Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1304). Services for accessing these data are described at the back of the journal.

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Manganese-rich natural Franklinite

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Abstract

A natural Franklinite has been characterized by X-ray diffraction techniques. The structure was refined in the space group $Fd\bar{3}m$. The almost normal spinel structure was confirmed. All the Zn^{2+} ions are located on tetrahedral sites. The best cation distribution was determined to be $(Zn_{0.65(1)}Mn_{0.35(1)})[Fe_2]O_4$, zinc manganese diiron tetraoxide.

Comment

AB_2O_4 spinels are some of the most studied substances in the solid-state sciences because of their magnetic, optical, dielectric and other properties (Banerjee, 1991; Cornell & Schwertmann, 1996). There are two basic types of spinel structure: if the tetrahedral *T* site is occupied by the divalent cation and the octahedral *M* site is occupied by the trivalent cation, the structure is called normal, and if the *T* site is occupied by the trivalent cation and the *M* site is occupied by a random arrangement of divalent and trivalent cations, the structure is called inverse spinel (Verwey *et al.*, 1947). An intermediate cation distribution may be represented as $(A_{1-i}B_i)[B_{2-i}A_i]O_4$ (the ( ) and [ ] sets of parentheses refer to *T* and *M* sites, respectively), where *i* is the so-called degree of inversion, which ranges from 0.0 (normal structure) to 1.0 (inverse structure) (Hill *et al.*, 1979). Spinels can also form a series of substitutional solid solutions in which the cation introduced normally replaces a cation of the same charge and similar size. The structure of Franklinite, $ZnMnO_4$, has been determined by X-ray powder diffraction methods (O'Neill, 1992). The structure of some natural Mn-rich spinels have been reported by Lucchesi *et al.* (1997), including the Mn-substituted Franklinite $Zn_{0.34}Mn_{0.30}Mg_{0.02}Al_{0.064}Ti_{0.025}Fe_{2.26}O_4$. This work is part of a project aimed at studying the cation distribution in natural ferrites.

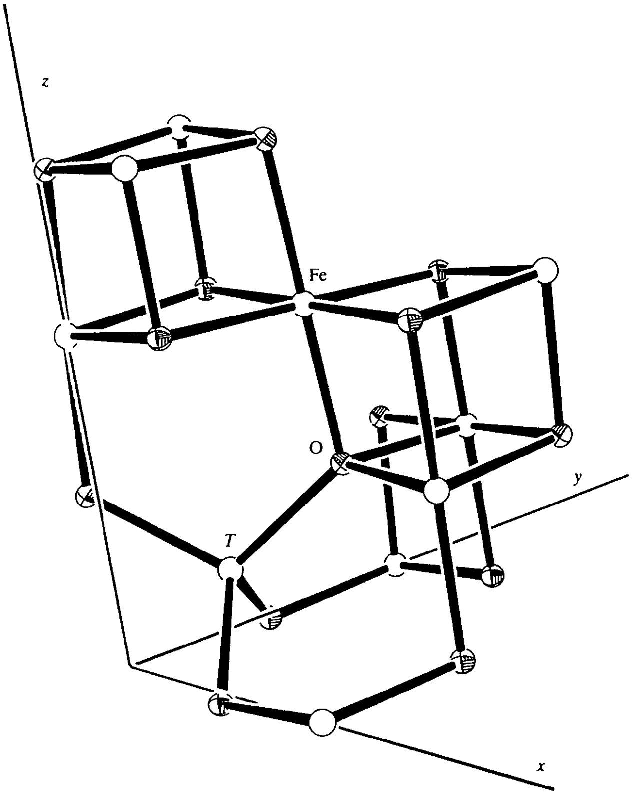

Fig. 1. *ORTEP*III (Burnett & Johnson, 1996) drawing of the structure of Franklinite, showing the atom designation (origin at the inversion center $\bar{3}m$). The Zn^{2+} and Mn^{2+} tetrahedral cations are represented together by the *T* label. $0 < x < \frac{1}{2}$, $0 < y < \frac{1}{2}$ and $0 < z < \frac{3}{4}$ is shown. Ellipsoids are drawn at the 50% probability level.

Experimental

The Franklinite crystals are from the Sterling Hill deposit (Ogdenburg, New Jersey, USA). They were collected by Professor Vochten. The treatment and chemical analysis of the sample were reported by De Grave *et al.* (1996). A single crystal was ground into a sphere.

Crystal data

$(Zn_{0.65}Mn_{0.35})Fe_2O_4$
$M_r = 237.7$
Cubic
$Fd\bar{3}m$
$a = 8.4551\,(3)$ Å
$V = 604.44$ Å^3
$Z = 8$
$D_x = 5.222$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 90 reflections
$\theta = 23.6$–$32.0°$
$\mu = 15.94$ mm^{-1}
$T = 293\,(2)$ K
Spherical
0.06 mm (radius)
Black

Data collection

Siemens *P*4 diffractometer
θ–2θ scans
Absorption correction: spherical (Flack & Vincent, 1978)
$T_{\min} = 0.257$, $T_{\max} = 0.315$
1393 measured reflections
236 independent reflections
235 reflections with $I > 0$

$R_{\rm int} = 0.060$
$\theta_{\max} = 56.76°$
$h = -11 \rightarrow 19$
$k = -11 \rightarrow 19$
$l = -11 \rightarrow 19$
3 standard reflections every 297 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R(F) = 0.017$
$wR(F^2) = 0.026$
$S = 1.30$
236 reflections
9 parameters
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 1.75$ e Å^{-3}
$\Delta\rho_{\min} = -0.98$ e Å^{-3}

Extinction correction: Becker & Coppens (1974), type 1, Gaussian isotropic
Extinction coefficient: 0.100 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C) (Zn^{2+}, Mn^{2+}, Fe^{3+}) and Rez *et al.* (1994) (O^{2-})

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x†	y	z	$U_{\rm eq}$
Fe	1	1/2	1/2	0.5	0.00512 (2)
Mn	0.35 (1)	1/8	1/8	1/8	0.00544 (2)
Zn	0.65 (1)	1/8	1/8	1/8	0.00544 (2)
O	1	0.26103 (4)	0.26103 (4)	0.26103 (4)	0.00547 (3)

† Origin at center ($\bar{3}m$), at ($\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$) from $\bar{4}3m$.

Table 2. *Selected geometric parameters (Å, °)*

Zn,Mn—O	1.9921 (3)	Fe—O$^{\rm i}$	2.0248 (3)
O$^{\rm i}$—Fe—O$^{\rm ii}$	84.60 (1)		

Symmetry codes: (i) $1 - y, \frac{1}{4} + x, \frac{1}{4} + z$; (ii) $\frac{1}{4} + z, 1 - y, \frac{1}{4} + x$.

The structure was refined in space group $Fd\bar{3}m$. It should be mentioned that the 200 reflection forbidden in this space group was observed. Some authors have suggested this intensity is due to multiple reflection conditions (Samuelsen, 1975; Fleet, 1986). De Grave *et al.* (1996) reported the chemical composition as $Zn_{0.68}Mn_{0.36}Fe_{1.96}O_4$. Moreover, from Mössbauer spectroscopy, they concluded that the sample is free of an Fe^{2+} component, however, approximately 0.06 Fe^{3+} cations per formula unit should be located on tetrahedral sites. Therefore, in view of the results, the general formula should be considered to be $(Zn_{0.68-x}Mn_{0.36-y}Fe_{0.06})[Fe_{1.9}Zn_xMn_y]O_4$, where $x + y = 0.1$, in order to maintain the spinel stoichiometry. On the other hand, in an X-ray diffraction experiment, one cannot distinguish between Mn^{2+} and Fe^{3+} since they are isoelectronic. Therefore, several models were tested, two of which are: (i) $(Zn_xMn_y)[Fe_yZn_z]O_4$; this refinement gave an unrealistic negative value for the occupancy for Zn^{2+} on the octahedral site, which means that there is no Zn^{2+} on the octahedral site; (ii) $(Zn_xMn_y)[Fe_2]O_4$, with $x = 0.65\,(1)$, $y = 0.35\,(1)$ and constraints on displacements, $U_{ij}(Zn^{2+}) = U_{ij}(Mn^{2+})$; the refinement gave $R = 0.0174$, $wR = 0.0255$ and $S = 1.30$. In refinements for which the constraints are relaxed on occupancy and displacements, the stoichiometry is retained and they provide similar discrepancy factors, even in a refinement in which Mn^{2+} and Fe^{3+} are partitioned on both sites, *i.e.* tetrahedral and octahedral. In this way, refinement (ii) seems to be the best model for cation distribution obtained in this X-ray diffraction experiment. It means that this system has almost a normal spinel structure. From this point of view, the results of this work agree with those reported by De Grave *et al.* (1996).

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *XS* in *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *JANA'*98 (Petricek & Dusek, 1998). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Tl_2MoO_4 at 350 K

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Abstract

The structure of the title compound, dithallium molybdate, is isotypical with the glaserite structure and Tl_2WO_4. The Mo ion is coordinated tetrahedrally by oxygen, with bond lengths ranging from 1.699 (16) to 1.725 (16) Å, and angles between 107.6 (4) and 111.3 (4)°. The shortest O–O edge length is 2.83 (2) Å. Three independent Tl ions are observed in the structure. The coordination polyhedron around Tl1 can be described as a distorted octahedron, with Tl—O distances of 2.769 (10) Å. Tl2 has a coordination number of 12, with six O atoms at a distance of 2.941 (10) Å and the remaining six at a distance of 3.622 (10) Å. The polyhedron around Tl3 is formed by ten O atoms, with distances ranging between 2.467 (16) and 3.682 (16) Å. The observed bond distances in Tl_2MoO_4 are in good agreement with those in Tl_2WO_4.

Comment

Tl_2MoO_4 was first investigated by Gaultier & Pannetier (1972), who found three phase transitions, presumably all of first order, at temperatures of 776, 673 and 311 K. The lattice parameters given at room temperature are a = 7.919 (5), b = 11.026 (7) and c = 6.179 (5) Å, in space group *Pnam*. Above 323 K, the structure is supposed to be trigonal in space group $P\bar{3}m$, with lattice parameters a = 6.257 (3) and c = 8.085 (4) Å. These authors further reported that the phase transition at 673 K leads to the destruction of the crystals. Later investigations (Sleight *et al.*, 1975) reaffirmed that Tl_2MoO_4 at 298 K is orthorhombic, although the authors reported the non-centrosymmetric space group $Pna2_1$ with similar lattice parameters. They could only observe the phase transitions at 310 and 772 K and did not detect that at 673 K. They also presumed the intermediate phase to have space group $P\bar{3}m$ and proposed the space group $P6_3/mmc$ for the high-temperature phase.

Our investigations corroborate the space group $P\bar{3}m$ for the intermediate phase, which we measured at 350 K. The refinement of the structure shows it to be isostructural with glaserite, $K_3Na(SO_4)_2$ (Okada & Ossaka, 1980), and with Tl_2WO_4 (Okada *et al.*, 1979).

In Tl_2MoO_4 (Fig. 1), the Mo ions are coordinated tetrahedrally by the O atoms, with bond lengths ranging from 1.699 (16) to 1.725 (16) Å, and angles between 107.6 (4) and 111.3 (4)°.

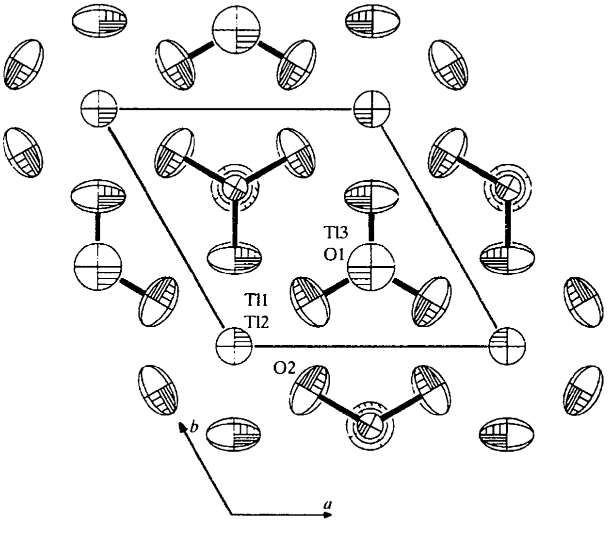

Fig. 1. The a,b projection of the structure of Tl_2MoO_4. Displacement ellipsoids are drawn at the 50% probability level.

As pointed out by Moore (1973), in the glaserite structure, and consequently in Tl_2MoO_4, three different monoivalent cations can be observed. These are now discussed.