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A NOTE ON THE STRUCTURAL CHEMISTRY OF HEMATOPHANITE¹ROLAND C. ROUSE, *Department of Geology and Mineralogy, The University of Michigan, Ann Arbor, Michigan 48105.*

ABSTRACT

Hematophanite, $Pb_4(Fe...)_4O_9(OH,Cl)_2$, is tetragonal with diffraction symmetry $P4/mmm$ and unit cell parameters $a=3.92 \text{ \AA}$ and $c=15.31 \text{ \AA}$. The crystal structure is based on a stacking of four perovskite-like cells along $[001]$ and has been refined to an R-factor of 19%. Relationships to chemically similar phases and other perovskite derivative structures are noted.

The first and only description of hematophanite appears in a paper by Johansson (1928). No morphological data were available, but from Laue photographs the symmetry was found to be tetragonal, space group $P4/mmm$, $P\bar{4}2m$, $P4mm$, or $P422$. Unit cell dimensions as determined from rotating crystal and powder photographs were $a=7.82$ and $c=15.26 \text{ \AA}$. Two chemical analyses yielded the formula $Pb(Cl, OH)_2 \cdot 4PbO \cdot 2Fe_2O_3$ or $Pb_5Fe_4O_{10}(OH, Cl)_2$ with 3 formula weights per unit cell. Berger and Pawlek (1957) in a study of the system $PbO-Fe_2O_3$ found an apparently similar phase, $2PbO \cdot Fe_2O_3$ or $Pb_2Fe_2O_6$, which was tetragonal with $a=7.79$ and $c=15.85 \text{ \AA}$. They also synthesized a compound of composition $PbCl_2 \cdot 4PbO \cdot 2Fe_2O_3$, whose color and density were similar to those of hematophanite and whose powder pattern could be indexed on the hematophanite cell. Mountavala and Ravitz (1962) in a restudy of the system $PbO-Fe_2O_3$ verified the existence of the phase $2PbO \cdot Fe_2O_3$. Strunz (1970) places hematophanite with the boleite group and assigns it, without explanation, to the space group $I4/mmm$.

This investigation of hematophanite was carried out on a specimen from Långban, Sweden kindly supplied by Dr. P. B. Moore of the University of Chicago. The specimen contained small reddish brown tabular grains of hematophanite associated with calcite, native copper, and plumboferrite. A number of crystals were examined by the Weissenberg and precession methods and all proved to be tetragonal with diffraction symmetry $P4/mmm$. As reported by Berger and Pawlek (1957) for $2PbO \cdot Fe_2O_3$, $hk0$ reflections were sharp and well-defined while those of classes $0kl$ and $h0l$ were diffuse and even arc-shaped. The unit cell dimensions as determined by Bradley-Jay extrapolations of single crystal diffractometer data are $a=3.92$ and $c=15.31 \text{ \AA}$, the former value

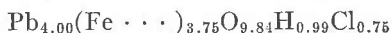
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being one half of Johansson's. Johansson, however, determined a as 7.82 Å from the powder pattern. If one very weak line, indexed as (310), (302) is discarded, the rest of the pattern can be indexed on the 3.92 Å cell.

Using the new cell parameters and Johansson's chemical analysis and density, the unit cell contents are



Assuming that the measured density of 7.70 g/cc is too low and normalizing to 4 Pb, the formula becomes



or ideally $\text{Pb}_4\text{Fe}_4\text{O}_9(\text{OH},\text{Cl})_2$. This is close to Johansson's formula $\text{Pb}_5\text{Fe}_4\text{O}_{10}(\text{OH},\text{Cl})_2$ and to the synthetic $\text{Pb}_2\text{Fe}_2\text{O}_5$. Since the volume of Johansson's (7.82 Å) cell is four times that of the 3.92 Å cell and since the density and chemical analysis used in the calculation are the same, the extra PbO in Johansson's formula must be an error. For the same reason the number of formula weights in the 7.82 Å cell must be 4 and not 3 as originally reported.

The single crystal photographs show three different substructures. Levels parallel to [001] indicate the presence of two subcells of periodicities $c/4 = 3.83$ Å and $c/2 = 7.65$ Å. A much less pronounced substructure appears in levels normal to [001] having $l = 4n$, where n is an integer. On alternate levels reflections with $h+k = 2n$ and $h+k = 2n+1$ are intense.

Judging from the formula and cell dimensions of hematophanite, the mineral is a structural derivative of the cubic perovskite structure. The very pronounced $c/4$ subcell corresponds to a perovskite-like subcell of dimensions $A = 3.92$ and $C = c/4 = 3.83$ Å with composition $\text{Pb}(\text{Fe} \cdot \cdot \cdot)\text{O}_{2.25}(\text{OH},\text{Cl})_{0.50}$ or $\text{ABO}_{2.75}$. Since perovskite is ABO_3 , there must be anion vacancies in addition to substitution of OH^- and Cl^- for O^{2-} .

The formula $\text{Pb}_4(\text{Fe} \cdot \cdot \cdot)_4\text{O}_9(\text{OH},\text{Cl})_2$ has an analogue in another perovskite-type compound $\text{Ca}_4(\text{Fe},\text{Cr})_4\text{O}_{11}$ (Johnson, 1960). It is reported on the basis of powder data to be orthorhombic Pbnm with $a = 5.415$, $b = 5.489$, and $c = 7.480$ Å. a and b correspond to the $a\sqrt{2} = 5.54$ Å translation in hematophanite and c to $c/2 = 7.65$ Å in hematophanite. Ignoring the small inequality of a and b , the index transformation $\text{Ca}_4(\text{Fe},\text{Cr})_4\text{O}_{11}$ to hematophanite is

$$\begin{aligned} h &= \frac{1}{2}(h' + k') \\ k &= \frac{1}{2}(-h' + k') \\ l &= 2l' \end{aligned}$$

When the powder pattern reported by Johnson (1960) is indexed on the hematophanite cell, the observed interplanar spacings are within ~ 2 percent of the calculated ones. Moreover, when the observed intensities for $\text{Ca}_4(\text{Fe,Cr})_4\text{O}_{11}$ and hematophanite (single crystal data) are compared, the correspondence in relative magnitudes is very good. It therefore seems probable that these two phases are closely related structurally with Ca and Pb playing the same structural role in a perovskite-like subcell.

The author has attempted to determine the structure of hematophanite using $\text{CuK}\alpha$ and $\text{FeK}\alpha$ intensity data gathered on a single crystal diffractometer. Using the simple model implied by the cell parameters, that is four PbFeO_3 perovskite-like cells stacked one on top of the other, conventional R-factors as low as 19 percent were obtained. The structure was refined in both $P4/mmm$ and $P4mm$, but the R-factor could not be reduced below this value. Since the usual methods of attack have not revealed any errors in the trial model, no further progress has been possible. This may be a case of twinning and if so would not be resolvable by x-ray diffraction alone.

The trial structure is related to a number of perovskite derivative structures, all composed of a congruent "vertical" stacking of perovskite-like subcells. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (Aurivillius, 1949), for example, is orthorhombic, pseudotetragonal $I4/mmm$ with $a=3.84$ and $c=32.83$ Å. Strunz's listing of hematophanite with the boleite group may have some validity as it appears that some of these phases are also related to perovskite (Rouse, 1970, in press)

The identity of $\text{PbCl}_2 \cdot 4\text{PbO} \cdot 2\text{Fe}_2\text{O}_3$ and hematophanite remains in doubt. The synthetic phase contains one extra PbO and no (OH,Cl) relative to the hematophanite formula derived here. It is, in fact, unclear just how Pawlek and Berger determined the composition of their product. That the two phases are not the same chemically is suggested by intensity differences between corresponding reflections in their powder patterns. These same differences appear when hematophanite single crystal intensities are used.

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