

Structural Investigation of a New Iron Germanate $\text{Fe}_8\text{Ge}_3\text{O}_{18}$

V. AGAFONOV, A. KAHN, D. MICHEL, AND M. PEREZ Y JORBA

*Laboratoire de Chimie Appliquée de l'Etat Solide—UA 302 CNRS, CECM
15 rue G. Urbain, 94407 Vitry, France*

Received July 29, 1985

The complete structure of $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ (monoclinic, space group $P2_1/c$, $Z = 2$) has been determined from X-ray diffraction data on single crystals grown by chemical vapor transport. Oxygen atoms form an array of six close-packed layers ABACBC. Iron ions are located in octahedral sites, whereas the six germanium ions of the unit-cell are distributed on four tetrahedral and two octahedral positions.

© 1986 Academic Press, Inc.

Introduction

New compounds have been previously reported by one of us in the Fe_2O_3 - GeO_2 system (1). Fe_2GeO_5 is isomorphous with kyanite and is stable in a limited range of temperature (950–1050°C). Another phase with a larger amount of Fe_2O_3 is stable from room temperature to 1150°C, but its structure and precise composition were still unknown. In addition, a metastable phase Fe_4GeO_8 can be prepared as an intermediate product from dehydration of coprecipitates. Its powder diagram has been indexed with a hexagonal unit-cell with parameters similar to that of the molybdenum compounds $\text{M}_2\text{Mo}_3\text{O}_8$ ($M = \text{Fe}, \text{Ni}, \text{Co}, \text{Zn}, \text{Cd}$) (2).

Recently, single crystals obtained from chemical vapor transport confirmed the existence of the two stable phases Fe_2GeO_5 and $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ (3). For this last compound, the definite composition $4\text{Fe}_2\text{O}_3 \cdot 3\text{GeO}_2$ has been established by electron microprobe and neutron activation analyses. Its crystal symmetry is monoclinic with the fol-

lowing unit-cell parameters $a = 8.754(2) \text{ \AA}$, $b = 5.110(1) \text{ \AA}$, $c = 14.280(3) \text{ \AA}$, $\beta = 101.80(2)^\circ$.

The present paper reports the structural features of $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ obtained from single crystal data.

Experimental

Most of the crystals grown by CVT are twinned and form pseudo-hexagonal platelets. Fortunately, some rod-like small crystals are untwinned and suitable for structural studies. All experimental details on the crystal selected for intensities measurements are gathered in Table I.

Approximate atomic coordinates of cations have been determined from a Patterson map. Refinements were then performed to determine the site occupancy and atomic positions. The relative positions of the oxygen atoms were determined as follows.

When considering the theoretical density of the kyanite-type Fe_2GeO_5 compound ($D_c = 5.05 \text{ g/cm}^3$) and that of $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ ($D_c = 5.03 \text{ g/cm}^3$) it can be assumed that this

TABLE I
CRYSTALLOGRAPHIC DATA AND STRUCTURE
REFINEMENT PARAMETERS

Crystal size	Needle-like crystal (50 × 50 × 200 μm)
Lattice constants	Monoclinic symmetry Space group $P2_1/c$ $Z = 2$ $a = 8.754$ (2) Å $b = 5.110$ (1) Å $\beta = 101.80$ (2)° $c = 14.280$ (3) Å
Density	$D_o = 5.0 \pm 0.1$ g/cm ³ $D_c = 5.03$ g/cm ³
Data collection	C.A.D. 3 Enraf-Nonius diffractometer with graphite monochromator $\lambda_{MoK\alpha} = 0.7109$ Å $3 < \theta < 35^\circ$ $\sin \theta/\lambda_{max.} = 0.81$ $-10 \leq h \leq 10$ $0 \leq k \leq 8$ $0 \leq l \leq 20$
Data corrections	1900 measured reflections of which 594 unobserved with $I < 3\sigma(I)$ Lorentz and polarization effects. Absorption corrections based on the crystal morphology: $\mu_{MoK\alpha} = 168$ cm ⁻¹
Resolution of the structure	Patterson and Fourier syntheses Atomic scattering factors from Cromer and Waber (Int. Tables for Crystallography, 1974, Vol. IV) Refinement: adaptation of ORXFLS routine from Busing, Martin, and Levy (1973)
Agreement factor R	$R = 0.039$ (with 1306 reflections)

compound also consists of a close-packed oxygen network, as the kyanite does.

From the assumption of an ideal anionic lattice having the same volume as $Fe_8Ge_3O_{18}$, it is possible to derive a correspondence between the experimental unit-cell and a theoretical one made of six packed layers of oxygen atoms (interatomic distances $d \approx 2.9$ Å). This correspondence is given in Table II and involves 36 oxygen atoms which determine 36 octahedral and 72 tetrahedral sites where the 22 cations are to be distributed.

The conditions limiting the observed reflections lead to a unique group $P2_1/c$:

$$\begin{aligned} hkl & \text{ no conditions} \\ h0l & l = 2n \\ 0k0 & k = 2n \end{aligned}$$

This group contains a general set of Wyckoff positions (4e) and four different special positions on inversion centers. Therefore,

among the 22 cations, at least two will be necessarily set on a special position with fixed coordinates. We have then arbitrarily set a cation on the unit-cell origin (2a position) because the four special positions are equivalent after translation. This determines the relative position of the oxygen sublattice with regard to this fixed cation.

From the Patterson map, a model has been drawn for the distribution of cations on five different general positions (5×4 atoms) and on one 2a position (2 atoms). All correspond to octahedral environments except one (4e) set of tetrahedral sites.

A perfectly ordered structure would be obtained by setting the six germanium atoms in the (4e) group of tetrahedral sites plus two in (2a) octahedral ones, and the sharp decrease of the value of the R agreement factor in the first steps of refinement indicated that this model was nearly correct. Nevertheless, a fully satisfactory agreement between observed and calculated intensities could not be obtained. The R factors remained too high (8–10%) in following steps and the thermal factors were especially bad for two sets of atoms. B values were too high for the 2a Oct (1) position and too low for the 4e Oct (2). This suggested that the 2a position is at least partly occupied by lighter atoms (iron), whereas some germanium atoms are to be found on Oct (2) sites. It appeared that the assignment of germanium atoms to the 4e tetrahedral positions was correct. Therefore, the

TABLE II
COMPARISON WITH AN IDEAL UNIT-CELL BUILT FROM THE STACKING OF SIX DENSE PLANES WITH OXYGEN-OXYGEN SPACING 2.9 Å

Ideal unit-cell	Actual unit-cell
$a = 3d \rightarrow a = 8.70$ Å	$a = 8.754$ Å
$b = d\sqrt{3} \rightarrow b = 5.03$ Å	$b = 5.110$ Å
$c = 5d \rightarrow c = 14.50$ Å	$c = 14.280$ Å
$\beta = \cos^{-1}\left(\frac{1}{2\sqrt{6}}\right) \rightarrow \beta = 101.8^\circ$	$\beta = 101.8^\circ$

TABLE III
FINAL POSITIONAL PARAMETERS OF $\text{Fe}_8\text{Ge}_3\text{O}_{18}$

	x	y	z	B (\AA^2)
Oct(1)—Fe (1)	0	0	0	0.41(2)
Oct(2)—M (2) (2.7 Fe + 1.3 Ge)	0.5388(1)	0.1878(2)	0.1801(1)	0.32(1)
Oct(3)—M (3) (3.3 Fe + 0.7 Ge)	0.9134(2)	0.1841(3)	0.1824(1)	0.33(2)
Oct(4)—Fe (4)	0.3370(2)	-0.0614(3)	0.0024(1)	0.31(1)
Oct(5)—Fe (5)	0.2793(2)	0.1678(3)	0.3393(1)	0.32(2)
Tetr. —Ge	0.7900(1)	-0.0252(2)	0.3791(1)	0.33(1)
O (1)	0.1912(8)	-0.2119(14)	0.0728(5)	0.54(5)
O (2)	0.3558(8)	0.2882(14)	0.0846(5)	0.53(6)
O (3)	0.0378(8)	0.2982(14)	0.0885(5)	0.52(5)
O (4)	0.5401(8)	-0.1101(15)	0.0880(5)	0.64(5)
O (5)	0.6931(9)	0.3280(14)	0.1007(5)	0.63(5)
O (6)	0.8484(8)	-0.1006(15)	0.0842(6)	0.72(6)
O (7)	0.0843(8)	0.0214(14)	0.2637(5)	0.64(5)
O (8)	0.2523(8)	0.5086(14)	0.2489(5)	0.53(5)
O (9)	0.4267(8)	0.0191(14)	0.2618(5)	0.72(6)

distribution of 16 iron and 2 germanium atoms among the 18 available octahedra has been reconsidered.

Occupancy factors were refined, assuming an initial statistical occupation and using an average scattering factor (16 Fe + 2 Ge)/18. It results in the following effective distribution of cations:

—the positions Oct (1), Oct (4), Oct (5) are only occupied by Fe

—Oct (2) and Oct (3) are shared by Fe and Ge.

TABLE IV
ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$)

	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Fe (1)	5	37	8	-1	2	-4
M (2)	4	25	7	-1	2	0
M (3)	4	25	7	0	1	-1
Fe (4)	3	31	7	-2	1	2
Fe (5)	5	27	8	-1	2	0
Ge	6	28	7	1	1	0
O (1)	17	25	8	3	2	9
O (2)	11	44	10	7	3	-2
O (3)	17	32	9	-10	1	-5
O (4)	4	104	7	-2	1	5
O (5)	20	35	11	5	3	3
O (6)	0	108	12	1	2	3
O (7)	14	52	10	-4	2	4
O (8)	11	49	8	0	2	-2
O (9)	20	63	9	5	3	-2

With this cation distribution, satisfactory values of R and B factors were obtained with a few more steps of refinement. The final value of R is 0.039 for the atomic pa-

TABLE V
PRINCIPAL INTERATOMIC DISTANCES IN
 $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ (IN \AA)

Fe (1)—O	Ge—O
2 Fe (1) — O (3) : 1.964(7)	Ge — O (3) : 1.737(7)
2 Fe (1) — O (6) : 2.031(8)	Ge — O (1) : 1.737(7)
2 Fe (1) — O (1) : 2.084(7)	Ge — O (2) : 1.754(8)
	Ge — O (8) : 1.798(7)
Mean value:	Mean value:
Fe(1) — O = 2.03	Ge — O = 1.76
M (2) — O	M (3) — O
(M (2) = 2.7 Fe + 1.3 Ge)	(M (3) = 3.3 Fe + 0.7 Ge)
M (2) — O (9) : 1.880(8)	M (3) — O (7) : 1.886(7)
M (2) — O (9') : 1.882(7)	M (3) — O (7') : 1.889(7)
M (2) — O (2) : 1.948(6)	M (3) — O (3) : 1.980(8)
M (2) — O (4) : 2.013(8)	M (3) — O (6) : 2.020(8)
M (2) — O (5) : 2.061(8)	M (3) — O (8) : 2.110(8)
M (2) — O (8) : 2.110(7)	M (3) — O (5) : 2.168(7)
Mean value:	Mean value:
M(2) — O = 1.98	M(3) — O = 2.00
Fe (4) — O	Fe (5) — O
Fe (4) — O (1) : 1.938(8)	Fe (5) — O (5) : 1.930(7)
Fe (4) — O (4) : 1.957(7)	Fe (5) — O (7) : 1.971(7)
Fe (4) — O (5) : 1.984(7)	Fe (5) — O (9) : 2.013(8)
Fe (4) — O (6) : 2.007(7)	Fe (5) — O (4) : 2.048(7)
Fe (4) — O (4') : 2.040(8)	Fe (5) — O (6) : 2.084(9)
Fe (4) — O (2) : 2.125(7)	Fe (5) — O (8) : 2.152(7)
Mean value:	Mean value:
Fe(4) — O = 2.01	Fe(5) — O = 2.03

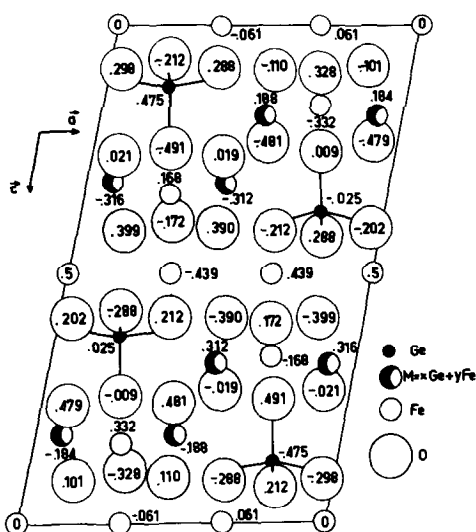


FIG. 1. Projection along [010] of the $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ structure. Tetrahedral GeO_4 groups are indicated.

rameters and thermal factors given in Tables III and IV.

Description of the $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ Structure

A projection of $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ on the plane (010) is shown on Fig. 1. Main interatomic distances are gathered in Table V.

GeO_4 tetrahedra are isolated and rather regular with an average Ge–O distance of 1.76 Å which fits well with the values usually found in tetrahedral GeO_4 groups. The O–Ge–O angles are in the range 106.5–113.6° (average 109.4). In the octahedral sites Oct (1), Oct (4) and Oct (5) occupied with iron the values of Fe–O bond lengths are in the usual range of 2.01–2.03 Å. As expected, slightly shorter distances are found in Oct (2) and Oct (3) sites statistically occupied by Fe and Ge. These values are consistent with Ge–O bond lengths in octahedral coordination which are about 1.90 Å (as, for instance, in GeO_2 rutile).

To our knowledge, the structure of $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ is a new structural type in which octahedra and tetrahedra build up a three-

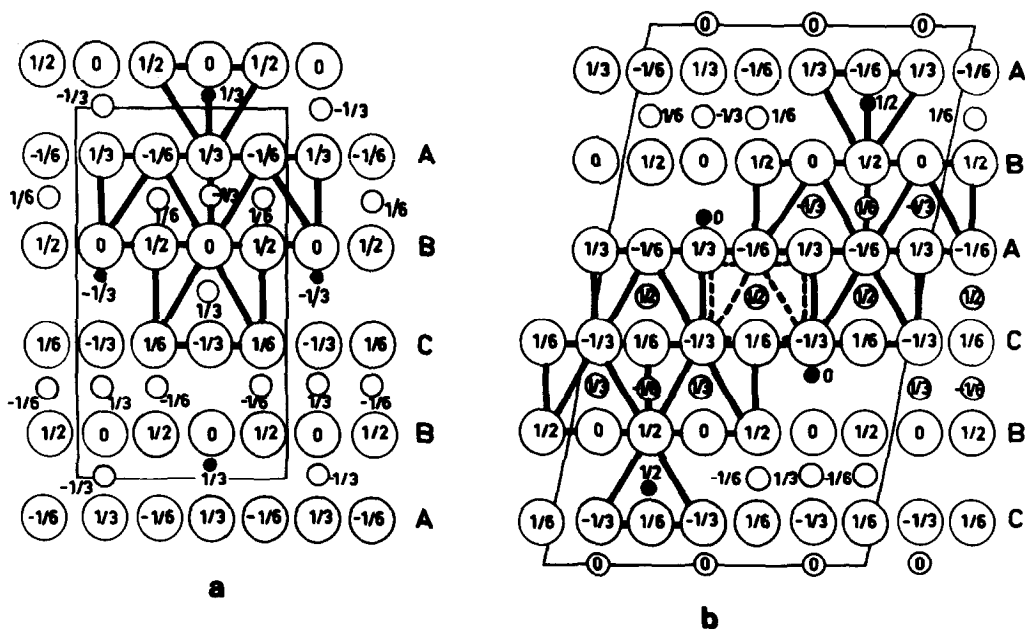


FIG. 2. Idealized projection of the structures of Fe_4GeO_8 ($\text{M}_2\text{Mo}_3\text{O}_8$ -type) (a) and $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ (b). The asymmetric unit of Fe_4GeO_8 consisting of four octahedra and one tetrahedron is underlined. In $\text{Fe}_8\text{Ge}_3\text{O}_{18}$, two similar groups are linked by one octahedron (dashed lines).

dimensional skeleton. Such a structure may be related to that of hexagonal $\text{M}_2\text{Mo}_3\text{O}_8$ compounds which is also that of the metastable phases Fe_4GeO_8 and Ga_4GeO_8 found by Perez y Jorba (1).

In the hexagonal $\text{M}_2\text{Mo}_3\text{O}_8$ structure ($P6_3mc$, $Z = 2$) the oxygen atoms form a double hexagonal network ABCB. The molybdenum atoms are in octahedral sites, the divalent atoms are shared between octahedra and tetrahedra (4). According to Raveau *et al.* (5–7), this may be described as a stacking of blocks built up with four octahedra (3 Mo + 1 M) and one tetrahedron. If we compare the projection of this structure (half unit-cell) on (100) and that of $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ on (010) (Fig. 2), one can see that the last one contains the same kind of blocks (4 Oct + 1 Tet) with a supplementary octahedron every second block. The corresponding stacking of oxygen dense planes is thus ABACBC. The main difference between Fe_4GeO_8 and $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ lies in the arrangement of the GeO_4 tetrahedra:

—In the $\text{M}_2\text{Mo}_3\text{O}_8$ structure, they are all oriented in the same direction along \vec{c} leading to polar materials exhibiting pyroelectric and ferroelectric properties (8, 9).

—In $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ on the contrary, the addi-

tional octahedron (giving an octahedra/tetrahedra ratio of 9/2) is located on an inversion center and two blocks Fe_4GeO_8 are symmetrically set apart from it.

Studies on magnetic behavior are now on way on these iron(III) germanates. $\text{Fe}_8\text{Ge}_3\text{O}_{18}$ exhibits a para \rightarrow antiferromagnetic transition at 230 K. Results on magnetic and Mössbauer properties will be published subsequently.

References

1. M. PEREZ Y JORBA, *Rev. Int. Hautes Temp. Refract.* **6**, 283 (1969).
2. W. H. MCCARROLL, L. KATZ, AND R. WARD, *J. Amer. Chem. Soc.* **79**, 5410 (1957).
3. V. AGAFONOV, D. MICHEL, M. PEREZ Y JORBA, AND M. FEDOROFF, *Mater. Res. Bull.* **19**, 233 (1984).
4. G. B. ANSELL AND L. KATZ, *Acta Crystallogr.* **21**, 482 (1966).
5. J. CHOISNET, M. HERVIEU, B. RAVEAU AND P. TARTE, *J. Solid State Chem.* **40**, 344 (1980).
6. J. CHOISNET, M. HERVIEU, B. RAVEAU, AND P. TARTE, *J. Solid State Chem.* **45**, 280 (1984).
7. J. CHOISNET, M. HERVIEU, B. RAVEAU, AND P. LACORRE, *J. Solid State Chem.* **51**, 44 (1984).
8. D. BETRANAU AND M. KERNER-CZESKLEBA, *J. Phys. (Paris)* **36**, 374 (1975).
9. P. STROBEL, Y. LE PAGE, AND S. P. MCALISTER, *J. Solid State Chem.* **41**, 242 (1982).