turnover point at 600 °C (0.65 mm² s⁻¹), then slightly increased with increasing temperature. Correspondingly, the thermal conductivity $\kappa$ was found to change from 2.79 at 20 °C to 2.05 W m⁻¹ °C⁻¹ at 700 °C, with the minimum $\kappa$ value $\sim$1.98 W m⁻¹ °C⁻¹ occurred at 600 °C. However, the ErCOB crystal was found to exhibit a similar trend to PrCOB, where the thermal conductivity $\kappa$ was found to maintain the same value, being around $\sim$2.00 W m⁻¹ °C⁻¹ in the same temperature range.
It is known that heat transfer occurs in solid by means of free electron diffusion and lattice wave, where the lattice wave plays an important role for thermal conduction in insulators, especially for the case of ReCOB crystals, due to their high resistivity ($\rho > 10^{14} \, \Omega \, \text{cm}$ at room temperature). The thermal conduction induced by a lattice wave can be regarded as a phonon scattering effect, relating to the phonon mean free path. According to the Debye mode, the thermal conductivity can be expressed as:

$$\kappa = \frac{1}{3} C \nu$$

where $l$ is the phonon mean free path, $C$ is the specific heat at constant volume and $\nu$ is the average sound velocity, which is considered as constant. The variation of thermal conductivity as a function of temperature is related to the temperature dependent phonon mean free path and specific heat. Thus, the less variation of the thermal conductivity for ErCOB and PrCOB crystals indicates the independence of the phonon mean free path over the temperature range, while the decrease of the thermal conductivity of YCOB crystal in the temperature range of 20–600 °C indicates the decrease of phonon mean free path, accounting for phonon scattering at elevated temperatures, associated with crystal defects. However, it should be noted that the thermal conductivity $\kappa$ of YCOB is higher than that of PrCOB, both at room temperature and elevated temperatures, demonstrating that the phonon mean free path for the YCOB crystal is longer than that of the PrCOB crystal, associated with the lower level of phonon scattering, and accounts for higher mechanical quality factor and resistivity in YCOB crystals. This phenomenon was consistent with the discussion in previous research.

**Conclusions**

PrCOB single crystals were grown by the Czochralski pulling method, crystal structure and thermal properties were investigated. The crystal structure of the PrCOB crystal was determined to be monoclinic phase (space group $Cm$), with unit cell parameters $a = 8.177 \, \text{Å}$, $b = 16.157 \, \text{Å}$, $c = 3.629 \, \text{Å}$ and $Z = 2$. The crystal density at room temperature was measured to be $3.47 \, \text{g cm}^{-3}$ and the density temperature coefficients were: $\alpha = 0.63 \, \text{Jg}^{-1} \, \text{K}^{-1}$ at room temperature to $0.85 \, \text{Jg}^{-1} \, \text{K}^{-1}$ at 700 °C. However, the thermal diffusivity was observed to decrease with increasing temperature, with $\lambda_{22}$ being on the order of $0.89 \, \text{mm}^2 \, \text{s}^{-1}$ at room temperature and $0.58 \, \text{mm}^2 \, \text{s}^{-1}$ at 700 °C. The increase of specific heat $C_p$ and decrease of thermal diffusivity $\lambda_{22}$ with increasing temperature were observed for PrCOB, ErCOB and YCOB crystals. However, different trends were found for thermal conductivity $\kappa_{22}$, where the $\kappa_{22}$ value of the YCOB crystal decreased from 2.79 to 2.05 W m$^{-1}$ K$^{-1}$, while PrCOB and ErCOB maintained the same value, being ~1.90 and ~2.00 W m$^{-1}$ K$^{-1}$ over the studied temperature range, respectively.

**Table 1** Crystal data and structure refinement for PrCOB crystals

<table>
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<tr>
<th>Crystal system, space group</th>
<th>Monoclinic, $Cm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 8.1772(12) , \text{Å}$, $b = 16.1572(2) , \text{Å}$, $c = 3.6286(5) , \text{Å}$, $\beta = 101.3990(10)^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>469.95(12) , $\text{Å}^3$</td>
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<tr>
<td>$Z_{\text{calculated}}$</td>
<td>2, 3.489 Mg m$^{-3}$</td>
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<tr>
<td>$\rho(000)$</td>
<td>7.407 mm$^{-1}$</td>
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<tr>
<td>Crystal size</td>
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<tr>
<td>Theta range for data collection</td>
<td>0.08 $\times$ 0.06 $\times$ 0.06 mm</td>
</tr>
<tr>
<td>Limiting indices</td>
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<tr>
<td>Reflections collected/unique</td>
<td>$-10 \le h \le 10$, $-20 \le k \le 20$, $-4 \le l \le 4$</td>
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<tr>
<td>Refinement method</td>
<td>Semi-empirical from equivalents</td>
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<td>Goodness-of-fit parameters</td>
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**Table 2** Atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters ($\lambda^2 \times 10^3$) for PrCOB. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor

<table>
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<th>$x$</th>
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<th>$z$</th>
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**Table 3** Anisotropic displacement parameters ($\lambda^2 \times 10^3$) for PrCOB single crystals. The anisotropic displacement factor exponent takes the form: $-2\pi^2/h^2 \lambda^2 U_{ij} + ... + 2ka^*b^*U_{ij}$

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Notes and references