Crystal Growth and Properties of β-Zn_3BPO_7

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A high-quality β-Zn_3BPO_7 crystal up to 43 × 43 × 12 mm in size has been grown from the melt by the top-seeded growth method. The obtained crystal crystallizes in a well-defined morphology of short triangular prism which is bound by {110} and {001} forms. The X-ray powder diffraction data of β-Zn_3BPO_7 crystal were indexed in a hexagonal system. The basic structure units of β-Zn_3BPO_7 crystal are planar BO_3 and tetrahedral PO_4 groups that have been confirmed by the IR spectrum. β-Zn_3BPO_7 crystals are transparent in the wavelength range of 250−3300 nm, with the UV absorption edge at about 250 nm. The refractive indices were measured by the minimum deviation technique and fitted to the Sellmeier equations. The nonlinear optical coefficient d_{11} of β-Zn_3BPO_7 measured by the Maker fringes technique is 0.69 pm/V.

Introduction

In the past years, much interest has focused on the exploration of novel nonlinear optical (NLO) materials for their important applications in laser field. Several NLO crystals such as β-BaB_2O_4 (BBO), LiB_3O_5 (LBO), and $KTiOPO_4$ (KTP)[1−3] have been developed for efficient second harmonic generation of Nd:YAG lasers. However, they suffer some limitations such as optical imperfections for KTP and growth difficulty for BBO and LBO. Therefore, soon after the introduction of BBO, LBO, and KTP as NLO materials, great effort has been spent on developing the new NLO crystals.

Seeing that the borates such as BBO and LBO or the phosphates such as KTP exhibit excellent NLO properties, we expect that the combination of the borate and the phosphate group in the same crystal may generate a whole new class of NLO materials. Until now, there have been few materials that contain both borate group and phosphate group. A broad search for new NLO materials in borophosphates led to a new NLO crystal β-Zn_3BPO_7 in our laboratory.[4]

β-Zn_3BPO_7 was first reported in 1982,[5] but large crystals of β-Zn_3BPO_7 have not been grown. In this paper, we describe the growth of a large β-Zn_3BPO_7 crystal by the top-seeded growth method in detail. X-ray powder diffraction, the IR spectrum, and linear and nonlinear optical properties are investigated.

Experimental Section

Microcrystalline samples of β-Zn_3BPO_7 were prepared by using the standard solid-state reaction. Analytical reagent grade materials were used. A stoichiometric mixture of $ZnCO_3$, H_3BO_3, and $(NH_4)_2HPO_4$ was finely ground in an agate mortar and then charged into a platinum crucible. The temperature was raised slowly to 450 °C in order to avoid ejection of raw materials from the crucible due to vigorous release of CO_2, NH_3, and H_2O. After being preheated at 450 °C for 10 h, the products were cooled, ground again, and sintered at 870 °C. The chemical reaction equation was as follows:

$$3ZnCO_3 + H_3BO_3 + (NH_4)_2HPO_4 \rightarrow Zn_3BPO_7 + 3CO_2\uparrow + 2NH_3\uparrow + 3H_2O\uparrow \quad (1)$$

The product was checked by X-ray powder diffraction. A single-phase powder of β-Zn_3BPO_7 was obtained when repeated heat treatment caused no further changes in the X-ray powder diffraction pattern.

The powder samples were melted in a platinum crucible of 50 mm diameter and 40 mm height. The melting point of β-Zn_3BPO_7 crystal is 927 °C. In the first run of growth, a platinum wire was dipped into the melt, and the temperature was reduced at a rate of 2 °C /h. The obtained crystals were cracked, but parts of them were usable as seeds.

To grow large and high-quality β-Zn_3BPO_7 crystals, the main efforts have been focused on the top-seeded growth. A platinum crucible containing the charge was put into the furnace; the temperature was rapidly raised to 1050 °C and held for 10 h in order to melt completely and mix homogeneously and then was decreased to 935 °C. A β-Zn_3BPO_7 seed attached to a platinum rod was dipped slowly into the melt; the temperature was kept at 935 °C to dissolve the outer surface of the seed. After half an hour, the melt was rapidly cooled to the melting point at 927 °C, and then the temperature was slowly reduced at a rate of 0.5 °C/day. The growing crystal was rotated at a rate of 20 rpm. When the growth was completed, the crystal was drawn out of the melt surface, cooled to 600 °C at a rate of 40 °C /h, and then slowly taken out from the furnace.

X-ray powder diffraction data were collected on a Bruker D8 ADVANCE X-ray diffractometer with a graphite monochromatized Cu Kα radiation. The diffraction pattern was

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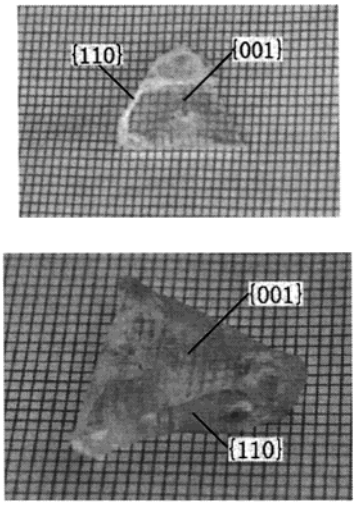

Figure 1. β-Zn_3BPO_7 crystal grown by the top-seeded growth method. (a, top) The temperature was reduced at a rate of 1 °C/day. (b, bottom) The temperature was reduced at a rate of 0.5 °C/day.

taken from 5° to 70° (2θ) with the step size of 0.02° and counting time of 5 s per step. The infrared (IR) spectrum of the pulverized β-Zn_3BPO_7 crystal was measured on a Bruker VECTOR-22 infrared spectrophotometer in the wavenumber range of 400−1500 cm^{-1} with KBr pellet as the reference. The transmittance spectrum of β-Zn_3BPO_7 was recorded using a Perkin-Elmer Lambda900 UV−vis−NIR spectrometer which can operate over 185−3300 nm.

Results and Discussion

Seeds oriented in different directions were attempted for the top-seeded growth of a β-Zn_3BPO_7 crystal. When a [100]-oriented seed was used, the crystal grown showed wedgelike morphology; however, a [120] seed resulted in a elongated tetragonal-prism-like crystal. The crystal grown in [001] direction crystallized in well-defined morphology. A β-Zn_3BPO_7 crystal with dimensions of 43 × 43 × 12 mm grown in the [001] direction is shown in Figure 1. It can be seen that the crystal is optically clear with no visible cracks, inclusions, or bubbles and exhibits the morphology of short triangular prism which is bounded by {110} and {001} forms.

In the process of crystal growth, the cooling rate of 1 °C/day often led to the spontaneous nucleation, and the crystalline grains initially floated on the melt surface and finally attached to the edge of the growing crystal. The different cooling rates were attempted; it was found that the spontaneous nucleation could be effectively avoided by a cooling rate of 0.5 °C/day. Figure 1 shows the β-Zn_3BPO_7 crystal grown by the cooling rates of 1 °C/day (a) and 0.5 °C/day (b).

The major problem that arises with crystal growth of borates is the high viscosity of the melt, which limits the mixing and the mass transport in the melt and causes low growth rates and therefore extends growth periods.[6,7] In comparison with borate crystals, it was encouragingly observed that the melt viscosity of β-Zn_3BPO_7 was low. It is easy to grow large, transparent, and inclusion-free β-Zn_3BPO_7 crystal in short period.

Table 1. X-ray Powder Diffraction Data of β-Zn_3BPO_7 Crystal

h k l	d_{obs}	d_{cal}	I/I_0	*h k l*	d_{obs}	d_{cal}	I/I_0
0 0 2	6.5124	6.5152	3.6	2 2 2	2.0050	2.0064	2.5
1 0 1	6.3650	6.3723	1.8	3 0 4	1.9499	1.9504	2.4
0 0 3	4.3461	4.3434	0.6	1 1 6	1.9313	1.9308	2.0
1 1 0	4.2113	4.2178	43.1	2 2 3	1.8968	1.8971	0.8
1 0 3	3.7324	3.7333	3.0	2 2 4	1.7702	1.7703	11.2
1 1 2	3.5366	3.5406	7.5	4 0 3	1.6834	1.6836	3.4
2 1 0	2.7599	2.7612	1.5	0 0 8	1.6285	1.6288	3.1
2 1 1	2.7006	2.7012	9.0	3 2 2	1.6223	1.6231	1.8
1 1 4	2.5761	2.5781	100	3 1 5	1.6000	1.5996	2.8
2 1 2	2.5418	2.5423	5.2	4 1 0	1.5946	1.5942	6.1
1 0 5	2.4529	2.4545	3.8	2 1 7	1.5443	1.5435	1.0
3 0 0	2.4334	2.4351	15.2	1 1 8	1.5192	1.5194	9.8
3 0 1	2.3924	2.3937	1.6	3 2 4	1.4914	1.4903	1.5
2 1 3	2.3281	2.3301	1.3	4 1 4	1.4325	1.4319	14.1
3 0 2	2.2813	2.2810	2.6	3 3 0	1.4068	1.4059	2.6
0 0 6	2.1705	2.1717	2.1	3 3 2	1.3742	1.3743	1.5
2 0 5	2.1220	2.1214	1.1	3 0 8	1.3542	1.3539	7.9
2 1 4	2.1064	2.1063	3.6	4 2 2	1.3504	1.3506	3.7

Because β-Zn_3BPO_7 crystals suffer a phase transition,[5] special care must be taken in order to prevent the occurrence of the phase transition. At the temperature above 600 °C, the β-Zn_3BPO_7 crystal is stable and can be cooled at a moderate cooling rate. However, the phase transition was observed to occur at about 600 °C, and the crystal should be cooled as rapidly as possible; otherwise, it will crack seriously and become opaque. In this experiment, the crystal was cooled to the temperature near 600 °C at a rate of 40 °C /h and then carefully taken out from the furnace. The obtained crystal was transparent and free of cracks.

The X-ray powder diffraction pattern was indexed by the trial-and-error program TREOR[8] in WIN-INDEX, and the cell parameters were refined by the program WIN-METRIC, available in the PC software package DIFFRAC^{plus} supplied by Bruker AXS. A hexagonal solution was found with the figures of merit of M_{20} = 38 and F_{20} = 50; the refined lattice parameters were a = 8.435(4) Å and c = 13.032(6) Å, which were in agreement with the data reported by Liebertz et al.[5] Table 1 gives the observed and calculated d values along with their indices and relative experimental intensities.

Figure 2 shows the IR spectrum of β-Zn_3BPO_7. The IR spectrum of β-Zn_3BPO_7 was assigned on the basis of results obtained from the vibration spectra measurements of other borate and phosphate groups.[9−11] It is clear that the observed wavenumber at 1230 cm^{-1} is characteristic of the planar BO_3 group; the strong absorption band at 1013 cm^{-1} and the weaker band at 1098 cm^{-1} are related to the asymmetric stretching vibration of PO_4 group. In the 550−650 cm^{-1} region there are three apparent absorption bands, which are expected to be the bending vibrations of the triangular BO_3 and tetrahedral PO_4 groups. The out-of-plane bending vibrations of BO_3 and PO_4 groups are observed in the IR spectrum, which correspond to the bands 728 and 438 cm^{-1}, respectively. The observed bands and the

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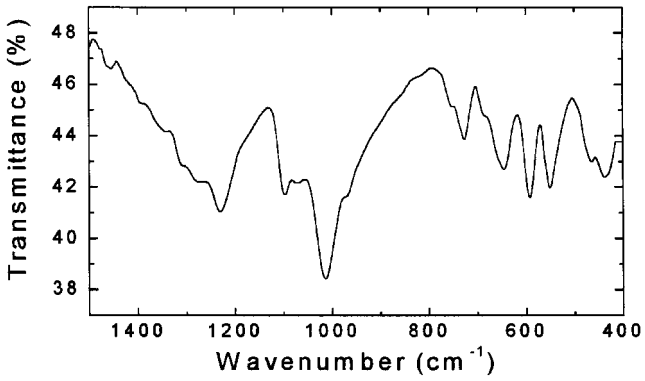

Figure 2. Infrared spectrum of β-Zn_3BPO_7.

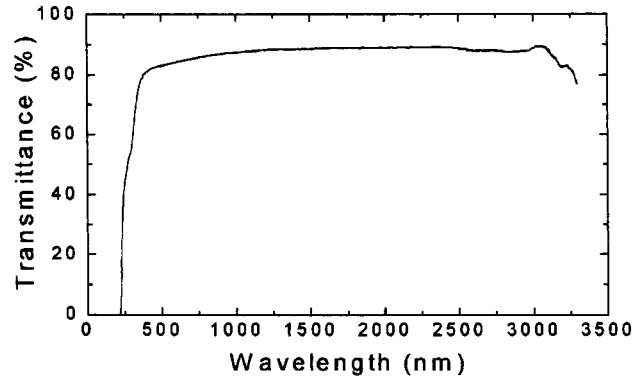

Figure 3. Transmittance spectrum of β-Zn_3BPO_7 crystal.

Table 2. Band Assignments in the IR Spectrum of β-Zn_3BPO_7

wavenumber(cm^{-1})	assignments
1230.4	ν_3 (BO_3)
1098.2, 1013.4	ν_3 (PO_4)
727.5	ν_2 (BO_3)
644.7, 592.2, 551.5	ν_4 (BO_3), ν_4 (PO_4)
438.0	ν_2 (PO_4)

assignments are listed in Table 2. Obviously, the β-Zn_3BPO_7 crystal contains planar BO_3 and tetrahedral PO_4 groups as its basic structural units.

A 1 mm thick sample of β-Zn_3BPO_7 crystal was cut and polished for optical transmission measurements; the transmittance spectrum was recorded with the (100) face as the incident surface. Figure 3 shows the transmittance spectrum of the β-Zn_3BPO_7 crystal. As shown in Figure 3, a wide transmission range from 250 to 3300 nm is observed in the UV-to-IR region, with the absorption edge at about 250 nm. There are no absorption peaks in the whole range of spectrum, but the transmission intensity gradually decreases below the wavelength of 400 nm.

The refractive index dispersion of β-Zn_3BPO_7 was determined by the minimum deviation technique at 16 different wavelengths between 404.7 and 1068.0 nm. Since β-Zn_3BPO_7 is a uniaxial crystal with point group symmetry $\bar{6}m2$, it is possible to measure both n_o and n_e using a prism cut with the edge at the apex parallel to the crystallographic *c*-axis and the (100) face as the incident surface (Figure 4). The incident polarized beam is perpendicular to (100) incident surface; n_o and n_e are the refractive indices of light polarized parallel and perpendicular to the optical axis (crystallographic *c*-axis), respectively. The values of room temperature refractive indices for both the ordinary and extraordinary polarizations measured at specific wavelengths are summarized in Table 3. The experimental data were fitted to the following Sellmeier equations:[4]

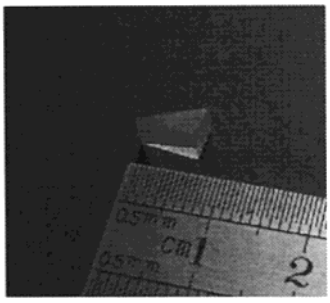

Figure 4. ZBP prism (6.4 × 3.6 × 4.2 mm).

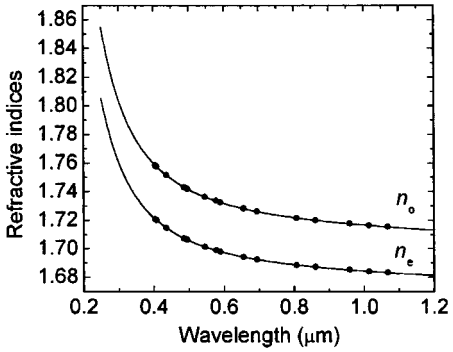

Figure 5. Refractive index dispersion curves of β-Zn_3BPO_7 crystal. Points are experimental values; curves are the fits given by the Sellmeier equation.

Table 3. Refractive Indices of the β-Zn_3BPO_7 Crystal

	n_o			n_e		
λ (μm)	exptl	calcd	errors	exptl	calcd	errors
0.4047	1.7585	1.7585	0.0000	1.7208	1.7208	0.0000
0.4078	1.7577	1.7577	0.0000	1.7202	1.7202	0.0000
0.4358	1.7516	1.7516	0.0000	1.7148	1.7148	0.0000
0.4861	1.7433	1.7433	0.0000	1.7075	1.7075	0.0000
0.4916	1.7426	1.7426	0.0000	1.7069	1.7069	0.0000
0.4962	1.7420	1.7420	0.0000	1.7063	1.7063	0.0000
0.5461	1.7364	1.7364	0.0000	1.7014	1.7015	−0.0001
0.5780	1.7336	1.7336	0.0000	1.6990	1.6990	0.0000
0.5893	1.7327	1.7327	0.0000	1.6982	1.6982	0.0000
0.6563	1.7284	1.7283	0.0001	1.6944	1.6944	0.0000
0.6943	1.7263	1.7263	0.0000	1.6927	1.6927	0.0000
0.8072	1.7218	1.7219	−0.0001	1.6887	1.6888	−0.0001
0.8617	1.7202	1.7202	0.0000	1.6874	1.6874	0.0000
0.9592	1.7178	1.7177	0.0001	1.6854	1.6853	0.0001
1.0140	1.7165	1.7165	0.0000	1.6842	1.6843	−0.0001
1.0680	1.7155	1.7155	0.0000	1.6835	1.6834	0.0001

$$n_e^2 = 2.82574 + 0.02026/(\lambda^2 - 0.01586) - 0.00856\lambda^2$$

$$n_o^2 = 2.93590 + 0.02336/(\lambda^2 - 0.01622) - 0.01210\lambda^2$$

where the wavelength, λ, is in microns. The values calculated from them are exactly consistent with experimental ones to the third decimal place, and there is only a small error even to the fourth decimal place. Figure 5 shows the measured and fitted refractive index data for both n_o and n_e.

The Sellmeier equations predict that the shortest second harmonic generation (SHG) wavelength for the crystal is 399 and 605 nm for type I and type II phase matching, respectively, so SHG of a Nd:YAG laser radiation (1064 nm) is possible for type I phase match-

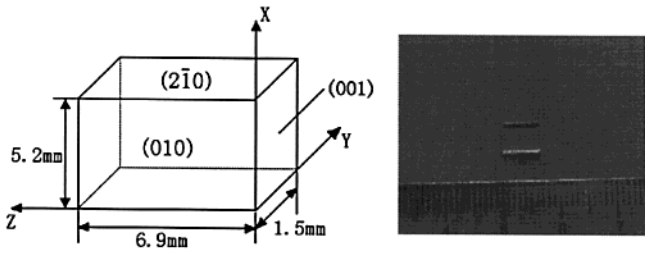

Figure 6. β-Zn_3BPO_7 plate for NLO coefficient determination.

ing. Phase matching angle for type I SHG of 1064 nm calculated from the Sellmeier equations is 52°.

Because β-Zn_3BPO_7 crystallizes in the hexagonal system with point group $\bar{6}m2$, only one NLO coefficient d_{11} needs to be considered. The nonlinear optical coefficient was measured using the Maker fringes technique,[12] with the d_{36} Maker fringe of KDP as a standard. Since the crystallographic axes are not orthogonal, we use the orthogonal crystallophysical coordinate system defined with the following convention: *x* and *z* are parallel to the *a* and *c* axes, respectively, and the *y* axis is perpendicular to the *xz* plane. Figure 6 shows the crystal plate of β-Zn_3BPO_7 used by Maker fringes technique. The plane of incidence is (010) faces which are carefully polished. The plate is rotated around the crystallophysical *x* axis, and fundamental 1064 nm light generated with a Nd:YAG laser propagates perpendicular to the *x* axis. The obtained NLO coefficient is $d_{11} = 0.69$ pm/V,[4] 1.8 times as large as that of d_{36} (KDP).

In conclusion, we have successfully grown large and transparent β-Zn_3BPO_7 single crystals by the top-seeded growth method. It is easy to grow a large single crystal of β-Zn_3BPO_7 due to the low viscosity of the melt. The β-Zn_3BPO_7 crystal contains BO_3 and PO_4 groups as its basic structural units and is transparent down to 250 nm. The Sellmeier equations predict that SHG of a Nd:YAG laser radiation (1064 nm) is possible for type I phase matching. The only NLO coefficient d_{11} measured by the Maker fringes technique is 0.69 pm/V.

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