Linear optical and thermo-physical properties of polar K$_3$B$_6$O$_{10}$Cl crystal

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Abstract

Single crystal of K$_3$B$_6$O$_{10}$Cl with size of 35 mm $\times$ 35 mm $\times$ 11 mm was grown by the TSSG method for the first time. In the crystal growth process, the cooling rate, the rotating speed and seed direction have been investigated. Based on the measurement of refractive-index from UV to NIR region, the limit of type-I phase matching second harmonic generation wavelength was calculated to be 272 nm, which is a little shorter than that of LiB$_3$O$_5$ (277 nm). Thermal properties including specific heat, thermal diffusion and thermal conductivity were performed on the crystal. In addition, polarization measurements demonstrate that although K$_3$B$_6$O$_{10}$Cl is polar, the material is not ferroelectric.

Keywords: K$_3$B$_6$O$_{10}$Cl; Optical property; Thermo-physical; Crystal growth; The relationship of structure-property

1. Introduction

Borates have attracted much attention from material scientists and chemists, which can be attributed to their outstanding linear and nonlinear optical (NLO), piezoelectric, luminescent and other functional properties for technical applications [1—8]. In the series of borate materials [9—14], K[B$_2$O$_4$(OH)$_4$]$_2$H$_2$O (KB5) was the first borate NLO crystal described for ultraviolet (UV) light generation [15]. After that, other borates [16—22], such as, $\beta$-BaB$_2$O$_4$ (BBO) [16], LiB$_3$O$_5$ (LBO) [17] in succession have been discovered. And a detailed review of above borate crystals was also reported by Becker and Sasaki et al. [23]. Among them, KBBF is the only NLO material used to direct second harmonic generation (SHG) down to 200 nm owing to wide phase-matching region. Thus, introducing halogen atom into the borate as a perspective system to explore the functional materials, receives much attention. Many borate halides have been reported in our and other groups [24—26]. For example, the borate halides K$_3$B$_6$O$_{10}$Cl (KBOC) [27—32], Ba$_4$B$_{12}$O$_{20}$F [33], M$_3$B$_6$O$_{11}$F$_2$ (M = Ba, Sr, Pb) [34—36], Li$_3$Ca$_9$(BO$_3$)$_7$$\cdot$$2$[LiF] [37], etc. have been reported in our group, some of them are promising UV NLO crystals.

KBOC has been reported that it possesses large SHG response, and short UV cut off edge [27]. In addition, Wang et al. have investigated the influence of pressure on SHG tensor of KBOC. At zero pressure, the calculated SHG response agrees well with the experimental results. And the large SHG response mainly results from the boron-oxygen framework. With the pressure increased, the large SHG response mainly comes from the perovskite-like ClK$_6$ octahedron distortion. Pressure changes the main source of SHG from the BO$_4$ tetrahedron to the ClK$_6$ octahedron [28]. Then, the centimetre-sized single crystal with dimensions up to 25 mm $\times$ 11 mm $\times$ 7 mm have been grown successfully in our group [29]. The limit of type-I phase matching SHG wavelength was calculated based on the measurement refractive index in visible region (400—700 nm), which indicates that KBOC may be promising for the fourth harmonic generation of a Nd: YAG laser. To well and accurately evaluate its UV application, the growth of large crystals with high quality is

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necessary. The growth of the KBOC crystal uses the high temperatures solution followed by cooling to room temperature. The measurement of their thermal properties is also necessary to confirm the appropriate choice of the optimum conditions for synthesis, and evaluate its effect on practical applications [38,39]. In addition, the thermal behaviour of material is interesting for developing solid state physics and chemistry, crystal chemistry, etc [40,41]. In the paper, the high quality KBOC crystal with size of 35 mm × 35 mm × 11 mm were grown by TSSG using the PbF2 flux for the first time. The effect on the growth including seed orientation, cooling rate and rotation speed on crystal morphology and quality are described. To further evaluate the application in UV region, the refractive index from UV to NIR region (0.2–2.4 μm) using a larger prism than before has been measured. The prism has an apex angle of 29.98°, and the height of KBOC prism (along the a-axis) is about 10 mm. Meanwhile, the phase matching curves of SHG, third and fourth harmonic generation (THG and FHG) in the fundamental wavelength region (0.5–4 μm) were discussed by detailed theoretical simulation, accordingly the walk-off and permittive angles have been calculated. The shortest phase matching wavelength 272 nm is a little shorter than that of LBO, which make that KBOC may be promising for the fourth harmonic generation (278 nm) of the 1112 nm laser. A preliminary measurement for the thermophysical properties including density, specific heat, thermal diffusion and thermal conductivity studies for KBOC is discussed. Additional functional properties, such as piezoelectricity, pyroelectricity and ferroelectricity have also been studied on the grown crystals.

2. Experimental section

2.1. Crystal growth

As we reported previously [29], KBOC melts incongruently. Centimeter sized KBOC crystals were grown by TSSG method. Several fluxes have been investigated for growing KBOC crystal, i.e. B2O3, K2CO3, K2CO3–PbO and KF, etc. However, there is still a small quantity of volatiles in the process of the crystal growth of KBOC, leading to the un-stabilization of crystal growth. Thus, to obtain optimal growth condition of KBOC, the more fluxes have been attempted. In the end, the PbF2 flux is proved to be suitable to grow KBOC crystal, which may overcome the high crystallization temperature and the high viscosity in the system, and KBOC is prone to crystallize. To study the best growth habits of KBOC crystal, seed crystals with different crystallographic directions ([101], [001] and [211]) were investigated. The growth technics of KBOC about the cooling rate and rotation speed have been also investigated in the process of crystal growth.

2.2. Refractive indices

The refractive indices of KBOC were determined from UV to NIR region (0.2–2.4 μm) by the minimum deviation method at room temperature, as shown in Table S1 in the Supporting Information. The prism used to measure its refractive indices has an apex angle of 29.98° and the height of KBOC prism (along the a-axis) is about 10 mm.

2.3. Raman spectrum measurement

Raman spectrum was obtained with on a LABRAM HR Evolution spectrometer using 532 nm radiations and a 50× Ultra-Long Working Distance MSPlan Olympus objective. The spectrum was recorded in the 400–1500 cm⁻¹ range.

2.4. Thermophysical property measurements

The high quality single crystal of KBOC was used for the measurement of specific heat and the thermal diffusivity. The specific heat was carried out in the temperature range of 25–300 °C at a heating rate of 10 °C/min using a simultaneous thermal analyzer (TGA/DSC1/1600HT, Mettler-Toledo Inc.), and sapphire was used as a reference. The thermal diffusivity was measured in the temperature range of 25–300 °C at a heating rate of 10 °C/min using NETZSCH LFA 457 NanoFlash equipment. The a- and c-cut wafers with dimensions of 4 × 4 × 1 mm³, respectively, coated with graphite on both sides were used to the measurements.

2.5. Piezoelectric measurements

A c-cut sample with the size of 6.0 × 6.0 × 0.5 mm³ was used to measure the piezoelectric coefficient. Direct piezoelectric coefficients were collected on YE2730A d33 m (APC international, Ltd). The c-cut sample coated with silver electrodes was used to measure the converse piezoelectric coefficients, and the applied voltages are in the range 500–1000 V. Converse piezoelectric measurements were carried out using a Radiant Technologies RT66A piezoelectric test system with a TREK (model 609B) high-voltage amplifier, Precision Materials Analyzer, Precision High-Voltage Interface, and MTI 2100 Fotonic Sensor.

2.6. Polarization measurements

The polarization and the pyroelectric coefficients were measured using the Radiant Technologies RT66A Ferroelectric Test system with a TREK high voltage amplifier. And the same c-cut sample coated with silver electrode was used to polarization measurements [42]. The polarization was carried out under different electric field and frequencies at room temperature. The pyroelectric coefficient was measured at electric field of 20 kV/cm and at 50 Hz in the temperature range 30–170 °C.

3. Results and discussion

3.1. Crystal growth and morphology of KBOC crystal

The KBOC crystals were grown using the PbF2 flux by TSSG method. To obtain optimal growth condition, the
influences including seed orientation, cooling rate and rotation speed on crystal morphology and quality are described. Based on the Bravais-Friedel and Donnay-Harker (BFDH) method, the theoretical morphology of KBOC exhibits \{210\}, \{110\}, \{101\} and \{111\} facets (Fig. 1a). However, for as-grown crystals, Figs. S1(a–c) in the Supporting Information show crystals with different oriented seeds. Using seeds oriented along the [101] direction, transparent crystal of KBOC is a regularly shaped rhombohedron with six developed faces. However, using the [001]-oriented seed, the profile morphology of grown KBOC is a headstand triangle as shown in Fig. S1b in the Supporting Information. The seed orientation is unfavourable for the growth of KBOC crystal since the growth interface (101) grows extremely slowly. Although a larger cooling rate is tried, the growth of KBOC crystal is still slower. Using seeds oriented along the [211] direction, although transparent crystal KBOC is obtained, the morphology is rarely observed (Fig. S1c in the Supporting Information). Through systematic experimental research, we found that the ideal growth morphology for KBOC crystal is a thick-tabular rhombus, which shows completely natural morphology and better transparency. And there are almost no inclusions in the crystal (Fig. 1b). However, the difference between growth and theoretical morphology mainly affect by multiple effects, such as the effect of thermodynamics and kinetics on the procession of crystal growth.

In addition, the cooling rate and rotation speed have been studied in the process of crystal growth. Figs. S2(a–c) in the Supporting Information show KBOC crystals grown by different cooling rates, apart from cooling rate, there are no differences in their growth conditions. The crystals exhibit almost the same shape, however, the fast cooling rate over 1 °C/day often makes the crystal growth become difficult since the minor thermodynamics deviation in the system may lead to the appearance of other nucleation, which will affect the crystal growth. The phenomenon may attribute to the little temperature gradient in the solution. When the solution drops the same temperature, the solution with small temperature gradient more inclines to saturate, which results in spontaneous nucleation appear. In the end, the more experiments suggest that the cooling rate of 0.2–0.5 °C/day is more suitable to the crystal growth of KBOC in existing temperature gradient. The rotation speed in the process of crystal growth has also been investigated. From Figs. S3 (a–c) in the Supporting Information, the differences between the crystals grown at different rotation speed are evident from the crystal growth interface (101) grows extremely slowly. Although a growth interface (101) grows extremely slowly. Although a diffusion layer and the transport of mass both affect the morphology and crystal quality of KBOC. In the end, the more experiments suggest that the suitable rotation rate for crystal growth of KBOC is about 3–10 rpm. From these experiments, we can see that in the case of growing KBOC crystal, the seed orientation and rotation speed have important effect on the crystal morphology, while, the cooling rate and rotation speed may affect the quality of KBOC crystal.

3.2. Refractive indices

The refractive indices from UV to NIR region have been measured. The experimental ordinary ($n_o$) and extraordinary ($n_e$) refractive indices of KBOC are summarized in Table S1 in the Supporting Information. The refractive index $n_i$ were fitted by the least squares method according to the Sellmeier equation. The equations are as follows:

$$n_o^2 = 2.40329 + \frac{0.012924341}{\lambda^2 - 0.015348131} - 0.012140921\lambda^2$$

$$n_e^2 = 2.25987 + \frac{0.010969635}{\lambda^2 - 0.015109462} - 0.0088335986\lambda^2$$

where $\lambda$ is the wavelength in micron. The calculated values are listed in Table S1 in the Supporting Information and consistent with experimental ones to the fifth decimal place. The fitted curves obtained from the Sellmeier equation agree well with the experimental data (Fig. S4 in the Supporting Information). In vision region, the values of the birefringence are only a little departure from the previous ones of the fifth decimal place. However, the four coefficients A, B, C and D of the Sellmeier parameters have obvious differences with that in the previous result [28]. These mainly affect by the adding measurement of UV and NIR refractive indexes. Meanwhile, the obvious

![Fig. 1. (a) Calculated morphology of the KBOC crystal. (b) The photograph of the KBOC crystal. (The minimum scale of the ruler is 1 mm).](image-url)
the refractive-index data for FHG of 1112 nm (1112 nm laser. The phase matching slab has been cut based on UV light generation by direct FHG from the fundamental KBOC extending the shortest achievable wavelength of KBOC. The phase matching (PM) region of KBOC crystal. The calculated difference of the Sellmeier parameters lead to the change of fundamental wavelengths over the 0.5–4 μm region are shown in Fig. 2a.

\[
\theta_m^o = \arcsin \left[ \frac{n_e^2(2\omega)}{n_o^2(2\omega)} \right] \left( \frac{n_o^2(2\omega)}{n_e^2(2\omega)} - \frac{n_o^2(2\omega)}{n_e^2(2\omega)} \right)^{1/2}, \text{ for type-I}
\]

\[
\left( \frac{\cos^2 \theta_m^o}{n_e^2(2\omega)} + \frac{\sin^2 \theta_m^o}{n_o^2(2\omega)} \right)^{1/2} = \frac{1}{2} \left\{ n_o(\omega) + \frac{\cos^2 \theta_m^o}{n_e^2(2\omega)} + \frac{\sin^2 \theta_m^o}{n_o^2(2\omega)} \right\}^{1/2}, \text{ for type-II}
\]

The calculated limit of type-I and type-II PM SHG wavelength are 272 and 374 nm, respectively. These make KBOC miss its potential application at 266 nm UV light by simple frequency doubling from the 1064 nm laser, however, the shortest phase matching wavelength is a little shorter than that of LBO (Table 1). In addition, an access to achieve deeper coherent light output through external pressure was proposed based on DFT simulated experiment, which shows that pressure-induced increase of polarizability anisotropy of \([B_6O_{10}]\) group can notably enlarge birefringence which assists KBOC extending the shortest achievable wavelength of KBOC [30]. Meanwhile, we can see that KBOC can achieve 278 nm UV light generation by direct FHG from the fundamental 1112 nm laser. The phase matching slab has been cut based on the refractive-index data for FHG of 1112 nm (θ = 77.32°, φ = 0°). In the laser experiment, we can observe the output of 278 nm laser from the fundamental laser at 1112 nm. Accordingly, the type-I and type-II PM curves for THG and FHG in the fundamental wavelengths (0.5–4 μm) are predicted. We can see that KBOC can achieve 355 nm UV light generation by direct THG or sum frequency generation from the fundamental 1064 nm laser (Fig. 2b). We usually use type II sum frequency \(\omega + 2\omega\) to realize the 355 nm UV light generation for 1064 nm laser. However, the beam \(2\omega\) produced by type I SHG, has a polarization perpendicular to the fundamental beam, using type-II sum frequency \(\omega(\omega) + e(2\omega) \rightarrow e(3\omega)\) type cannot obtain the sum frequency wavelength 355 nm. Thus, the usually used sum frequency technique for 355 nm UV light generation is type-II sum frequency \(e(\omega) + (2\omega) \rightarrow e(3\omega)\) type, which can use the half waveplate for 1064 nm and the full waveplate for 532 nm to change the polarization. In addition, KBOC does not allow realizing 266 nm UV light by simple frequency doubling from the fundamental laser at 1064 nm since the calculated limits of type-I PM SHG wavelength is 272 nm, which is a little greater than 266 nm. However, it can realize the UV fourth harmonic (266 nm) by sum frequency \(\omega + 3\omega\) with type-I arrangement (Fig. 2c). As shown in Table 1, we can see that the capability of producing UV harmonic generation for the KBOC crystal is comparable to that of LBO.

In addition, the walk-off and the permissive angles have been discussed. The detailed description of the calculation has been published elsewhere [43]. The walk-off and permissive angle curves for type-I SHG, THG and FHG are shown in Fig. 3a and b, respectively. The walk-off and permissive angles of KBOC for SHG from the fundamental laser at 1112 nm are 1.59° and 6.22 mrad mm, respectively. It is comparable with that of some practical applicable UV NLO crystal. These characters suggest that the KBOC crystal can be used for the generation of UV laser. Based on the analysis of structure and the dipole calculations [27], we found that the good NLO response arises from the distortion of \([B_6O_{10}]\) groups and C1K6 octahedra.

### 3.3. Raman spectrum measurement

In the Raman spectrum (Fig. S5 in the Supporting Information), the Raman-active mode of BO3 and BO4 have also been observed. The band at 1462 cm\(^{-1}\) normally corresponds to BO3 groups. The bands at 1154 and 1003 cm\(^{-1}\) are attributed to the asymmetric and the symmetric stretching of BO4. The bands at 718, 684, 636 and 595 cm\(^{-1}\) belong to the bending of BO3. The band at 567 cm\(^{-1}\) is attributed to the bending of BO4. The bands in the range 492, 480 cm\(^{-1}\) belong to the bending of BO4. It is clear that the spectrum exhibits BO3 and BO4 vibrations. The results are consistent with the reported IR spectrum [27] and the calculated Raman spectroscopy of KBOC based on the first-principles [32].
3.4. Density and specific heat

We calculated the density of KBOC using the formula \( \rho = \frac{MZ}{NV} \), where \( M \) is the molar weight of the crystal, \( Z \) is the number of molecules in the unit cell, \( N \) is Avogadro's number and \( V \) is the volume of the unit cell. The calculated density is 2.43 g/cm\(^3\). At the same time, the measurement value 2.37 g/cm\(^3\) using the Archimedes method [44] at 30 °C is similar with the calculated one. When the temperature is changed from 30 °C to \( T \), the dimensions of the sample will also change owing to the thermal expansion of the KBOC crystal. In the previous study, the two principal coefficients of thermal expansion along \( a \) and \( c \) axes were measured in the temperature range 50–400 °C [29]. Thus its density can be calculated:

\[
\rho = \frac{MZ}{NV} = \frac{1}{NV_0 \left(1 + \Delta a/a_0 \right) \left(1 + \Delta b/b_0 \right) \left(1 + \Delta c/c_0 \right)}
\]

where \( \rho_0 \) is the density of the crystal at \( T_0 \) (30 °C). The values of \( \Delta a/a_0 = \Delta b/b_0 \) and \( \Delta c/c_0 \) can be obtained based on the thermal expansion coefficient. The density almost linearly decreases from 2.43 g/cm\(^3\) at 30 °C to 2.34 g/cm\(^3\) at 400 °C as shown in Fig. 4a.

Additionally, as NLO crystals, the damage threshold and its possible applications could be affected by the specific heat [45]. Fig. 4b shows the specific heat vs temperature curves of the KBOC crystals. From the curve, it implies that the specific heat of KBOC linearly increases smoothly from 0.95 to 1.34 J (g K\(^{-1}\)) in the temperature range from 25 to 300 °C. The molar mass of KBOC is 377.61 g/mol; thus, the specific heat \( (C_p) \) of KBOC is calculated to be 358.73–506.00 J (mol K\(^{-1}\)) in the temperature range of 25–300 °C, demonstrating that KBOC can endure more thermal energy at high temperatures. In addition, the volume specific heat \( (C_V) \) can be calculated according to the Neumann-Kopp law and the Dulong-Petit law:

\[
C_V = \sum_{i=1}^{n} C_{V_i}
\]
Where the K atomic specific heat is about 25 J (mol K)$^{-1}$, while the specific heat of the light element B, O and Cl is about 11.3, 16.7 and 20.4 J (mol K)$^{-1}$ [46], respectively. For KBOC, there are 20 atoms in the chemical formula. Thus, the $C_V$ of KBOC is about 330.2 J (mol K)$^{-1}$, which is close to the experimental one at elevated temperature. The KBOC crystal possesses the high specific heat suggesting that it is not easily destroyed. When the pulsed laser beam irradiates on the KBOC crystal, which will absorb much energy, however it still can keep minimum temperature change.

3.5. Thermal diffusivity and thermal conductivity

Thermal diffusivity and conductivity affect the output beam quality of the laser crystal. High thermal conductivity will make the heat transfer easily to the air. The thermal diffusion coefficients of KBOC along $a$ and $c$ axes from 25 to 300 °C were measured directly (Fig. 5a), and its calculated thermal conductivity coefficients were given by the equation: $k = \lambda \rho C_p$, where $\lambda$, $\rho$, and $C_p$ denote the principal thermal conductivity, thermal diffusivity, density, and specific heat of the crystal, respectively. Along $a$ and $c$ axes, the calculated thermal conductivity is 2.21 and 1.98 Wm$^{-1}$K$^{-1}$ at 60 °C, respectively (Fig. 5b). Compared with commercialized BBO, KBOC possesses the larger thermal conductivity (1.98 Wm$^{-1}$K$^{-1}$; along $c$) than that of BBO (1.2 Wm$^{-1}$K$^{-1}$; along $c$). The large thermal conductivity also suggests that the KBOC crystal may have large damage threshold or long service life as the optical device.

3.6. Polarization and piezoelectric measurement of KBOC crystal

Under 1000 V at the frequency of 50 Hz from 20 to 170 °C, the pyroelectric coefficient has been obtained by measuring the polarization as a function of temperature. The temperature and frequency dependence of the pyroelectric coefficient is shown in Fig. S6 in the Supporting Information. The pyroelectric phenomenon has not been observed. In addition, piezoelectric measurements were performed on a $c$-cut crystal by direct and converse methods. We have not observed the piezoelectric property for the KBOC crystal. However, Han et al. have calculated the magnitudes of the piezoelectric constants of KBOC based on the first-principles. The largest non-zero piezoelectric tensor is 0.352 C/m$^2$ [31]. Thus, the difference between them has been discussed. Based on the structural analysis [27,29], we found that the acentric and polar units in KBOC are attributable to the CIK$_6$ octahedra and [B$_6$O$_{10}$] groups. And the distortions in CIK$_6$ octahedra and [B$_6$O$_{10}$] groups are not the result of second-order Jahn-Teller effects. Thus, the three dimensional network of [B$_6$O$_{10}$] and CIK$_6$ groups would be unfavourable for macroscopic deformation and the change of polarization, which may lead that the KBOC crystal doesn’t show piezoelectric and pyroelectric properties.

The ferroelectric measurements were also carried out to investigate any polarization reversibility. Obviously, there is a linear relationship between polarization and electric field (Fig. S7 in the Supporting Information), suggesting that KBOC is not ferroelectric. For a ferroelectric material, polarization can reverse, which suggests local polarization reversibility. For example, it is possible for the d$^0$ transition metals in octahedral coordination environments to be switched from one corner, edge, or face to the opposite, such as, BaTiO$_3$ (corner) and LiNbO$_3$ (face) [47,48], with an external electric field resulting in ferroelectric behaviour. However, local polarity in KBOC mainly attributes to the local dipole moments observed in the CIK$_6$ octahedra [27]. The CIK$_6$ octahedra connecting with each other to form the three dimensional framework will make polarization reversal for the CIK$_6$ octahedra be unfavourable for the energy and therefore KBOC is not ferroelectric.

4. Conclusion

High optical quality KBOC crystal using [101]-oriented seed with dimensions up to 35 mm × 35 mm × 11 mm has been obtained. Using seeds with the [101], [001] and [211] directions grow the crystals, and the most regularly shaped and high quality crystal was grown from the [101] seed. The optimal growth condition of KBOC has been obtained. In addition, the calculations indicate that the shortest type-I PM
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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jmat.2015.06.001.

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