A NEW SERIES OF SYNTHETIC BORATES ISOSTRUCTURAL WITH THE CARBONATE MINERAL HUNTITE

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ABSTRACT

A new series of rare earth aluminum borates has been synthesized from a molten solution with the general formula $RX_3(BO_3)_4$. Single crystals of these materials have been grown where R has been yttrium or a rare earth and X has been aluminum or chromium. All the members of this series made to date have been found to be piezoelectric as indicated by a positive test when placed in a Giebe-Scheibe circuit. The yttrium-aluminum borate, when doped with rare earth ions, and the rare earth-aluminum borates show a bright, sharp line fluorescence when excited by U.V. with the emitted fluorescence concentrated in only a very few lines.

The crystals are trigonal with a rhombohedral lattice and contain one formula weight in the rhombohedral unit cell. The yttrium-aluminum borate and the rare earth-aluminum borates crystallize as hexagonal rods elongated in the c direction and are colorless except where the rare earth ion imparts its characteristic color. The rare earth-chromium borates occur as distinct rhombohedra and are dark green in color. Optical examination of the yttrium-aluminum borate shows it to be uniaxial ($-$) with $\omega = 1.775 \pm 0.005$ and $\epsilon = 1.775 \pm 0.005$. H (Mohs' scale) $= ca.$ 7.5, and the pycnometric density is 3.701 g/cc as compared to a theoretical density of 3.72 g/cc based on x-ray measurements.

INTRODUCTION

During the course of investigation of a variety of molten solvents suitable for crystal growth, a new series of rare earth compounds was synthesized. This paper reports a method of preparation and some of the physical and chemical properties of these new materials.

EXPERIMENTAL

Small single crystals of rare earth-aluminum borates and rare earth-chromium borates were obtained by slowly cooling a molten solvent saturated with the component oxides in much the same manner previously used for the growth of ferrite (Remeika 1956) and garnet (Neilsen and Dearborn, 1958) single crystals.

A molten solution of potassium sulfate and molybdic anhydride (1:3 mole ratio) or lead fluoride and boric oxide (1:3 mole ratio) were two of the solvents successfully used to dissolve the component oxides in these experiments and produced single crystals ranging in size from about 0.1–10 mm when slowly cooled from 1150° C. to 900° C.

A typical run using a 100 ml platinum crucible follows:

K_2SO_4	0.1	Mole
MoO_3	0.3	Mole
Y_2O_3	0.04	Mole

Al_2O_3 0.12 Mole
B_2O_3 0.16 Mole

A four hour soak period at 1150° C. and a cooling rate of about 2°/hour down to 900° C. produced single crystals of the size mentioned. The grown crystals can be removed by dissolving the matrix in hot KOH, HCl or HNO_3.

RESULTS

To date, single crystals of the following compositions have been grown:

$RAl_3B_4O_{12}$ where R has been Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb and Er; $RX_3B_4O_{12}$ where R has been Gd and Sm, and X has been Cr and Al. Attempts to date at producing the yttrium-chromium borate and the yttrium-gallium borate have not been successful nor have attempts at fully substituting iron in the X position. The gadolinium-chromium borate, however, has been iron doped, with the iron presumably substituting for the chromium.

The yttrium-aluminum borate and the rare earth-aluminum borates crystallize as hexagonal rods elongated in the c direction. The crystals are colorless except where the rare earth ion imparts its characteristic color; in such cases, pastel colors are produced. An interesting example showing a distinct color change is the neodymium-aluminum borate which is a light blue color when exposed to a fluorescent lamp and a light pink color when viewed in natural light.

Optical examination of the yttrium aluminum borate shows it to be uniaxial negative with indices of refraction, $\omega = 1.775 \pm 0.005$ and $\epsilon = 1.715 \pm 0.005$. The crystal hardness on a Mohs' scale is about 7.5 and the pycnometric density is 3.701 g/cc. The theoretical density based on x-ray measurement is 3.72 g/cc.

The borates appear to be insoluble in boiling KOH, HCl and HNO_3, and do not melt below 1400° C., although at this temperature an opaqueness develops which is indicative of crystalline decomposition.

The crystal system is trigonal with a rhombohedral lattice and the point group based on stereographic projection studies using the two circle reflection goniometer is D_3-32. The space group is D_3^7-R32 with the rare earth in site symmetry 32. The hexagonal lattice constants are $a_h = 9.287$ Å and $c_h = 7.256$ Å and for the rhombohedral lattice $a_r = 5.883$ Å and $\alpha = 104.26°$ (Mills, to be published).

The chemical composition of the yttrium-aluminum borate was determined by wet analysis and quantitative spectrochemical analysis, and the x-ray fluorescence technique was also used for yttrium. The results of these analyses with standard deviations follow:

Oxide	Theoretical ($YAl_3B_4O_{12}$)	Wet analysis	Quantitative spectrochemical Analysis	X-ray fluorescence
Y_2O_3	27.9%	32.96	26 ± 2	29.8 ± 0.0
Al_2O_3	37.7%	42.08	32 ± 5	—
B_2O_3	34.4%	35.85	40 ± 4	—
	100.0%	110.9	98.6 ± 9.9	

The formula indicated by the above analyses appears to be $YAl_3B_4O_{12}$. The agreement between the theoretical and the found composition is reasonable; further confirmation of this formula, however, was obtained by calculating the formula weight of the unit cell from the volume of the unit cell and the density. This calculation confirms the formula arrived at by analytical means and shows there to be one formula weight in the rhombohedral unit cell.

The fact that the compounds have been found to be isostructural with huntite (Faust 1953; Graf and Bradley, in press; Knox, 1961) and the line intensities and lattice spacings observed agree with calculated values clearly indicate the formula to be $RX_3(BO_3)_4$.

Using $YAl_3(BO_3)_4$ as a representative pattern for the $RX_3(BO_3)_4$ family of compounds the seven strongest lines are:

hk·l	I	d (obs.)
20.2 30.0	s	2.687
12.2 22.0	ms	2.322
10.1	m	5.343
02.1	m	3.504
11.3	m	2.140
13.1	m	2.128
22.3	m	1.673

This isomorphism between carbonate and borate structures is well known (Goldschmidt and Hauptmann, 1931–32) and is shown in the following examples (Levin, *et al.*, 1961):

$CaCO_3$	$LuBO_3$	Calcite Structure
$CaCO_3$	YBO_3	Vaterite Structure
$CaMg(CO_3)_2$	$CaSn(BO_3)_2$	Dolomite Structure
$CaMg_3(CO_3)_4$	$YAl_3(BO_3)_4$	Huntite Structure

Piezoelectricity

The entire series grown to date has been found to be piezoelectric as indicated by a positive test when placed in a Giebe-Scheibe circuit (Giebe and Scheibe, 1925; Perdox and Van Suchtelen, 1950), and a crystal of the yttrium-aluminum borate has been sectioned, and a plate has been made to oscillate over a series of resonant frequencies. Further studies to give a more quantitative measurement of the electrical properties are in progress. No ferroelectricity was noted at room temperature or liquid nitrogen temperature for several of the samples examined.

Fluorescence

The rare earth-aluminum borates and the yttrium-aluminum borate doped with rare earths show a bright, sharp line fluorescence when illuminated by U.V., with the emitted fluorescence concentrated in only a few lines. The most intense lines possess a width of about one wave number.

Acknowledgments

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