Crystal Growth of $Na_5[B_2P_3O_{13}]$

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(Received January 11, 2002; CL-020039)

Large crystals of $Na_5[B_2P_3O_{13}]$ with dimensions of $22 \times 24 \times 17\,mm^3$ and $35 \times 15 \times 5\,mm^3$ have been grown by the Kyropouls and Czochralski methods respectively for the first time. Parameters of crystal growth including the seed direction, cooling rate and rotation rate were investigated. The measured transmittance spectrum from 180 nm to 2800 nm indicates that the absorption edge lies at 186 nm. Furthermore, $Na_5[B_2P_3O_{13}]$ crystal exhibits an optical second harmonic generation effect about the same as that of KDP(KH_2PO_4).

In the past decades borate and phosphates crystals have received much attention because of their excellent properties for nonlinear optical materials. For example, $KTiOPO_4$(KTP), β-$BaBO_4$ (BBO) and LiB_3O_5 (LBO) are characterized by a large nonlinear coefficient, a broad transparency range, and high damage threshold.[1–3] In these materials, B_xO_y and PO_4 groups have a strong effect on their excellent properties. It is possible to produce new properties if we combine borate and phosphates to form borophosphates. On the basis of this idea, $Na_5[B_2P_3O_{13}]$ was investigated in our laboratory.

In 1995, $Na_5[B_2P_3O_{13}]$ compound was first prepared by Hauf et al.,[4] who pointed out that $Na_5[B_2P_3O_{13}]$ crystallizes in the noncentrosymmetric monoclinic space group C_2 with cell parameters $a = 6.71(2)$ Å, $b = 11.62(2)$ Å, $c = 7.69(2)$ and $\beta = 115.17(2)^\circ$, $Z = 2$[4]. In 1998, $Na_5[B_2P_3O_{13}]$ was synthesized by hydrothermal and microwave-assisted methods.[5] In the present study, we describe the synthesis in air, crystal growth by the Kyropouls and Czochralski methods.

Polycrystalline samples of $Na_5[B_2P_3O_{13}]$ were prepared by using solid state reaction techniques. The initial substances were analytical grade Na_2CO_3, H_3BO_3 and $NH_4H_2PO_4$. The mixture of the starting charges taken in stoichiometric proportion was thoroughly homogenized in an agate mortar, then packed into a platinum crucible. The temperature was raised slowly to 500 °C in order to avoid ejection of powdered raw material from the crucible arising from vigorous evolution of NH_3 and CO_2 and H_3BO_3 decomposition. After preheating at 500 °C for 10 h in air in a muffle furnace, the products were cooled, ground again, compressed, and sintered at 680 °C for 24 h. The purity of sample was checked by X-ray powder diffraction. A single phase powder of $Na_5[B_2P_3O_{13}]$ was obtained when repeated heat treatment caused no further changes in the X-ray powder diffraction pattern. The chemical equation can be expressed as follows:

$$5Na_2CO_3 + 6NH_4H_2PO_4 + 4H_3BO_3 = 2Na_5[B_2P_3O_{13}] + 5CO_2\uparrow + 6NH_3\uparrow + 15H_2O\uparrow \quad (1)$$

At the beginning of crystal growth, we used platinum wire as a seed. For the growth with seed of $Na_5[B_2P_3O_{13}]$ crystal from the stoichiometric melt, the temperature of the melt was kept at its melting point. The seed crystal of $Na_5[B_2P_3O_{13}]$ was attached to a platinum rod. We obtained the satisfactory seeds by sifting the spontaneous crystals in the several growth runs.

The experiments using the Kyropouls method were carried out in a resistance-heated furnace. An A1-708P controller was used to control the temperature. The procedure was as follows: The polycrystals were melted in a platinum crucible in several batches. Then the fully charged crucible was placed in the growth furnace. The temperature was raised at about 100–150 °C/h to 850 °C and held at that temperature for 10–24 h to ensure that the charge melts completely. After the melt was firstly cooled at a rate of 10 °C/h to 800 °C (about 13 °C above the melting point 787 °C), a seed was slowly introduced into the furnace, dipped into the melt and kept at constant temperature for 10 minutes to dissolve the outer surface of the seed. The temperature was first decreased at a rate of 5 °C/h to the initial growth temperature and then decreased at a rate of 0.5 °C per day. The growing crystal was rotated at a rate of 15 rpm. When the growth was completed, the crystal was drawn out of the melt surface and cooled down together with the furnace to room temperature at a rate of 50 °C/h. Finally, the colorless transparent crystal with a dimension of $35 \times 15 \times 5\,mm^3$ was obtained. Figure 1 shows the crystal $Na_5[B_2P_3O_{13}]$ by the Kyropouls method.

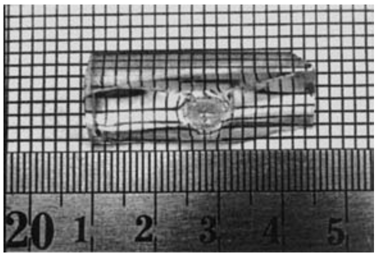

Figure 1. Crystal of $Na_5[B_2P_3O_{13}]$ grown by Kyropouls method, using a [001] seed.

The crystal growth by the Czochralski method was carried out in a two-zone cylindrical electric furnace.[6] The temperature was controlled by a YCC computer programmer controller. The desired thermal gradient can be obtained by controlling the power independently. The manipulation of the crystal growth was the same as the Kyropouls method. The moderate growth parameters of $Na_5[B_2P_3O_{13}]$ crystal were as follows: the thermal gradient 20–40 °C/cm, the cooling rate 0.15 °C/h, the pulling rate 0.25–0.5 mm/h and rotation rate 10–20 rpm. It took three days to grow a large crystal with the dimensions of $22 \times 24 \times 17\,mm^3$. Figure 2 shows the crystal $Na_5[B_2P_3O_{13}]$ by the Czochralski method.

$Na_5[B_2P_3O_{13}]$ crystal grown shows clear facets that the morphology of the crystals strongly depends on the seed crystal orientation. The morphological faces of $Na_5(B_2P_3O_{13})$ are the forms (010), (100), and (001) etc. During the crystal growth by the

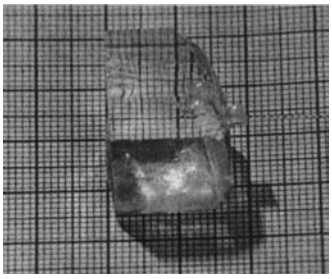

Figure 2. Crystal of $Na_5[B_2P_3O_{13}]$ grown by CZ method, using a [010] seed.

Kyropouls and Czochralski method, $Na_5(B_2P_3O_{13})$ crystals grown using [001]-seed always show a bar-shaped, while the fast growth rate is along [010] direction. However, crystals grown with [010]-seed show a lozenge-shaped and a larger volume can be achieved easily. Crystal grown by Czochralski method sometimes have a slight color, it will be colorless after annealing for 48 hours in a muffle furnace. Controlling over the growth parameters carefully, the high optical grade crystals can be grown by the two methods.

The obtained crystals using the Kyropouls method and the Czochralski method were identified by X-ray powder diffraction, respectively, using a D8 ADVANCE (Bruker Analytical X-ray Systems) X-ray diffractmeter with graphite monochromatized CuKα radiation ($\lambda = 0.15405$ nm). The scanning step width of 0.02 °C and the scanning rate of 0.1 °C/s were applied to record the patterns in the 2θ range of 10–70 °C. Figure 3 shows the X-ray powder diffraction pattern of the crystal $Na_5[B_2P_3O_{13}]$. All peaks in the pattern correspond to the phase of $Na_5[B_2P_3O_{13}]$ reported by Hauf et al.[4]

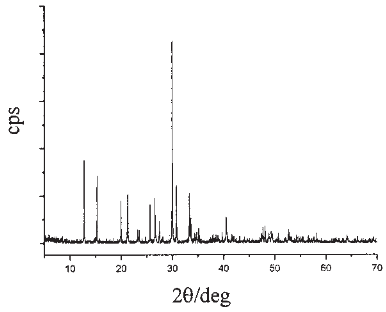

Figure 3. X-ray powder diffraction pattern of $Na_5[B_2P_3O_{13}]$ crystal.

The measured range of $Na_5(B_2P_3O_{13})$ was from 180 nm to 2800 nm by a Lambda 900 UV-VIS-NIR spectrometer. The transmission curve around the shorter cutoff wavelength is shown in Figure 4. $Na_5(B_2P_3O_{13})$ crystal has a absorption edge at approximate 186 nm.

The light and shade striations have been observed in the (010) slice of $Na_5[B_2P_3O_{13}]$ under the polarized microscope (Figure 5). This phenomenon indicates that the $Na_5[B_2P_3O_{13}]$ crystal may be twinning. Further investigations are in progress.

The investigation of optical second harmonic generation

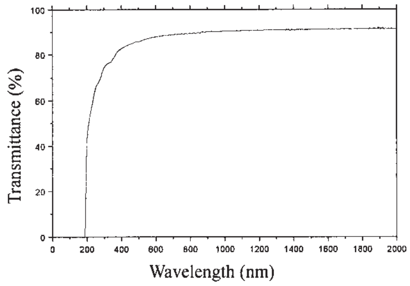

Figure 4. Transmission spectrum of $Na_5[B_2P_3O_{13}]$.

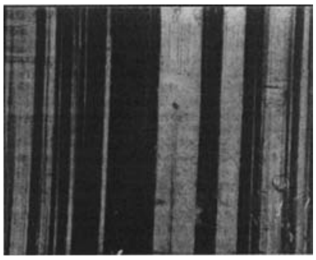

Figure 5. Photograph of $Na_5[B_2P_3O_{13}]$ crystal under polarized microscope.

(SHG) was carried out on the $Na_5[B_2P_3O_{13}]$ polycrystalline sample. Fundamental 1064 nm light was generated with a Q-switched Nd:YAG laser. Microcrystalline KDP(KH_2PO_4) served as the standard. Green light was observed and its intensity was about the same as that of KDP.

In conclusion, we have grown large crystals of $Na_5[B_2P_3O_{13}]$ with dimensions of $22 \times 24 \times 17$ mm^3 and $35 \times 15 \times 5$ mm^3 by the Kyropouls and Czochralski methods, respectively, and the moderate parameters of crystal growth such as the seed direction, cooling and rotation rate have been investigated. $Na_5[B_2P_3O_{13}]$ crystal grown always shows clear facets and has a large transparent range, while its ultraviolet cutoff is 186 nm. The powder SHG effect of $Na_5[B_2P_3O_{13}]$ is almost the same as that of KDP.

This work was supported by the National Fundamental Key Research Program of China.

References

1 F. C. Zumsteg, J. D. Bierlein, and T. E. Gier, *J. Appl. Phys.*, **47**(11), 4980 (1976).
2 C. T. Chen, B. C. Wu, A. D. Jiang, and G. L. You, *Sci. Sin. B*, **28**, 235 (1985).
3 C. T. Chen, Y. C. Wu, A. D. Jiang, G. L. You, and R. C. Li, *J. Opt. Soc. Am. B*, **6**, 616 (1989).
4 C. Hauf, T. Friedrich, and R. Kniep. *Z. Kristallogr.*, **20**, 446 (1995).
5 C. Hauf, A. Yilmaz, M. Kizilyalli, and R. Kniep, *J. Solid State Chem.*, **140**, 154 (1998).
6 P. Z. Fu, J. X. Wang, Z. G. Hu, Y. C. Wu, S. T.Yin, and Z. Y. Xu, *J. Synth. Cryst.*, **28**(3), 215 (1999).