Growth of a New Nonlinear Optical Crystal $Ba_2Be_2B_2O_7$ by TSSG Method

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(Received January 16, 2001; CL-010043)

In this work, a new nonlinear optical $Ba_2Be_2B_2O_7$ crystal was grown by top-seeded solution growth method using BaB_2O_4–$BaCO_3$–NaF fluxes. The differential thermal analysis curve and a typical angle-tuned curve of $Ba_2Be_2B_2O_7$ crystal were also investigated. The measured ultraviolet absorption edge of the title crystal was found to be about 215 nm.

Many borate crystals are qualified for being nonlinear optical (NLO) materials because of their wide transparent region, high damage threshold, moderate birefringence, chemical stability, and so on. These virtues have impelled many researchers continuously to search for new NLO materials among borate crystals. After BBO (β-BaB_2O_4)[1] and LBO (LiB_3O_5)[2] were found in 1980s', many other borate crystals, such as CBO (CsB_3O_5),[3] CLBO ($CsLiB_6O_{10}$),[4] KBBF ($KBe_2BO_3F_2$),[5] SBBO ($Sr_2Be_2B_2O_7$),[6] YCOB ($YCa_4O(BO_3)_3$)[7] and GdCOB ($GdCa_4O(BO_3)_3$)[8] were successively developed. As one of them, SBBO possesses the above-mentioned excellent properties that the NLO materials should have. However, it is not easy to grow large crystal of SBBO. This led to the limitation of its practical application.

In this work, we aimed to find a new NLO crystal that may be grown easier and may possess the similar properties as SBBO does. On the basis of this idea, we have successfully grown a new crystal, $Ba_2Be_2B_2O_7$ (TBO).[9] The preliminary second harmonic generation (SHG) test of the crystal demonstrated that TBO possesses larger SHG coefficient, about twice as large as that of KH_2PO_4 (KDP). This implied that TBO was a promising NLO crystal. Structure analysis results indicated that this crystal crystallizes in the hexagonal space group $P\bar{6}2c$ in a cell dimensions of $a = b = 8.289(2)$ Å, $c = 8.048(2)$ Å and $V = 479.4(1)$ Å^3. In spite of different space groups, TBO and SBBO had the similar basic structure unit $[Be_2B_2O_6]$. Herein, we report the growth and the ultraviolet absorption edge of TBO crystal. Besides, we also discuss its melting behavior.

The raw materials of TBO crystal growth were synthesized at about 950 °C by sintering in an ambient atmosphere with a stoichiometric ratio of analytical reagent grade $BaCO_3$, H_3BO_3, and chemical pure BeO. The solid-state reaction equation was as follows:

$$2BaCO_3+2H_3BO_3+2BeO \rightarrow Ba_2Be_2B_2O_7+2CO_2\uparrow+3H_2O\uparrow$$

The starting materials were mixed and heated in a platinum crucible at about 950 °C for two days. The powder was ground carefully 2–3 times at room temperature between heatings. Thus synthesized products were examined by the powder X-ray diffraction technique and revealed to be $Ba_2Be_2B_2O_7$. Caution: a particular protective system must be employed in the whole preparation process to prevent the toxicity of BeO.

Using the synthesized products, we employed the top-seed solution growth (TSSG) method to grow TBO crystal. The growth was carried out in a vertical cylindrical electric furnace, with a nickel–chrome wire as the heating element. AI-708P controller and Pt-Rh/Pt thermocouples were used to control the temperature of the furnace. The crystal growth was performed in air, using a platinum crucible with the size of 40 × 40 mm. A platinum wire was used as a cold finger for the first seeding in place of a seed crystal.

The temperature was kept at about 30–50 °C above the melting temperature for 36 h in order to ensure the mixtures melt completely and mix homogeneously. The seed crystal of TBO was attached to a platinum rod and then touched the melt surface at a temperature 20 °C above the saturation temperature for half an hour to dissolve the outer surface. The cooling rate of furnace was about 0.5–1.0 °C/d in the process of crystal growth. The seed was rotated unidirectionally at a rate of 9 rpm. As the growth completed, the crystal was removed from the solution surface and cooled down to room temperature at a rate of 20 °C/h.

It is necessary to choose proper flux to carry out the crystal growth. BaB_2O_4 was selected as self-flux to grow the expected TBO crystal from the melt. However, the result of X-ray powder diffraction analysis indicated that the obtained crystal was $BaBe_2B_2O_6$[10] rather than the expected $Ba_2Be_2B_2O_7$. We therefore made an attempt to add an appropriate amount $BaCO_3$ into the melt. In practice, we mixed $BaCO_3$ with BaB_2O_4 and chose several mole ratios of them to perform experiments. We found that the mixtures of BaB_2O_4:$BaCO_3$ with ratios from 1.5:1 to 2.3:1 were suitable to the crystal growth. Interestingly, we also found that the viscosity of the melt increased with the increase of the added $BaCO_3$ content, leading to the decline of the solute molecule transportation. Additional experiments showed that the addition of NaF in an amount of 5–10 % by weight of TBO could effectively change this situation. The X-ray powder diffraction analysis confirmed that the obtained crystal using BaB_2O_4–$BaCO_3$–NaF fluxes was TBO.

During the process of crystal growth, while the melt viscosity increased gradually with the volatilization of NaF, the melt temperature decreased with the crystallization of TBO. In our experiments, the saturation temperature in the range of 1000 °C–890 °C proved suitable for growth of TBO crystal.

Figure 1(a) shows a photograph of TBO crystal with the dimensions of 28 × 20 × 10 mm^3 grown by the TSSG technique using BaB_2O_4–$BaCO_3$–NaF as fluxes. Inclusions were found on the crystal surface and inside the crystal, respectively. These inclusions led to the partially opaque of the crystal. Figure 1(b) shows a piece of completely transparent TBO crystal with the dimensions of 6 × 5 × 2 mm^3, obtained after the originally grown TBO crystal was cut, selected and polished.

We have also checked the melting behavior of TBO crystal by the differential thermal analysis (DTA). A sample (33.75 mg) of the title crystal was placed in a platinum cup and heated

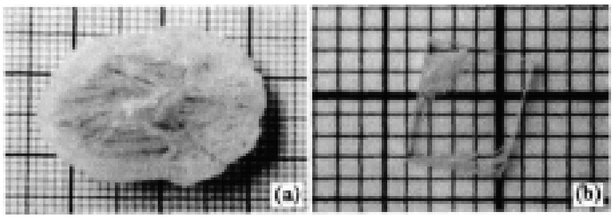

Figure 1. TBO crystal grown by TSSG method. (a) Inclusions were found on the crystal surface and inside the crystal, which led to the partially opaque of the crystal. (b) Transparent crystal with the dimensions of $6\times5\times2$ mm^3, obtained from the crystal shown in (a) through cutting, selection and polishment.

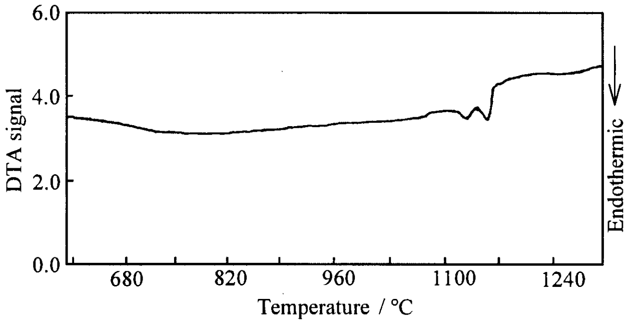

Figure 2. The differential thermal analysis curve of TBO crystal.

from 600 °C to 1300 °C at 10 °C/min under flowing N_2. DTA signal was simultaneously recorded during this process. It was shown in Figure 2. Clearly, two endothermic peaks in the DTA curve were successively observed ranging from 1110 °C to 1135 °C and 1135 °C to 1165 °C, respectively. We suggested that the former was associated with the melting of TBO and the latter was linked with the decomposition of the melting TBO during the process of increasing temperature.

Additionally, it is important to measure the absorption edge for a nonlinear optical crystal. Figure 3 shows the transmission spectrum (185–2200 nm) of TBO crystal. It could be seen from the spectrum that the transparency of TBO was above 50% at wavelengths larger than about 224 nm. The transparency of TBO crystal decreases sharply starting from 224 nm and reaches zero at about 215 nm. Ultraviolet absorption edge, 215 nm, could thus be obtained. This implies that TBO crystal may be used in the UV wave band as NLO material.

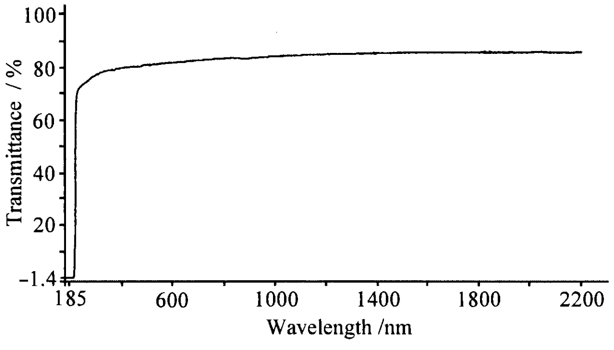

Figure 3. The transmission spectrum of TBO crystal.

We have also measured a typical angle-tuned curve for SHG ($\lambda_{2\omega}$ = 532 nm) of TBO crystal, as shown in Figure 4. The preliminary measurement indicates that the acceptance angles of TBO crystal is 1.92 mrad-cm at $\lambda_{2\omega}$ = 532 nm with θ = 38.4°.

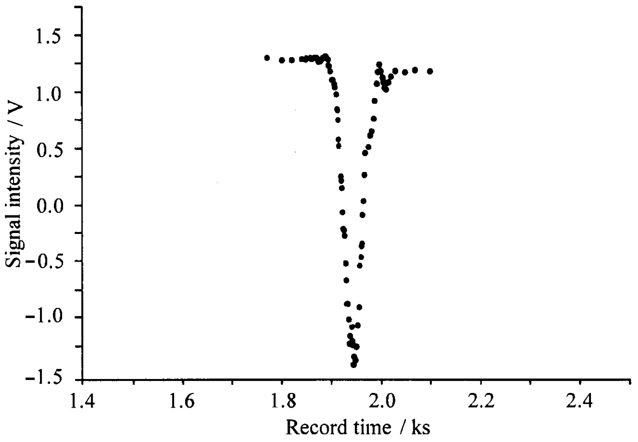

Figure 4. Angle-tuned curve of SHG for TBO crystal at 532 nm.

In summary, TBO crystal, a new nonlinear optical material, has been successfully grown from the BaB_2O_4–$BaCO_3$–NaF fluxes by TSSG method. We consider that it is possible to produce larger TBO crystal if more suitable fluxes were found. Two endothermic peaks were observed in the DTA curve for TBO crystal. Besides, ultraviolet absorption edge of TBO crystal was also obtained from the transmission spectrum. We think that TBO crystal shows promise to become a promising UV NLO material. Studies on NLO properties of TBO crystal are in progress.

We would like to thank Mr. Zhong-yu Wei for his help in taking the pictures of TBO crystal. This work was supported by the financial support from the Chinese Academy of Sciences and the Chinese National "Climb-up" project.

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