SUBSTITUTIONS OF THE TYPE $(Sb_{0.5}{}^{5+}Fe_{0.5}{}^{3+})\rightleftarrows(Ti^{4+})$: THE CRYSTAL STRUCTURE OF MELANOSTIBITE

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Abstract

Melanostibite, $Mn^{2+}(Sb_{0.5}{}^{5+}Fe_{0.5}{}^{3+})O_3$, is shown to be fully disordered and isostructural with members of the ilmenite-pyrophanite group on the basis of three-dimensional crystal structure analysis. Pertinent cell data are $a_{hex}=5.226$ Å, $c_{hex}=14.325$ Å, $R\bar{3}$, $Z=6$. Atom coordinates are (6)Mn: O, O, $0.1378\pm.0002$; (6)(Sb Fe): O, O, 0.3473 ± 0.0001; and (18) O, 0.2873 ± 0.0016, -0.0252 ± 0.0016, 0.2559 ± 0.0005. Sb^{5+}, if present in ilmenite— or rutile-bearing ores, may be concealed by the coupled substitution $(Sb_{0.5}{}^{5+}Fe_{0.5}{}^{3+})\rightleftarrows(Ti^{4+})$.

Introduction

Melanostibite was one of many new minerals described for the first time by L. J. Iglestrom (1893) during the course of his studies on the mineralogy of the Sjö Mine, Grythyttan, Örebro Province, Sweden. Originally named "melanostibian," its status as a mineral species was uncertain until recently, when a detailed crystallochemical investigation was undertaken on type specimens by Moore (1968) (Table 1). The mineral was renamed *melanostibite* to conform to present mineral nomenclature. It was shown that melanostibite is a member of the important hematite-ilmenite-pyrophanite group of minerals and that the composition is nearly Mn_2SbFeO_6.

Experimental Procedure

Several small crystal fragments of type material were singled out for study on the basis of their propitious shapes and dimensions. Most of the crystals were found to be not single but aggregates twinned by rotation on c {0001}. Only two crystals were found suitable for study after seeking matched diffraction spectra through successive 120° rotation of the crystals about c [0001]. Alignment was facilitated by the perfect c

TABLE 1. STRUCTURE CELL DATA FOR MELANOSTIBITE

a_{hex}	5.226 Å
c_{hex}	14.325
a_{rhomb}	5.648 ± 0.005 Å
c_{rhomb}	55°08′
Density (calc.)	5.63 g/cc
Z_{rhomb}	2
Space group	$R\bar{3}$
Formula	$Mn^{2+}(Sb_{0.5}{}^{5+}Fe_{0.5}{}^{3+})O_3$

{0001} cleavage (or parting) planes. Throughout this study the triply primitive hexagonal coordinate system was used.

One crystal, nearly a cube in shape of 0.00077 mm³ volume, yielded 249 independent diffraction spectra of the *hk0* to *hk,20* levels. Intensities were gathered on a manual Weissenberg geometry counter-diffractometer employing Zr-filtered Mo radiation. The data were then processed to obtain F_{obs} after a suitable polyhedral transmission correction was applied.
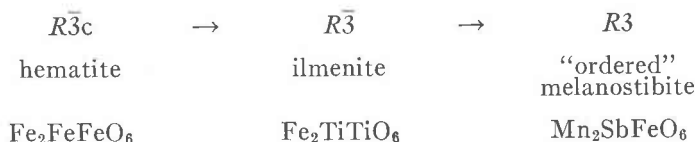
SOLUTION OF THE STRUCTURE

The three possible space groups $R\bar{3}$, $R3$, and $R32$ could not be distinguished by X-ray diffraction spectra alone. The space group $R32$ was eliminated because it cannot accommodate structures of the ilmenite type. Two models were then tested by a full-matrix atomic coordinate-isotropic temperature factor refinement. Atomic parameters for ilmenite in Wyckoff (1964) were used initially. The first model assumed complete ordering of Sb and Fe with the subsequent space group $R3$. Since ilmenite is centrosymmetric $R\bar{3}$, Ti has equivalent positions of the type $(00z, 00\bar{z})$. Atoms were placed in the following manner, referring to the ilmenite structure: $Mn(1)$ $(00z)_{Fe}$, $Mn(2)$ $(00\bar{z})_{Fe}$, $Sb(00\bar{z})_{Ti}$, $Fe(00\bar{z})_{Ti}$, $O(1)$ $(xyz)_O$, $O(2)$ $(\bar{x}\bar{y}\bar{z})_O$. The free parameters were allowed to vary. After five cycles, R_{hkl} converged to 0.120. The isotropic temperature factors were unrealistic: Fe was negative and Sb was positive but large. This suggested an arrangement of partial to complete disorder of (Sb+Fe) over the Ti sites in ilmenite as the temperature factors effectively added electron density at the Fe site and subtracted electron density from the Sb site. Further convergence of the refinement was hindered by the fact that the scattering curve for Sb is not congruent over $(\sin\theta/\lambda)$ to that of Fe.

The fully disordered model has space group $R\bar{3}$ and the following atomic substitutions over an asymmetric unit of ilmenite are: $Mn\rightarrow Fe$, $(Sb_{0.5}+Fe_{0.5})\rightarrow Ti$, $O\rightarrow O$. Scattering curves were prepared for Mn^+, $(Sb_{0.5}^{3+}+Fe_{0.5}^{2+})$, and O^- from International Tables for X-ray Crystallography, Vol. III (1962). Refinement converged to $R_{hkl}=0.086$ and after removal of five strong reflections showing extinction followed by two more cycles, $R_{hkl}=0.060$, all shifts being within their limits of error. The atomic coordinates and isotropic temperature factors are given in Table 2 and the F(obs)–F(calc) data are given in Table 4.[1] The reasonable temperature factors demonstrate that this model is correct and it may be further stated that melanostibite is close to a pure stoichiometric compound,

[1] Table 4 has been deposited as Document No. 9982 with the American Documentation Institute, Auxiliary Publications Department, Photoduplication Service, Library of Congress, Washington, D.C., 20540. Copies may be secured by citing the document numbers, and remitting in advance $1.25 for photographs or $1.25 for 35 mm microfilm.

its formula being written $Mn(Sb_{0.5}Fe_{0.5})O_3$, isostructural with pyrophanite and ilmenite.

It may be remarked that if melanostibite were fully ordered, there would exist an interesting series of progressive symmetry loss

$R\bar{3}c$	$\rightarrow$	$R\bar{3}$	$\rightarrow$	$R3$
hematite		ilmenite		"ordered" melanostibite
Fe_2FeFeO_6		Fe_2TiTiO_6		Mn_2SbFeO_6

DISCUSSION OF THE STRUCTURE

The structures of the hematite-ilmenite group consist of gibbsite-type layers stacked six high normal to the c-axis. Successive layers are obtained by inversion of the octahedra through centers of their horizontal faces

TABLE 2. MELANOSTIBITE. ATOMIC COORDINATES AND
ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	$B(Å^2)$
Mn	0	0	0.1378(2)	0.50(4)
Sb+Fe	0	0	.3473(1)	0.22(2)
O	0.2873(16)	−0.0252(16)	.2559(5)	0.59(9)

and by 60° rotation of the layers about any three-fold axis (Blake, *et al.*, 1966).

Each octahedron in melanostibite shares three of its edges with other octahedra within a gibbsite layer and one face with an octahedron in a successive layer. The polyhedral distances for each of the two non equivalent octahedra include two independent metal-oxygen distances and four independent oxygen-oxygen edge distances: those associated with the shared face, those with the shared edges, those with unshared edges, and those with unshared edges opposite the shared face. These distances are summarized in Table 3 and the two polyhedra are shown in Figure 1.

The distortions observed for the Mn-O and (Sb Fe)-O octahedra closely parallel those observed for hematite as noted by Blake, *et al.* (1966). The metal-O distances toward the shared faces are considerably longer than those toward the opposing unshared faces. The O-O distances are consistent with cationic repulsions, with the edges on shared faces <shared edges<unshared edges. Finally, the larger Mn-O octahedron suffers more relative distortion than the (Sb Fe)-O octahedron.

TABLE 3. POLYHEDRAL DISTANCES FOR MELANOSTIBITE

Mn-O			(Sb Fe)-O	
(3) Mn-O	2.309 Å		(3) (Sb Fe)-O	2.049 Å
(3) MnO^I	2.110		(3) (Sb Fe)-O^{IV}	1.967
aver.	2.209 Å		aver.	2.008 Å
O-O Distances			O-O Distances	
(3) O-O^{II}	2.722	edges on shared face	(3) O-O^{II}	2.722
(3) O-O^I	3.118	shared edges	(3) O^{II}-O^{IV}	2.761
(3) O^I-O^{II}	3.150	unshared edges	(3) O-O^{IV}	2.873
(3) O^I-O^{III}	3.343	unshared edges opposite shared face	(3) O^{IV}-O^V	3.225
aver.	3.083 Å		aver.	2.895 Å

Estimated errors: Me-O ± 0.011 Å, O-O ± 0.016 Å

The mean Mn-O and (Sb Fe)-O distances of 2.209 Å and 2.008 Å respectively are entirely consistent with the formal charge interpretation: $Mn^{2+}(Sb_{0.5}^{5+}Fe_{0.5}^{3+})O_3$.

DISCUSSION ON THE (Sb^{5+} Fe^{3+}) COUPLE

It was suggested by Moore (1968) that substitutions involving Sb^{5+}, Fe^{3+}, and Ti^{4+} are possible if ionic crystal radii alone are considered. Numerous reported crystal structure analyses show that Me-O distances
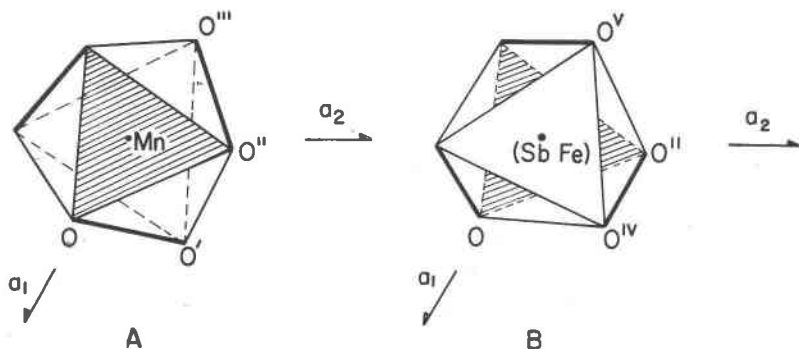

FIG. 1. Polyhedral diagram of (A) the Mn-O octahedron and (B) the (Sb Fe)-O octahedron in the crystal structure of melanostibite. The shared faces are ruled and shared edges in the gibbsite layers are drawn bold. Labelling of the symmetry equivalent oxygen atoms correspond to those cited in the text.

range from 1.98 to 2.02 Å for Sb^{5+} and Fe^{3+} and 1.92 to 1.98 Å for Ti^{4+} when the oxygen coordination is octahedral. It is possible then, that a substitution of the general type $[Sb_{0.5x}^{5+} Fe_{0.5x}^{3+} Ti_{1-x}^{4+}]^{4+}$ may exist.

The existence of melanostibite in nature has interesting implications augmented by the fact that another important compound with this type of substitution exists in the laboratory, having never been reported from a natural occurrence. This is $(Sb_{0.5} Fe_{0.5})O_2$, shown by Brandt (1943) to be a rutile structure. It was synthesized by heating $Fe_2O_3 + Sb_2O_3$ for seven days at 1300°C. Ordering of Fe and Sb in this compound can be easily tested since the diagonal glide plane would be lost and the great difference in the scattering powers of Fe and Sb would result in noticeable superstructure lines on powder photographs. These were not observed by Brandt.

It would appear likely that $(Sb_{0.5} Fe_{0.5})^{4+}$ substitutions for Ti^{4+} in other structure types may be possible at least where Ti atoms occur in fairly regular octahedral coordination. In certain cases, however, Ti^{4+} does not occur in regular octahedra but in hybrid coordination best described as square pyramidal with a sixth oxygen atom displaced at a much greater distance. This is demonstrated in the crystal structure of narsarsukite, $Na_2(TiO)(Si_4O_{10})$, as determined by Peacor and Buerger (1962), where there are (4)Ti-O 1.966, (1)Ti-O 1.904, and (1)Ti-O 2.070 Å. The existence of Ti^{4+} in square pyramidal coordination is offered by Moore and Louisnathan (1967) for fresnoite, $Ba_2(TiO) (Si_2O_7)$. Consequently, it is suggested that if routine syntheses of (Sb Fe) isotypes of Ti^{4+} compounds are contemplated, a close look at the Ti-O polyhedra may be instructive. To my knowledge, there are no examples of oxygen square pyramidal coordination about Fe^{3+} or Sb^{5+} in structures other than represented by organometallic compounds or coordination complexes with forced ligancy.

Information on the geochemistry of Sb^{5+} in moderately high to high temperature assemblages is scanty. There are but few occurrences where Sb^{5+} forms its own minerals such as complex oxides or antimoniosilicates. The Sjö Mine and the nearby Långban and Nordmark orebodies are such localities and the antimony minerals occur associated with the ores, in skarn assemblages, and in low temperature hydrothermal parageneses. All these orebodies include hematite-magnetite-braunite-hausmannite ores.

Based on the evidence offered here, it is reasonable that the ilmenite structure type could accommodate Sb^{5+} via the coupled substitution mentioned previously; hence, Sb^{5+}, if present, may be concealed in the Mn-Fe oxide ores in ilmenite-type structures.

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