

## Flux Growth of Single Crystals of BaBPO<sub>5</sub>

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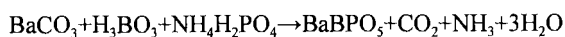
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The powder barium borophosphate BaBPO<sub>5</sub> was synthesized by solid-state reaction techniques. Single crystals BaBPO<sub>5</sub> with sizes up to 20 mm × 15 mm × 10 mm were grown by top-seeded solution growth method using H<sub>3</sub>BO<sub>3</sub>–NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> as fluxes. The crystals and the components volatilized were characterized by the method of X-ray powder diffraction.

In the last forty years the first few compounds combining both borate and phosphate groups were synthesized and structurally characterized. High-temperature syntheses have produced handful of metal borophosphates. These are the following: MBPO<sub>5</sub>, where M= Ca, Sr, or Ba,<sup>1–4</sup> M<sub>3</sub>BP<sub>3</sub>O<sub>12</sub>, where M=Ba or Pb,<sup>1,5</sup> Na<sub>5</sub>B<sub>2</sub>P<sub>3</sub>O<sub>13</sub>,<sup>6</sup> Co<sub>5</sub>BP<sub>3</sub>O<sub>14</sub>,<sup>7</sup> M<sub>3</sub>BPO<sub>7</sub>, where M=Mg, or Zn.<sup>8</sup> The main structural features in them is that boron is trigonally or tetrahedrally coordinated by oxygen, and that the BO<sub>3</sub> or BO<sub>4</sub> and PO<sub>4</sub> tetrahedra share corners and build infinite chains or networks. Therefore, the considerable variety in crystal structure of borophosphate compounds provides a great deal objects for the study aiming at exploring new functional materials.

The compound BaBPO<sub>5</sub> was first prepared by Bauer,<sup>1</sup> who defined the chemical formula as 2BaO·B<sub>2</sub>O<sub>3</sub>·P<sub>2</sub>O<sub>5</sub>. X-ray powder diffraction data of this compound was reported,<sup>1</sup> and the structure of BaBPO<sub>5</sub> was also analyzed from powder data.<sup>2,3</sup> To our knowledge, all these investigations were performed on the powder of BaBPO<sub>5</sub> and never on single crystals. The present paper reports the growth of BaBPO<sub>5</sub> crystals from H<sub>3</sub>BO<sub>3</sub>–NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> flux using the top-seeded solution growth method.

In this work, polycrystalline samples of BaBPO<sub>5</sub> were prepared by using solid-state reaction techniques. The initial substances were analytical grade BaCO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The starting materials in the stoichiometric proportion were mixed homogeneously in an agate mortar, and then packed into a platinum crucible. The temperature was raised to 500 °C at a rate of 2 °C /min in order to avoid ejection of powdered raw material from the crucible due to vigorous evolution of CO<sub>2</sub>, NH<sub>3</sub> and decomposition of H<sub>3</sub>BO<sub>3</sub>. After preheating at 500 °C for 10 h in a muffle furnace, the products were cooled to room temperature, and ground up again; the mixture was heated at 700 °C for 24 h, and then cooled to room temperature. The purity of sample was checked by X-ray powder diffraction. A single-phase powder of BaBPO<sub>5</sub> was obtained when repeated heat treatment caused no further changes in the X-ray powder diffraction. The solid products were then pulverized, and ground into fine powder. The chemical equation can be expressed as follows:

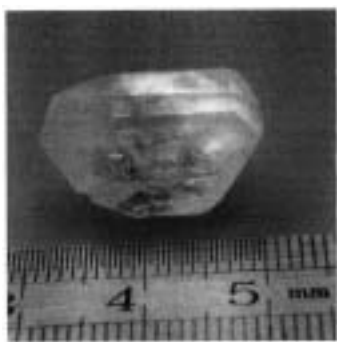


Since BaBPO<sub>5</sub> melts incongruently,<sup>4</sup> the flux method is necessary for the purpose of its crystal growth. The success of

growth depends to a large extent on whether an appropriate flux can be found. For this reason, efforts have been made to search for the best flux to suit the growth of BaBPO<sub>5</sub> crystals. According to the choice rules of fluxes, if a surplus of constituents of the compounds can act as the flux for the growth of the crystals of that compound, it will be possible to prevent the flux from contaminating the grown crystal. The crystals grown in such a melt will be of high purity and of good quality. So several self-fluxes were firstly investigated for growing BaBPO<sub>5</sub>, such as BaCO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The results indicate that H<sub>3</sub>BO<sub>3</sub>–NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> flux system is more suitable than others. Several ratios of BaCO<sub>3</sub>: H<sub>3</sub>BO<sub>3</sub>: NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> were tested for growing BaBPO<sub>5</sub> crystals. Taking a wider crystallization zone and higher crystal yield into account, the suitable molar ratios of BaCO<sub>3</sub>: H<sub>3</sub>BO<sub>3</sub>: NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> for the growth of BaBPO<sub>5</sub> crystals turned out to be 1:1.8:1.8. The growth temperature decreased with decreasing of solute concentration, and the growth temperature at 840–915 °C proved suitable for the growth of BaBPO<sub>5</sub> in our experiment.

At the beginning of our experiment, BaBPO<sub>5</sub> seeds were unavailable. Therefore our first seed was a Pt wire seed, the raw materials were polycrystalline form BaBPO<sub>5</sub> powder, analytical grade H<sub>3</sub>BO<sub>3</sub>, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The charges were weighed in the appropriate ratio, ground, mixed thoroughly, and then a platinum crucible of 40 mm in height and 40 mm in diameter containing the crystal growth charge was mounted in a vertical, temperature programmable furnace. When the initial charge was melted in the platinum crucible, new portions of the starting material were added until the proper amount of melt was made. The crucible position was fixed at the center of the furnace. We then dipped a platinum wire into the solution, the solution was slowly cooled, and then the BaBPO<sub>5</sub> crystals were obtained. Most of the crystals were cracked, but parts of new crystals were usable as seeds.

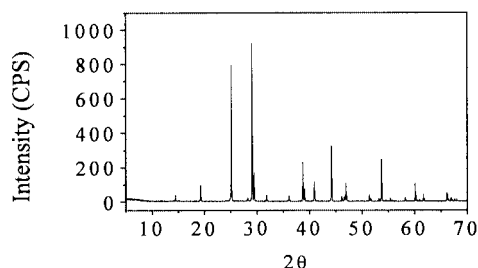
A spontaneous growth method was performed in this early stage; however, in order to obtain larger crystals BaBPO<sub>5</sub>, the main efforts have been focused on top-seeded solution growth method. The experiment processing is as follows: A platinum crucible containing the crystal growth charge was put into the furnace. Then the furnace was sealed with a cover that had a hole for insertion of the seed. The furnace was heated rapidly to a temperature of 1050 °C and maintained at this temperature for 24 h. Then it was cooled rapidly to 920 °C. A seed crystal of BaBPO<sub>5</sub> attached to a platinum rod was inserted slowly into the crucible and kept in contact with the surface of the solution, while a temperature of 920 °C was maintained for half an hour to dissolve the outer surface of the seed. The growing crystal was rotated at a rate of 20 rpm. The solution was then cooled rapidly to the saturation temperature of 915 °C determined by repeated seeding, and then the temperature was slowly reduced to 840 °C at a rate of 1 °C /day until the end of the growth. The



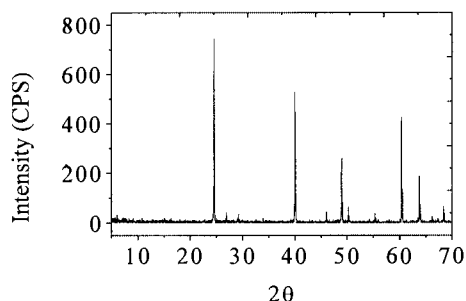
**Figure 1.** Photograph of BaBPO<sub>5</sub> grown by the top-seeded growth method using H<sub>3</sub>BO<sub>3</sub>–NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> as fluxes.

crystal thus obtained was drawn out of the melt surface and then cooled down together with the furnace to room temperature at a rate of 30 °C/h. A BaBPO<sub>5</sub> crystal with dimensions of 20 mm × 15 mm × 10 mm was grown under this condition. Figure 1 shows the crystal BaBPO<sub>5</sub> by the top-seeded solution growth method using H<sub>3</sub>BO<sub>3</sub>–NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> as fluxes. From the figure, we can see that the obtained crystal is colorless, partially transparent and the crystal exhibits fairly distinguishable facets.

The obtained crystal was identified by X-ray powder diffraction method, operating on a D8 ADVANCE (Bruker AXS) powder diffractometer with Cu K $\alpha$  radiation (40 KV, 40 mA)



**Figure 2.** X-ray powder diffraction pattern of as-prepared single crystals BaBPO<sub>5</sub>.



**Figure 3.** X-ray powder diffraction pattern of the components of evaporation during the growth of single crystals.

by a graphite monochromator. The X-ray powder diffraction data for phase identification was collected at ambient temperature. The scattering slit is 1.0°, the divergence slit 1.0° and the receiving slit 0.1 mm. The scanspeed of the X-ray powder diffraction data is 0.2 s per step, and the 2 $\theta$  range is from 5° to 70°. Figure 2 shows the X-ray powder diffraction pattern of as-prepared single crystals BaBPO<sub>5</sub> by top-seeded solution growth method.

All peaks in the pattern correspond to the phase of BaBPO<sub>5</sub>, and the refined cell parameters are in good agreement with the reported data.<sup>3</sup> The X-ray powder diffraction data of single crystal by top-seeded solution growth method shows that the crystals are well crystallized.

During the growth, a thin layer of white substance was observed around the seeding-rod near the cover of the furnace. These are the components volatilized of the melt. Figure 3 shows the X-ray powder diffraction pattern of the components volatilized during the growth of single crystals BaBPO<sub>5</sub>.

An X-ray powder diffraction pattern recorded for the components of evaporation was found to match almost well with the data of BPO<sub>4</sub> reported in the reference.<sup>9</sup> Therefore, the main components volatilized were BPO<sub>4</sub>.

In addition, our experiment indicates that although a solution of the H<sub>3</sub>BO<sub>3</sub>–NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> flux system can grow BaBPO<sub>5</sub> crystals, it exhibits a high viscosity, which limits the mixing and mass transfer in the melt and leads to the formation of such defects as inclusions of the solution in the growing crystal. We intend to test new complex flux and try some suitable dopants to improve the crystal quality. Further study of the present crystal is in progress.

In conclusion, we synthesized the powder barium borophosphate BaBPO<sub>5</sub> in ambient atmosphere and we grew single crystals BaBPO<sub>5</sub> with dimensions of 20 mm × 15 mm × 10 mm by top-seeded solution growth method using H<sub>3</sub>BO<sub>3</sub>–NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> as fluxes. The crystals BaBPO<sub>5</sub> and the components were characterized by X-ray powder diffraction.

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## References

- 1 H. Bauer, *Z. Anorg. Allg. Chem.*, **337**, 183 (1965).
- 2 R. Kniep, G. Gozel, B. Eisenmann, C. Rohr, M. Asbrand, and M. Kizilyalli, *Angew. Chem., Int. Ed. Engl.*, **33**, 749 (1994).
- 3 A. Baykal, M. Kizilyalli, G. Gozel, and R. Kniep, *Cryst. Res. Technol.*, **35**, 247 (2000).
- 4 H. Bauer, *Z. Anorg. Allg. Chem.*, **345**, 225 (1966).
- 5 C. H. Park and K. Bluhm, *Z. Naturforsch., B*, **50**, 1617 (1995).
- 6 C. Hauf, T. Friedrich, and R. Kniep, *Z. Kristallogr.*, **210**, 446 (1995).
- 7 R. P. Bontchev and S. C. Sevov, *Inorg. Chem.*, **35**, 6910 (1996).
- 8 J. Liebertz and S. Stahr, *Z. Kristallogr.*, **160**, 135 (1982).
- 9 G. E. Schulze, *Z. Phys. Chem.*, **B24**, 215 (1934).