Article

Flux Growth and Properties of Volatile Bromine-Containing UV Nonlinear Optical Crystal $K_3B_6O_{10}Br$

Huaiyu Hu ^{1,2,†}, Chen Zhou ^{1,†}, Jiahao Jiao ^{1,2}, Siru Guo ^{1,2}, Yanna Chen ¹ and Min Zhang ^{1,*}

¹ Xinjiang Key Laboratory of Electronic Information Materials and Devices, Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, Urumqi 830011, China; huhuaiyu960719@163.com (H.H.); chenzhou@hit.edu.cn (C.Z.); h8glass@163.com (J.J.); guosiru18@mail.ucas.ac.cn (S.G.); ynchenaa@163.com (Y.C.)

² University of the Chinese Academy of Sciences, Beijing 100049, China

* Correspondence: zhangmin@ms.xjb.ac.cn

† These authors contributed equally to this work.

Abstract: A UV Nonlinear optical (NLO) crystal is one of the key devices in all-solid-state laser technology, and borate halides show outstanding potential due to their abundant structural diversity and short UV cut-off edges. In this article, the sizable UV NLO crystal of $K_3B_6O_{10}Br$ (KBOB) has been grown with lead-containing and lead-free fluxes systems using the high-temperature top-seeded solution growth (TSSG) method. Energy Dispersive X-ray Spectroscopy (EDS) and transmittance spectra illustrate the influence of Pb^{2+} ions on the transmittance properties and laser-induced damage threshold (LDT). The thermal property, namely, thermal expansion, thermal conductivity, and thermal diffusivity curves, were characterized. Moreover, a small variation of thermal refractive indexes was analyzed to illustrate the advantage of KBOB in the application for temperature-fluctuated specific regions.

Keywords: top-seeded solution growth; $K_3B_6O_{10}Br$; nonlinear optical crystal; lead-free fluxes; optical property; thermal property

Citation: Hu, H.; Zhou, C.; Jiao, J.; Guo, S.; Chen, Y.; Zhang, M. Flux Growth and Properties of Volatile Bromine-Containing UV Nonlinear Optical Crystal $K_3B_6O_{10}Br$. *Crystals* **2022**, *12*, 33. <https://doi.org/10.3390/cryst12010033>

Academic Editors: Zsuzsanna Szaller and Shanpeng Wang

Received: 1 December 2021

Accepted: 22 December 2021

Published: 26 December 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Due to the good monochromaticity, strong directivity, and high brightness, lasers have been used extensively in the fields of industry, communication, and information technology, through applications such as laser welding, laser etching, and free special optical. Benefiting from the frequency conversion by NLO crystals, a UV laser can be expediently and efficiently obtained [1–4]. Nowadays, some well-known borates, such as β -BaB₂O₄ (β -BBO) [5], (LiB₃O₅) (LBO) [6], CsLiB₆O₁₀ (CLBO) [7] have been commercially applied. While these classic crystals cannot meet practical needs, the investigation of NLO crystals with a UV absorption deeper than 400 nm, a large second harmonic generation (SHG) response, and a moderate birefringence is of urgent demand.

Notably, introducing halide elements into borate can regulate the structure configuration and increase the structure diversity, and this strategy leads to the discovery of plenty of excellent UV NLO materials [8–12]. In 2006, KBOB was firstly synthesized by Belokoneva et al. via the hydrothermal method [13], which crystalized in the $R3m$ space group. Then, centimeter-sized KBOB crystals were grown by our group via the high-temperature TSSG method using lead-containing fluxes to reduce the crystallizing temperature and hinder the volatilization of bromine [14–16]. The property characterizations of the crystal indicates that KBOB crystals have a short UV absorption edge (about 182 nm), large SHG response ($d_{22} = 0.83$ pm/V), moderate birefringence (0.0506@355 nm), and short type I phase-matching SHG wavelength (290 nm), which was regarded as a potential UV NLO crystal. Due to the thriving performance, R.K. Li et al. [17–19] continued the growth of KBOB and estimated the optical properties. The autonomous studies by these groups verified the promising application of KBOB crystals for laser frequency conversion in the UV

region, such as 355 nm laser outputting by frequency tripling of Nd: YAG. However, in the previous sizable growth of KBOB, the lead-containing fluxes were adopted to decrease the viscosity and crystallization temperature of the solution. At the same time, the introduction of Pb^{2+} cations causes UV absorption below 280 nm. Although decreasing the content of the PbO in the flux can reduce absorption, the issue remains unsolved [17]. Hence, we propose the exploration of lead-free fluxes to completely remove the absorption and propose the dominant application fields of KBOB crystal.

In this article, we present research regarding growing the KBOB crystal to analyze the difference of optical absorption between lead-containing and lead-free fluxes systems. Additionally, the thermal expansion, thermal conductivity, thermal diffusivity, and thermal refractive index of KBOB were compared with the benchmark UV NLO crystal LBO. The results indicate that KBOB is preponderant in the circumstance with temperature fluctuation due to the weak temperature dependence of physical properties of KBOB.

2. Materials and Methods

KBOB has been grown by the top-seeded solution growth (TSSG) method as KBOB melts incongruently. All of the reagents are analytically pure and were used as received. The method to grow KBOB with lead-containing fluxes (KBOB-L) can be found in a previously published article. For the lead-free fluxes (KBOB-LF), H_3BO_3 , KBr, K_2CO_3 , and KF were mixed in the proper molar ratio and pre-calcined, then the mixture was transferred to the center of a vertical, programmable temperature furnace with a platinum plate to restrain the volatilization and heated to at 740 °C for 24 h. Then, the temperature was rapidly cooled to 720 °C, and a seed crystal was dipped into the solution. After this operation, the rotation speed of the seed crystal was set to 20 rpm, and the cooling rate was set as 0.1 °C per day. Finally, a crystal with the size of 25 mm × 10 mm × 30 mm was obtained, and the experiment was completed by removing the crystal from the solution.

The powder X-ray diffraction (PXRD) was recorded by Bruker's D2 PHASER XRD diffractometer (Germany) at room temperature. The sample was ground and placed in the instrument. Comparing the results with the powder diffraction file (PDF) cards in Jade helped to identify the composition of the powder.

The energy dispersive X-ray spectrum of the crystals was recorded by OXFORD INSTRUMENTS X-MaxN's (Britain) microscopic analysis instrument consisting of SEM (Scanning Electron Microscope) and EDS. A piece of crystal was taken from the bulk crystal and was placed in the equipment to be tested.

The transmittance spectrum was recorded by Shimadzu SolidSpec-3700 DUV UV-VIS-IR spectrometer (Japan) at room temperature, and the measurement range extends from 180 nm to 1600 nm. Polished crystal plates of KBOB-L and KBOB-LF were used in the characterization.

The thermal expansion coefficients were measured with a thermal-mechanical analyzer (Netzsch DIL402PC, Germany). Two crystal plates, oriented in the direction of [100] and [001], respectively, were used to study the thermal expansion coefficients of KBOB along the different crystallographic axis. The measuring directions of the crystal plates were polished to 4.359 mm and 5.017 mm, respectively. The thermal conductivity and thermal diffusion coefficient were tested by laser thermal conductivity analyzer (Netzsch LFA 457, Netzsch, Selb, Germany).

The thermal refractive index of KBOB was measured using the prism coupling technique (Metricon Model 2010, Metricon, Pennington, NJ, USA), and a [001] crystal plate was used for the test at temperatures of 25, 40, 60, 80, and 100 °C, respectively.

The LDT was measured on a pulsed Q-switched Nd: YAG laser (Continuum, 1064 nm, 5 ns, 10 Hz) using KBOB-L and KBOB-LF crystal plates with 1 mm thickness. An optical concave lens was used to obtain the appropriate laser beam diameter (0.5 mm).

The rocking curves were recorded by a high-resolution X-Ray Diffractometer (D2 phaser, Germany), using polished KBOB-L and KBOB-LF crystal plates with the size of 5 mm × 5 mm × 1 mm.

3. Results and Discussion

3.1. The Crystal Growth of KBOB with Lead-Containing and Lead-Free Fluxes

The following reagents were purchased and were not further purified: H_3BO_3 (Aladdin, Shanghai, China, 99.99%), KBr (Aladdin, Shanghai, China, 99.99%), KF (Tianjin Hengxing, Tianjin, China, $\geq 99.0\%$), PbO (Aladdin, Shanghai, China, 99.9%), K_2CO_3 (Tianjin Hengxing, Tianjin, China, $\geq 99.0\%$), $\text{KF}\cdot 2\text{H}_2\text{O}$ (Tianjin Hengxing, Tianjin, China, $\geq 99.0\%$).

For the KBOB-L (the ratio of the raw materials was $\text{H}_3\text{BO}_3\text{:KBr:KF:PbO} = 6\text{:}1\text{:}2\text{:}1$), the orientation of the seed crystal was selected as described in [101], and a high-quality, transparent crystal ($30\text{ mm} \times 30\text{ mm} \times 10\text{ mm}$) with the developing faces of [101], [211], and [110] was obtained (Figure 1a). The volatile was collected and characterized, and the result indicates that the volatile mixture consists of PbBr_2 , PbBrF , and KPb_2Br_5 . At the same time, the prior fluxes used were, the self-fluxes for the TSSG method to avoid introducing the impurities. Our group explored the fluxes in the system of $[\text{H}_3\text{BO}_3\text{-KBr-KF}]$, $[\text{H}_3\text{BO}_3\text{-KBr-K}_2\text{CO}_3\text{-KF}]$, $[\text{H}_3\text{BO}_3\text{-KBr-K}_2\text{CO}_3\text{-KF}\cdot 2\text{H}_2\text{O}]$, and $[\text{B}_2\text{O}_3\text{-KBr-K}_2\text{CO}_3\text{-KF}]$, respectively. Speculated from the experiment results, $[\text{H}_3\text{BO}_3\text{-KBr-K}_2\text{CO}_3\text{-KF}]$ was the best growing system, as the main phase of the crystallization product was KBOB. Finally, the ratio of $\text{H}_3\text{BO}_3\text{:KBr:K}_2\text{CO}_3\text{:KF}$ was selected as $6\text{:}0.6\text{:}0.5\text{:}1$. Additionally, a block KBOB crystal with the size of $25\text{ mm} \times 10\text{ mm} \times 30\text{ mm}$ was obtained (Figure 1b). Apparently, the inclusion was found in the crystal, which is due to the heavy volatilization, (Mainly potassium bromide) leading to deviated components at the high growth temperature. The transmittance spectra indicate that the KBOB-LF performs better than KBOB-L in the UV region (Figure 1c) due to the absence of lead compounds. Specifically, the removal of lead can result in a 70 nm blueshift, which is effective for application in shortwave regions, for example, 266 nm laser frequency doubling via sum-frequency. Hence, the optimized growth technique, such as the closed high-temperature solution method, needs to be developed to prevent volatilization in future studies. We recorded the PXRD of KBOB-L and KBOB-LF, and both of were in accordance with those that were calculated (Figure 2a). The Raman bands (Figure 2b) around $1011\text{--}1159\text{ cm}^{-1}$ can be attributed to the BO stretching vibrations of both the trigonal and tetrahedral boron, and the bands located from 600 cm^{-1} to 800 cm^{-1} are attributed to the bending modes of trigonal and tetrahedral boron, which means both KBOB-L and KBOB-LF consisted of the ideal KBOB structure.

Figure 1. (a,b) The photographs of KBOB-L and KBOB-LF crystals, respectively. (c) The transmittance spectra of KBOB-LF and KBOB-L, respectively.

Figure 2. (a) The XRD patterns and (b) the Raman spectra of KBOB-L and KBOB-LF crystals, respectively.

3.2. The EDS Analysis of KBOB Crystals

In order to identify whether the fluxes, especially for the non-self fluxes, intrude into the crystal lattice as doped ions, EDS tests were performed to investigate the quantity and distribution of the elements (Figure 3). The abundance of the elements is uniformly distributed, which means the crystals are of high quality. When PbO flux was used, the lead ion was found to be distributed homogeneously in the transparent zone of KBOB-L, which means that the impurity ions were relatively evenly distributed in the crystal lattices. Furthermore, the distribution of lead and fluorine ions was localized in the inclusion zone (Figure 4). Although the concentrations of lead ions are very low, they significantly influence the optical performance, such as the transmittance in the UV region. For KBOB-LF, the main elements are K, B, O, and Br (Figure 5), and no other impurity elements were found. This means that the objective of removing the absorption in the UV region caused by the Pb element was achieved.

Figure 3. Element analysis of the transparent zone of KBOB-L. (a) Element analysis photography. (b) The picture of KBOB crystal (c) Surface topography photography. (d–g), and (h) EDS digital images of elements K, B, O, Br, and Pb, respectively. (i) The SEM photograph of the transparent zone of KBOB-L.

Figure 4. Element analysis of the inclusion zone of KBOB-L. (a) Element analysis photography. (b) The picture of KBOB crystal (c) Surface topography photography. (d–h), and (i) EDS digital images of elements K, B, O, Br, F, and Pb, respectively. (j) The SEM photograph of the inclusion zone KBOB-L.

Figure 5. Element analysis of KBOB-LF. (a) Element analysis photography. (b) The object picture of KBOB crystal (c) Surface topography photography (d–g) EDS digital images of elements K, B, O, and Br, respectively. (h) The SEM photograph of KBOB-LF.

3.3. Rocking Curves and Laser Damage Threshold

Both of the rocking curves of KBOB-LF and KBOB-L have ideal symmetric shapes, and the full width at half maximum (FWHM) is relatively small, at 30.706'' and 28.044'', respectively, which means both of these two crystals are of high quality (Figure 6).

Figure 6. (a,b) the rocking curves of KBOB-L and KBOB-LF, respectively.

Additionally, the LDTs of KBOB-LF and KBOB-L are 2.5 and $1.4 \text{ GW} \cdot \text{cm}^{-2}$, respectively, which means that the lead impurity can cause absorption and significantly affect the laser's damage resistance.

3.4. The Thermal Properties

The thermal expansion coefficients (α) of KBOB in different directions are $\alpha_{[100]} = 8.84 \times 10^{-6}/\text{K}$, and $\alpha_{[001]} = 13.86 \times 10^{-6}/\text{K}$, respectively (Figure 7). The ratio of the thermal expansion coefficients between the c direction and a direction is 1.6, which is relatively smaller than LBO ($\alpha_{[100]} = 66.4 \times 10^{-6}/\text{K}$, $\alpha_{[001]} = -52.8 \times 10^{-6}/\text{K}$, and $\alpha_{[110]} = 27.3 \times 10^{-6}/\text{K}$, respectively [20]). The thermal conductivity and thermal diffusivity were also considered for the applied perspective of the crystals, and these properties are shown in Figure 7b. Both of them decrease with increasing temperature, and the values of different crystallographic axis were kept approximate, which is beneficial for the uniform distribution of heat in different directions. The small thermal anisotropy of KBOB is beneficial for avoiding cracks in the process of crystal growth and application in laser devices.

Figure 7. (a) Thermal expansion curves, (b) thermal conductivity curves, and thermal diffusivity curves of KBOB crystal along the different crystallographic axis.

3.5. Thermal Refractive Index

As the heating effect of the laser system, the thermal refractive index is very important for the application. As shown in Table 1, the refractive index waned slightly with the increased temperature, as did the birefringence. Then, the Sellmeier equation was fitted to map the curves of the type I phase matching angle (frequency-doubling of Nd: YAG laser) versus temperature (Figure 8). It is clear that the phase-matching angles of KBOB changed

slightly (about 0.5°) when the temperature ranged from 25°C to 100°C . This suggests that the NLO property of KBOB is less affected by temperature, and it is not necessary to use the temperature control system during the frequency doubling applications, which is of benefit to the miniaturization of the equipment system and for applications in temperature-fluctuated circumstances.

Table 1. Thermal refractive index at different temperatures.

λ (μm)/T ($^{\circ}\text{C}$)		25	40	60	80	100
0.405	n_o	1.60344	1.60301	1.60259	1.60220	1.60179
	n_e	1.55386	1.55394	1.55357	1.55317	1.55303
	$n_o - n_e$	0.04958	0.04907	0.04902	0.04903	0.04876
0.514	n_o	1.59120	1.59098	1.59071	1.59030	1.59014
	n_e	1.54350	1.54340	1.54299	1.54282	1.54260
	$n_o - n_e$	0.04770	0.04758	0.04772	0.04748	0.04754
0.636	n_o	1.58358	1.58340	1.58320	1.58280	1.58251
	n_e	1.53652	1.53630	1.53624	1.53602	1.53599
	$n_o - n_e$	0.04706	0.04710	0.04696	0.04678	0.04652
0.965	n_o	1.57488	1.57456	1.57444	1.57412	1.57390
	n_e	1.52895	1.52934	1.52886	1.52868	1.52856
	$n_o - n_e$	0.04593	0.04522	0.04558	0.04544	0.04534
1.547	n_o	1.56611	1.56542	1.56531	1.56517	1.56490
	n_e	1.52193	1.52182	1.52179	1.52170	1.52135
	$n_o - n_e$	0.04418	0.04360	0.04352	0.04347	0.04355

Figure 8. The type I phase-matching angles of KBOB at different temperatures.

4. Conclusions

In conclusion, the UV NLO crystal, KBOB, has been grown by the TSSG method with lead-containing and lead-free fluxes, respectively. The lead impurities in the crystal lattice cause UV absorption below 280 nm, and the problem was solved by exploring lead-free fluxes. The UV absorption edge of KBOB-LF has a blueshift of 70 nm above KBOB-L. The small differences in the thermal expansion, thermal conductivity, and thermal diffusivity between different crystallographic axes endow KBOB with excellent mechanical properties

for wafer fabrication and application. Moreover, the KBOB crystals' refractive indexes show weak temperature dependence, which indicates that KBOB crystals can avoid phase mismatching with temperature severely changing. Hence, KBOB is a potential material for the application in UV nm laser frequency doubling. Notably, upgraded equipment needs to be developed to restrain volatilization during the growth of KBOB-LF.

Author Contributions: The manuscript was written through the contributions of all authors. M.Z. conceptualized and designed the experiment. H.H., C.Z., J.J., S.G. and Y.C. performed the entire experiment and analyzed the results. H.H. wrote the manuscript. M.Z. revised the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Youth Innovation Promotion Association of CAS (2020429), the CAS Project for Young Scientists in Basic Research (YSBR-024), the National Natural Science Foundation of China (22122509, 52002398, and 11774414), and the Xinjiang Major Science and Technology Project (2021A01001-3).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhang, W.G.; Yu, H.W.; Wu, H.P.; Halasyamani, P.S. Crystal Growth and Associated Properties of a Nonlinear Optical Crystal— $\text{Ba}_2\text{Zn}(\text{BO}_3)$. *Crystals* **2016**, *6*, 68. [\[CrossRef\]](#)
2. Chen, Q.L.; Luo, M.; Lin, C.S. $\text{Na}_4\text{Yb}(\text{CO}_3)_3\text{F}$: A New UV Nonlinear Optical Material with a Large Second Harmonic Generation Response. *Crystals* **2018**, *8*, 381. [\[CrossRef\]](#)
3. Zou, G.H.; Lin, C.S.; Kim, H.G.; Jo, H.; OK, K.M. $\text{Rb}_2\text{Na}(\text{NO}_3)_3$: A congruently Melting UV-NLO Crystal with a Very Strong Second-Harmonic Generation Response. *Crystals* **2016**, *6*, 42. [\[CrossRef\]](#)
4. Shen, C.Y.; Zhang, H.J.; Wang, D.L.; Wang, J.Y.; Boughton, R.I. Optical Properties of the Fresnoite $\text{Ba}_2\text{TiSi}_2\text{O}_8$ Single Crystal. *Crystals* **2017**, *7*, 53. [\[CrossRef\]](#)
5. Fedorov, P.P.; Kokh, A.E.; Kononova, N.G. Barium borate $\beta\text{-BaB}_2\text{O}_4$ as a material for nonlinear optics. *Russ. Chem. Rev.* **2002**, *71*, 651–671. [\[CrossRef\]](#)
6. Lin, S.J.; Sun, Z.Y.; Wu, B.C.; Chen, C.T. The nonlinear optical characteristics of a LiB_3O_5 crystal. *J. Appl. Phys.* **1990**, *67*, 634–638. [\[CrossRef\]](#)
7. Sasaki, T.; Mori, Y.; Yoshimura, M. Progress in the growth of a $\text{CsLiB}_6\text{O}_{10}$ crystal and its application to ultraviolet light generation. *Opt. Mater.* **2003**, *23*, 343–351. [\[CrossRef\]](#)
8. Wu, H.P.; Pan, S.L.; Poeppelmeier, K.R.; Li, H.Y.; Jia, D.Z.; Chen, Z.H.; Fan, X.Y.; Yang, Y.; Rondinelli, J.M.; Luo, H.S. $\text{K}_3\text{B}_6\text{O}_{10}\text{Cl}$: A New Structure Analogous to Perovskite with a Large Second Harmonic Generation Response and Deep UV Absorption Edge. *J. Am. Chem. Soc.* **2011**, *133*, 7786–7790. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Liu, H.K.; Wang, Y.; Zhang, B.B.; Yang, Z.H.; Pan, S.L. $\text{CsAlB}_3\text{O}_6\text{F}$: A beryllium-free deep-ultraviolet nonlinear optical material with enhanced thermal stability. *Chem. Sci.* **2019**, *11*, 694–698. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Yu, H.W.; Young, J.S.; Wu, H.P.; Zhang, W.G.; Rondinelli, J.M.; Halasyamani, S. The Next-Generation of Nonlinear Optical Materials: $\text{Rb}_3\text{Ba}_3\text{Li}_2\text{Al}_4\text{B}_6\text{O}_{20}\text{F}$ —Synthesis, Characterization, and Crystal Growth. *Adv. Opt. Mater.* **2017**, *5*, 1700840. [\[CrossRef\]](#)
11. Wu, B.C.; Tang, D.Y.; Ye, N.; Chen, C.T. Linear and nonlinear optical properties of the $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) crystal. *Opt. Mater.* **1996**, *5*, 105–109. [\[CrossRef\]](#)
12. Mutailipu, M.; Zhang, M.; Wu, H.P.; Yang, Z.H.; Shen, Y.H.; Sun, J.L.; Pan, S.L. $\text{Ba}_3\text{Mg}_3(\text{BO}_3)_3\text{F}_3$ polymorphs with reversible phase transition and high performances as ultraviolet nonlinear optical materials. *Nat. Commun.* **2018**, *9*, 3089. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Al-Ama, A.G.; Belokoneva, E.L.; Stefanovich, S.Y.; Dimitrova, O.V.; Mochenova, N.N. Potassium Bromo-Borate $\text{K}_3[\text{B}_6\text{O}_{10}]\text{Br}$ —A New Nonlinear Optical Material. *Crystallogr. Rep.* **2006**, *51*, 225–230. [\[CrossRef\]](#)
14. Zhang, M.; Pan, S.L.; Fan, X.Y.; Zhou, Z.X.; Poeppelmeier, K.R.; Yang, Y. Crystal growth and optical properties of a noncentrosymmetric haloid borate, $\text{K}_3\text{B}_6\text{O}_{10}\text{Br}$. *CrystEngComm* **2011**, *13*, 2899–2903. [\[CrossRef\]](#)
15. Zhang, M.; Su, X.; Pan, S.L.; Wang, Z.; Zhang, H.; Yang, Z.H.; Zhang, B.B.; Dong, L.Y.; Wang, Y.; Zhang, F.F.; et al. Linear and Nonlinear Optical Properties of $\text{K}_3\text{B}_6\text{O}_{10}\text{Br}$ Single crystal: Experiments and Calculation. *J. Phys. Chem. C* **2014**, *118*, 11849–11856. [\[CrossRef\]](#)
16. Fan, X.Y.; Zhang, M.; Pan, S.L.; Yang, Y.; Zhao, W.W. Top seeded solution growth and optical properties of a bromic borate crystal: $\text{K}_3\text{B}_6\text{O}_{10}\text{Br}$. *Mater. Lett.* **2012**, *68*, 374–377. [\[CrossRef\]](#)
17. Xia, M.J.; Xu, B.; Li, R.K. Growth and nonlinear optical properties of $\text{K}_3\text{B}_6\text{O}_{10}\text{Br}$ crystal. *J. Cryst. Growth* **2014**, *404*, 65–68. [\[CrossRef\]](#)

18. Xia, M.J.; Xu, B.; Liu, L.J.; Wang, X.Y.; Li, R.K.; Chen, C.T. Thermo-physical properties of nonlinear optical crystal $K_3B_6O_{10}Br$. *J. Appl. Cryst.* **2016**, *49*, 539–543. [[CrossRef](#)]
19. Meng, L.P.; Zhang, L.; Hou, Z.Y.; Wang, L.R.; Xu, H.; Shi, M.; Wang, L.W.; Yang, Y.Y.; Qi, Y.Y.; He, C.J.; et al. Frequency-doubled green picosecond laser based on $K_3B_6O_{10}Br$ nonlinear optical crystal. *Optlastec* **2018**, *101*, 401–403. [[CrossRef](#)]
20. Guo, R.Y.; Markgraf, S.A.; Furukawa, Y.; Sato, M.; Bhalla, A.S. Pyroelectric, dielectric, and piezoelectric properties of LiB_3O_5 . *J. Appl. Phys.* **1995**, *78*, 7234–7239. [[CrossRef](#)]