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Preparation of Barium Tetrahydroxo Borate Crystals ($Ba[B(OH)_4]_2$)

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The preparation and properties of a new compound bariumtetrahydroxoborate ($Ba[B(OH)_4]_2$) are described. The crystal belongs to the monoclinic system with a = 8.33 Å, b = 16.52 Å, c = 10.22 Å, β = 107°. The properties are as follows; density = 2.83 $g \cdot cm^{-3}$, refractive indexes; $\alpha = 1.567_6$, $\beta = 1.547_6$, $\gamma = 1.517_8$.

Single crystal of β-BaB_2O_4,[1-3] which belongs to the trigonal system with the space group of C^6_{3v}-R3c and its density is 3.83 g/cm^3, is an excellent new nonlinear optical material with a good pyroelectric properties. In optoelectronic applications the crystals of high quality are severely demanded.

The present paper describes the preparation and properties of $Ba[B(OH)_4]_2$ compound, which was obtained in the course of the preparation of the high quality raw material for growing β-BaB_2O_4 single crystal.

Both solutions of barium chloride ($BaCl_2$) and sodium borate ($NaBO_2$) are prepared by dissolving 1.0 mol of analytical-grade $BaCl_2$ and 2.0 mol of $NaBO_2 \cdot 4H_2O$ into 1.0 L. of distilled water, respectively. The apparatus used is a 500 mL. four-necked round-bottomed flask with a stirring bar, a Hg-thermometer (1/100 °C) and two 100 mL. additional separatory funnels in which contain $BaCl_2$ and $NaBO_2$ solutions, respectively. The flask is placed on a mantle heater and the precipitaion reaction is carried out at 20 °C and at 80 °C in 100 mL. diluted hydrochloric acid or sodium hydroxide solutions. The three concentrations as 1.0×10^{-1}, 1.0×10^{-3} and 1.0×10^{-5} (mol/l) for the acid or base solution are used for adjusting a pH of the whole solution in a precipitation reaction. Barium chloride and sodium borate solutions are added slowly drop by drop into the acid or base solution in 1 h while continuously stirred at a speed of 500 rpm with a stirrer. After the solutions were added, stirring is continued for 30 min., then the liquid is kept standing for 1 h.

Colorless crystals of monoclinic prism form having the size of about 0.1 x 0.1 x 0.1 mm^3 have precipitated at the bottom of the flask at 20 °C. At 80 °C, powder-like BaB_2O_4 crystals (γ-type) precipitated. There have been no data concerning the chemical and physical properties of crystals precipitated at 20 °C. Table 1 shows the powder x-ray data of crystals precipitated at 20 °C, which were calculated by the Rad-B system computer program (Rigaku Denki Co). The crystal belongs to the monoclinic system consisting of the unit cell of a = 8.33 Å, b = 16.52 Å, c = 10.22 Å and β = 107° , and has the refrative indexes; $\alpha = 1.567_6$, $\beta = 1.547_6$, $\gamma = 1.517_8$. The density was 2.83 $g \cdot cm^{-3}$. On the basis of DAT data, water content of the crystals was evaluated to be 4.0 mol in a chemical unit. Moreover, from the chemical analysis by the ICP method it was determined that the concentrations of barium, boron and oxygen are 46.5, 7.3, and 46.2 in wt% respectively. Consequently, it was found that the crystals precipitatied at 20 °C were a new compound, $Ba[B(OH)_4]_2$). The measurement of chemical and physical properties as well as crystal structure analysis are now under way, and will be reported elsewhere in detail.

Table 1. Powder X-ray data of $Ba[B(OH)_4]_2$ crystals

d	I/I_o	h k l
5.764	100	1 2 0
5.487	10	1 2 1
4.905	22	0 0 2
4.186	53	1 2 2
4.005	95	2 0 0
3.813	28	0 4 1
3.400	33	1 2 2
3.318	10	1 1 3
3.212	17	0 1 3
3.162	44	0 4 2
2.930	12	2 1 3
2.878	10	2 4 1
2.736	25	2 0 2, 2 4 2
2.636	28	3 2 1
2.560	54	0 4 3, 3 2 2
2.534	24	3 2 0
2.442	25	1 2 4
2.308	11	1 3 4
2.285	14	2 4 2
2.215	10	2 5 3, 2 3 4, 1 6 2
2.134	15	1 6 3, 2 6 1
2.108	14	0 4 4
2.068	21	4 0 2
2.024	21	0 8 1, 1 1 5
1.962	16	2 4 3, 3 6 1
1.850	18	2 8 1, 4 4 2, 6 3 5

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