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Synthesis and Structure of $BiFe_{1.35}Al_{1.65}(BO_3)_4$

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Single crystals of the title composition have been grown from a Bi_2O_3/B_2O_3 flux. The compound crystallizes in the huntite structure (space group $R32$) and constitutes the first example with Bi occupying the (a) site in such a composition. The X-ray powder diffraction pattern and cell parameters are reported.

Introduction

In recent years, the mineral "huntite," $CaMg_3(CO_3)_4$, has become a structural prototype for numerous new compositions. The actual mineralogical specimen from Currant Creek, Nevada was originally described by Faust (*1*) as being orthorhombic. More recently Graf and Bradley (*2*) refined the structural data and described huntite as an ordered rhombohedral double carbonate crystallizing in the $R32$ space group. More commonly huntite itself, as well as isostructural analogs, is described by a hexagonal cell which is quite similar to that of the simpler carbonates $CaCO_3$ and $MgCO_3$. It is interesting to note that all attempts to synthesize the actual huntite composition have failed, and only boron-containing analogs are known to date. Blasse and Bril (*3*), for instance, described some rare earth aluminum and rare earth gallium "huntites" of the types $YAl_3B_4O_{12}$ and $EuGa_3B_4O_{12}$. The structural analogy to huntite is better represented by formula designations of the type $YGa_3(BO_3)_4$. More recently Joubert, et al. (*4*) published on some Fe^{3+}-containing rare earth compositions of the type $GdFe_3(BO_3)_4$. All these compounds crystallize on the hexagonal huntite structure with the rare earth ions occupying the Ca^{2+}(a) site and the Fe^{3+} ions the octahedrally coordinated Mg^{2+}(d) position. Boron, of course, occupies the trigonal C^{4+} position of huntite.

It is the purpose of the present paper to describe the first bismuth containing huntite, $BiFe_{1.35}Al_{1.65}(BO_3)_4$.

Experimental

The single crystal of the new huntite-type compound was prepared by standard flux growth techniques, using a flux similar to the one used by Bernal (*5*) for the preparation of calcite-type $FeBO_3$ compositions. Typically, 25.00 g Bi_2O_3, 15.00 g B_2O_3, 5.00 g Fe_2O_3, and 2.50 g Al_2O_3 were weighed, mixed, and melted in a covered Pt crucible at 1150°C. The melt was then slowly cooled with a programmer controlled at the rate of 3°C/hr to 600°C; then furnace-cooled to room temperature. The crucible contents were leached with 50% HNO_3 and the pale yellow acicular crystals were recovered by final washing with water, alcohol and drying at 120°C.

Results and Discussion

A. Analysis

Since a calcite-type (Fe, Al) BO_3 composition had been anticipated, chemical analyses were originally carried out only for Fe, Al, and B. However, the sum of the oxides at these components repeatedly accounted for only about 60% of the total sample weight. Bi was not sought in the analyses because the products from other flux plus oxide combinations such as Fe/In/B/Bi, Fe/Cr/B/Bi, Fe/Co/B/Bi, Fe/Ni/B/Bi, or Fe/Ga/B/Bi invariably contained Bi at a level of less than 0.1%. When sought in the Fe/Al/B/Bi case, however, 37.0% Bi was found. Thus, it was only this combination with the relatively small Al^{3+} ion that yielded a Bi-containing and a huntite-type product.

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TABLE I

OBSERVED AND CALCULATED D-VALUES FOR $BiFe_{1.35}Al_{1.65}(BO_3)_4$

N	I	H	K	L	$D_{(\text{obsd})}$	$D_{(\text{calcd})}$
2	90	1	0	1	5.480	5.488
3	70	1	1	0	4.710	4.717
4	90	0	2	1	3.576	3.577
5	50	0	1	2	3.372	3.374
7	85	2	1	1	2.849	2.850
8	100	2	0	2	2.746	2.744
9	75	3	0	0	2.724	2.724
10	65	1	2	2	2.371	2.372
11	80	2	2	0	2.360	2.359
12	35	1	1	3	2.186	2.188
13	55	1	3	1	2.167	2.167
14	50	4	0	1	1.969	1.969
15	40	3	1	2	1.933	1.933
16	30	3	0	3	1.830	1.830
17	55	4	1	0	1.784	1.783
18	50	2	2	3	1.706	1.706
19	30	0	2	4	1.691	1.687
20	35	2	3	2	1.672	1.672
21	20	0	5	1	1.595	1.595
22	25	2	4	1	1.511	1.511
23	20	5	0	2	1.495	1.495
24	30	5	1	1	1.441	1.440
25	20	4	2	2	1.426	1.425
26	5	6	0	0	1.362	1.362
27	20	4	3	1	1.321	1.321
28	30	5	2	0	1.308	1.308

The analyses for the remaining ions were as follows: Fe, 13.3%, Al, 8.2%, B, 7.7%. This compares favorably with the theoretical amounts calculated for $BiFe_{1.35}Al_{1.65}(BO_3)_4$ of Bi, 37.05%, Fe, 13.36%, Al, 7.89%, B, 7.67%.

B. X-ray Study

Single crystal information was obtained by the precession method using Mo radiation. Powder patterns were taken with CuK_{α_1} radiation in a Hägg–Guinier type camera. The parameters were refined by a least-squares method. Table I gives the observed d-values for $BiFe_{1.35}Al_{1.65}(BO_3)_4$ compared with those calculated on the basis of the refined parameters:

$$a_h = 9.43 \pm 1$$

$$c_h = 7.410 \pm 3$$

$$V = 571.201 \text{ Å}$$

In the original rhombohedral assignment by Graf (*1*), this corresponds to $a_{rh} = 5.98$ $\alpha = 104.28°$. What we have then, in this composition, is a statistical distribution of Fe^{3+} and Al^{3+} over the octahedral Mg^{2+} sites in huntite, while the larger Bi occupies the eight-fold coordinated Ca^{2+} site. Since Fe_2O_3 and Al_2O_3 were charged in equimolar amounts to the original mixture and the crystals are slightly richer in Al^{3+}, one can state that the distribution coefficient for Al relative to Fe is larger and greater than one. It is interesting to note that despite the considerable excess of Bi in the flux, it was incorporated into the structure exactly at the level dictated by the huntite structure.

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