Crystal Growth of Magnesium Zinc Borophosphate

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Single crystal of solid solution magnesium zinc borophosphate was first grown by the Czochralski method. The crystal obtained shows thick plate-like morphology with sizes up to 20 mm × 15 mm × 7 mm. The crystal is transparent in the wavelength range of 200–2500 nm, with the UV absorption edge at about 200 nm. The powder second harmonic generation effect of the crystal is similar to that of KH_2PO_4.

Nonlinear optical (NLO) crystals have received much attention because of their potential in various laser applications. Many NLO materials are either borates or phosphates, for example, BBO (β-BaB_2O_4),[1] LBO (LiB_3O_5),[2] KTP ($KTiOPO_4$)[3] and KDP (KH_2PO_4)[4] are well-known NLO crystals and heavily used for frequency conversions in laser spectroscopy. However, there have been few materials in borophosphates that contain both borate group and phosphate group. We recently characterized a new borophosphate NLO crystal β-Zn_3BPO_7.[5] This crystal melts congruently with the melting point of 927 °C and can be grown by Czochralski method, but it suffers a phase transition at about 600 °C, special care must be taken during the crystal growth, otherwise it will crack seriously and became opaque. Therefore, continued effort has been made to explore new NLO crystals in borophosphates.

The existence of Zn_3BPO_7 and Mg_3BPO_7 was first reported by Liebertz et al.[6] Both Mg_3BPO_7 and Zn_3BPO_7 occur in two forms. The transition of the high-temperature form β-Zn_3BPO_7 into the low-temperature form α-Zn_3BPO_7 is very sluggish, the growth of larger crystals is restricted to β-Zn_3BPO_7. However, The transition of β-Mg_3BPO_7 into α-Mg_3BPO_7 is prompt, β-Mg_3BPO_7 can not be quenched to room temperature. α-Zn_3BPO_7 and α-Mg_3BPO_7 crystallize in orthorhombic system, the lattice parameters of α-Zn_3BPO_7 are $a = 8.438(5)$ Å, $b = 4.884(5)$ Å, $c = 12.746(5)$ Å, $V = 525.3$ Å^3 and α-Mg_3BPO_7 is $a = 8.497(5)$ Å, $b = 4.880(5)$ Å, $c = 12.558(5)$ Å, $V = 520.7$ Å.[3] It was found that both of the two forms have SHG effects. In the course of the investigation on the phase relations of Zn_3BPO_7 and Mg_3BPO_7, we found that α-Zn3BPO7 and α-Mg_3BPO_7 formed solid solution named $Mg_xZn_{3-x}BPO_7$ (MZBP). In this paper, we report the crystal growth of MZBP by Czochralski technique. The X-ray powder diffraction, transmittance spectrum and powder second harmonic generation effect are also investigated.

Microcrystalline samples of MZBP were prepared by using standard solid state reaction techniques. Analytical reagent grade materials were used. Mixtures of MgO, ZnO, H_3BO_3 and $NH_4H_2PO_4$ in the mole ratio 1.8 : 1.2 : 1 : 1 were finely ground in an agate mortar, then charged into a platinum crucible. The temperature was slowly raised to 450 °C in order to avoid ejection of raw materials from the crucible arising from vigorous release of NH_3 and H_2O. After preheated at 450 °C for 10 h, the powder was sintered at 950 °C for 48 h with intermittent grindings and its X-ray powder diffraction measurements were performed. The process was repeated until the X-ray powder diffraction pattern had no further changes. The chemical reaction equation was as follows:

$$1.8MgO + 1.2ZnO + H_3BO_3 + NH_4H_2PO_4 \rightarrow Mg_{1.8}Zn_{1.2}BPO_7 + NH_3\uparrow + 3H_2O\uparrow \qquad (1)$$

The growth experiments were carried out in a two-zone vertical resistance furnace. The principal component is a cylindrical resistance furnace with two independently powered and controlled zones, which allow the establishment of the desired temperature profile within the furnace chamber.

The powder samples were melted in a platinum crucible in several batches. In the first run of growth, a platinum wire (0.5 mm in diameter) was fixed at the one end of alumna ceramic rod and immersed in the melt, the temperature was reduced at a rate of 2–3 °C/day. The obtained crystals were cracked, but parts of them were usable as seeds.

In order to grow large MZBP crystals, the main efforts have been focused on Czochralski growth. A platinum crucible (ϕ50mm × 40 mm) containing the charge was put into the furnace, the temperature was raised to 1180 °C and held for 10 hours in order to melt completely and mix homogeneously, and then decreased to 1120 °C. A seed crystal attached to a platinum rod contacted the melt, the pulling rate was 0.4 mm/h and the seed rotation rate was 20 rpm. The temperature gradient above the melt was about 30–40 °C/cm. When the growth was completed, the crystal was drawn out of the melt surface and cooled to room temperature at a rate of 50 °C/h.

Figure 1 shows the as-grown MZBP crystal by the Czochralski technique. Its size is 20 mm × 15 mm × 7 mm. It is colorless and crack-free, and shows thick plate-like morphology. Most part of the crystal is transparent except that little inclusion is observed at the top of the crystal.

The sample of MZBP crystal was pulverized to carry out the X-ray powder diffraction analysis on a MXP18AHF X-ray

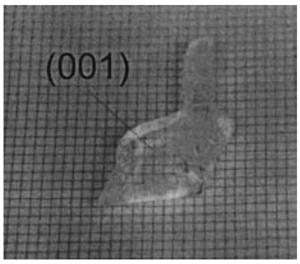

Figure 1. MZBP crystal grown by Czochralski method.

diffractometer with a graphite monochromatized CuKα radiation. The powder diffraction pattern was recorded over the angular range 5–70° (2θ). Figure 2 shows the X-rays powder diffraction pattern of MZBP crystal grown by Czochralski technique. The X-ray powder diffraction pattern was indexed by ITO program and the cell parameters were refined by the program WIN-METRIC, available in the PC software package DIFFRAC^{plus} supplied by Bruker AXS. An orthorhombic solution was found with the lattice parameters $a = 8.473$ Å, $b = 4.877$ Å, $c = 12.641$ Å, $V = 522.29$ Å,[3] which were similar to those of α-Zn_3BPO_7 and α-Mg_3BPO_7 reported by Liebertz et al..[5]

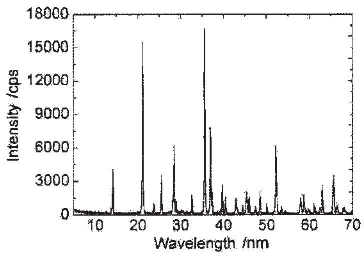

Figure 2. The X-ray powder diffraction pattern of MZBP crystal.

Optical transmittance measurements were performed on the as-grown MZBP crystal. The transmittance spectrum was recorded on a Shimadzu UV-240 UV-VIS-NIR Spectrometer. Figure 3 shows the transmittance spectrum of MZBP single crystal. As shown in Figure 3, a wide transmission range from 200 nm to 2500 nm is observed in the UV-to-IR region, with the absorption edge at about 200 nm. Also it was shown that the transmittance is lower than 50%. The low transmittance is owing to the scattering and the thickness of the crystal. The unpolished incident surfaces may cause scattering as the transmittance measurement was carried out on the as-grown crystal. Moreover, the thickness of the incidence, which is 7 mm, may cause the heavy absorption.

A powder second harmonic generation (SHG) test was carried out on the MZBP sample. Fundamental 1064 nm light was

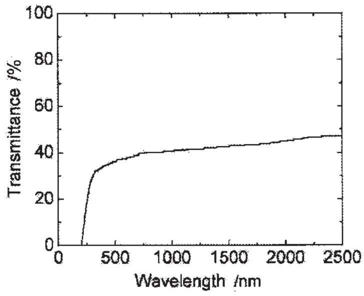

Figure 3. The transmittance spectrum of MZBP crystal.

generated with a Q-switched Nd:YAG laser. Microcrystalline KDP (KH_2PO_4) served as the standard. The powder SHG effect of MZBP crystal is similar to that of KDP.

There was no weight change after one week when a crystal sample of 6.5 g was soaked into water, which indicated that MZBP crystal is insensitive to water. MZBP has good mechanical properties for easy cutting and polishing.

In conclusion, we have grown large and transparent MZBP single crystal by the Czochralski method. The crystal exhibits wide transmittance range. The powder second harmonic generation effect is similar to that of KDP. MZBP crystal has good mechanical properties and is chemically stable and insensitive to moisture.

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