The Canadian Mineralogist
Vol. 34, pp. 1287-1297 (1996)

NEŽILOVITE, A NEW MEMBER OF THE MAGNETOPLUMBITE GROUP, AND THE CRYSTAL CHEMISTRY OF MAGNETOPLUMBITE AND HIBONITE

VLADIMIR BERMANEC
Mineraloško-petrografski zavod, Geološki odsjek, Prirodoslovno-matematickog fakulteta, Sveučilišta u Zagrebu, Demetrova 1, Zagreb, Croatia

DAN HOLTSTAM[1]
Sektionen för mineralogi, Naturhistoriska riksmuseet, Box 50 007, SE-104 05 Stockholm, Sweden

DARKO STURMAN
Department of Mineralogy, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6

ALAN J. CRIDDLE
Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

MALCOLM E. BACK
Department of Mineralogy, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6

STJEPAN ŠĆAVNIČAR
Mineraloško-petrografski zavod, Geološki odsjek, Prirodoslovno-matematickog fakulteta, Sveučilišta u Zagrebu, Demetrova 1, Zagreb, Croatia

ABSTRACT

Nežilovite, ideally $PbZn_2(Mn^{4+},Ti^{4+})_2Fe_8O_{19}$, is a newly recognized member of the magnetoplumbite group from Nežilovo, FYR Macedonia. It forms black, magnetic crystals up to 1 mm with a tabular, hexagonal outline. Electron-microprobe analyses yielded PbO 19.01, CaO 0.03, Sb_2O_5 0.25, ZnO 13.23, Fe_2O_3 41.96, Mn_2O_3 7.13, MnO_2 11.01, TiO_2 2.84, Al_2O_3 4.52, MgO 0.08, total 100.06 wt.%. The mineral is optically anisotropic and bireflectant. Reflectance values (R_o%) obtained in air and oil are: 23.8, 10.0 (470 nm), 22.4, 8.8 (546 nm) 21.7, 8.3 (589 nm) and 20.7, 7.7. (650 nm). D_{calc} = 5.69(1) g·cm^{-3} and VHN_{25} = 735. The strongest reflections in the powder XRD pattern [d in Å (I/I_0)(hkl)] are: 3.811(100)(006), 2.858(75)(008), 2.745(50)(107), 11.39(45)(002), 2.605(40)(114) and 1.636(30)(0,0,14). The crystal structures of natural magnetoplumbite [a 5.902(2), c 23.185(8) Å], hibonite [a 5.613(1), c 22.285(8) Å] and nežilovite [a 5.849(1), c 22.809(2) Å] have been refined in the space group $P6_3/mmc$ to R indices of 6.9%, 5.3% and 4.5%, respectively, using Mo$K\alpha$ single-crystal X-ray-diffraction data. The general formula for the magnetoplumbite-group minerals is $A^{[6]}(M1)^{[5]}(M2)^{[4]}(M3)_2{}^{[6]}(M4)_2{}^{[6]}(M5)_6O_{19}$, with Z = 2. An important common feature is the tendency of M^{2+} and $M^{4+,5+}$ ions, hosted by these minerals, to order onto the $M3$ and $M4$ sites, respectively; for nežilovite, almost complete occupancy of $M3$ by Zn is demonstrated, which forms the basis for naming a new species. Al^{3+} strongly prefers $M1$. Mössbauer spectral data show that nežilovite is paramagnetic at room temperature; they also support the present model of cation distribution.

Keywords: magnetoplumbite, hibonite, nežilovite, new mineral species, cation ordering, Mössbauer spectrum, FYR Macedonia.

SOMMAIRE

La nežilovite, de composition idéale $PbZn_2(Mn^{4+},Ti^{4+})_2Fe_8O_{19}$, est un membre nouvellement établi du groupe de la magnétoplumbite, découvert à Nežilovo, en République macédonienne de l'ancienne Yougoslavie. Elle se présente en cristaux noirs et magnétiques, en tablettes hexagonales atteignant le millimètre. Les analyses à la microsonde électronique ont donné: PbO 19.01, CaO 0.03, Sb_2O_5 0.25, ZnO 13.23, Fe_2O_3 41.96, Mn_2O_3 7.13, MnO_2 11.01, TiO_2 2.84, Al_2O_3 4.52, MgO 0.08,

---

[1] *E-mail address:* mi-dan@nrm.se

total 100.06% (en poids). Le minéral est optiquement anisotrope et biréflectant. Les valeurs de la réflectance (R_0%), mesurées dans l'air et dans l'huile, sont: 23.8, 10.0 (470 nm), 22.4, 8.8 (546 nm) 21.7, 8.3 (589 nm) and 20.7, 7.7. (650 nm). D_{calc} = 5.69(1) g·cm^{-3} et VHN_{25} = 735. Les raies les plus intenses du cliché de diffraction X (méthode des poudres) [*d* en Å (I/I_0)(*hkl*)] sont: 3.811(100)(006), 2.858(75)(008), 2.745(50)(107), 11.39(45)(002), 2.605(40)(114) et 1.636(30)(0,0,14). Les structures cristallines de la magnétoplumbite naturelle [*a* 5.902(2), *c* 23.185(8) Å], hibonite [*a* 5.613(1), *c* 22.285(8) Å] et nežilovite [*a* 5.849(1), *c* 22.809(2) Å] ont été affinées par diffraction X sur cristaux uniques dans le groupe spatial $P6_3/mmc$, jusqu'à un résidu *R* de 6.9, 5.3 et 4.5%, respectivement, en utilisant un rayonnement Mo*K*α. La formule générale des minéraux du groupe de la magnétoplumbite est $A^{[6]}(M1)^{[5]}(M2)^{[4]}(M3)_2{}^{[6]}(M4)_2{}^{[6]}(M5)_6O_{19}$, avec $Z = 2$. Dans ces minéraux, les ions M^{2+} et $M^{4+,5+}$ ont une tendance à se concentrer dans les sites *M*3 et *M*4, respectivement; dans le cas de la nežilovite, nous montrons que le Zn occupe presque uniquement la position *M*3, ce qui nous permet de la proposer comme espèce nouvelle. Par contre, Al^{3+} montre une forte préférence pour les sites *M*1. Les spectres de Mössbauer montrent que la nežilovite est paramagnétique à température ambiante; les implications de ces données spectroscopiques appuient notre modèle de la distribution des cations.

(Traduit par la Rédaction)

Mots-clés: magnetoplumbite, hibonite, nežilovite, nouvelle espèce minérale, mise en ordre des cations, spectre de Mössbauer, République macédonienne de l'ancienne Yougoslavie.

INTRODUCTION

The present study started with the discovery of an unusually Zn-rich magnetoplumbite-related mineral from Nežilovo, FYR Macedonia (Bermanec *et al.* 1993) and new compositional data obtained for magnetoplumbite (Holtstam 1994a). Following a structural description of the zincian phase (Bermanec & Šćavničar 1993), a proposal for a new mineral with the name nežilovite was submitted to the Commission on New Minerals and Mineral Names (CNMMN) of the IMA and approved (CNMMN #94–020). Parts of the holotype specimen are preserved in the collections of the Natural History Museum, Zagreb (catalog #600:ZAG;8425MP1), Royal Ontario Museum, Toronto (#M46312) and the Swedish Museum of Natural History, Stockholm (#940002).

The structure of magnetoplumbite-group minerals, of general formula $AM_{12}O_{19}$, was originally solved by Adelsköld (1938), and subsequently refined by Obradors *et al.* (1985) and Moore *et al.* (1989), among others. It is based on ten layers of approximately closest-packed oxygen atoms perpendicular to **c** in the hexagonal cell. Two of these layers contain large *A* cations (usually Pb, Ba, Sr or Ca) proxying for every fourth oxygen atom. The sequence can be expressed as (·*chhhcchhhc*·), where *c* and *h* symbolize cubic and hexagonal closest-packed layers, respectively. The small M^{3+} ions are distributed over five independent interstitial sites, three with octahedral, one with tetrahedral and one with trigonal bipyramidal (5-fold) coordination. The cubic close-packed layers constitute blocks that have the spinel ($S = [M_6O_8]^{2+}$) structure. These are interlayered between blocks having the hexagonal close-packed character R (= $[AM_6O_{11}]^{2-}$). Thus the repeat is written *RSR'S'*, where *R'* and *S'* are rotated 180° around **c** relative the two first blocks. The structure type is an essential element in the members of the prolific hexagonal ferrite family (*e.g.*, Kohn *et al.* 1971).

A variety of cations is accommodated by magnetoplumbite (Burke 1980, Holtstam 1994a) and the isotypic mineral hibonite (Maaskant *et al.* 1980), which normally deviate significantly from their ideal end-member compositions ($PbFe_{12}O_{19}$ and $CaAl_{12}O_{19}$, respectively). With the rare exception of some meteoritic examples of hibonite (Allen *et al.* 1980), magnetoplumbite-group minerals are found to contain significant amounts of divalent as well as tetravalent and pentavalent cations occupying interstitial *M* sites. The mantle-derived phases yimengite, $K[Ti_3Cr_5Fe_2Mg_2]O_{19}$ (Dong *et al.* 1983), and hawthorneite, $Ba[Ti_3Cr_4Fe_4Mg]O_{19}$ (Haggerty *et al.* 1989), are examples of highly substituted members.

The formal description of the new mineral has been complemented with crystal-structure refinements of magnetoplumbite (Långban, Sweden) and hibonite (Madagascar) to obtain additional information about the intracrystalline behavior of the different cations in the members of crustal origin.

EXPERIMENTAL

The chemical composition of hibonite from Madagascar (Royal Ontario Museum catalogue #M23764) was determined by means of electron-microprobe analyses performed at the Canadian Museum of Nature on a JEOL 733 electron microprobe with Tracor Northern Task automation at an operating voltage of 15 kV and a beam current of 20 nA. Synthetic chrysoberyl was used as a standard for Al, rutile for Ti, diopside for Mg, Ca and Si, almandine for Fe, and rare-earth-element (*REE*) phosphate for the *REE*. The sample was also checked for U, K, Ba, Pb, Mn, Zn, Cr, Pr and Gd, which were found to be below the detection limit. Chemical data for magnetoplumbite (#910051 in Holtstam 1994a) and nežilovite (Bermanec *et al.* 1993) have been obtained by electron-microprobe analysis as well. The chemical formulae were calculated on the basis of 13 cations (Tables 1A, B).

X-ray-diffraction data sets were collected up to 30°θ on a Philips 1100 single-crystal diffractometer using filtered Mo*K*α radiation. Intensity data were empirically corrected for absorption with the ψ-scan method. Data reduction, including corrections for background, Lorentz and polarization effects, was performed by the SDP program system (Enraf–Nonius 1983). Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1974), and the refinements were done in the space group $P6_3/mmc$ with the program SHELX–76 (Sheldrick 1976) using the atomic positions of Moore *et al.* (1989) as a starting point. A unit-weight weighting scheme was employed. The choice of the space-group symmetry is fully supported by the outcome of the structural refinements and is in agreement with previous studies. Further experimental details are given in Table 2.

Reflectance spectra of nežilovite were obtained with spectrophotometric measurements (10-nm intervals) performed at normal incidence in air and oil (Zeiss, N_D = 1.515). Silicon carbide (Zeiss no. 472) was used as a standard.

A spectrometer system comprising, *i.a.*, a ^{57}Co(Rh) source with a nominal strength of 50 mCi, a proportional counter and a multi-channel analyzer, was used to obtain ^{57}Fe transmission Mössbauer data for nežilovite. Two mirror-image spectra with a velocity span of ±4.3 mm/s were collected at room temperature over 1024 channels. The Fe concentration of the powder absorber (mineral + transoptic powder) was ~3 mg/cm^2. An α-iron foil was used for velocity calibration and as centroid-shift reference. Spectra were reduced (folded) and fitted using new versions of the MDR and MDA programs (Jernberg & Sundqvist 1983). Owing to software and computer limitations, the final analysis was carried out on a spectrum with 256 "channels" (data points).

TABLE 1A. CHEMICAL DATA FOR NEŽILOVITE (1) AND MAGNETOPLUMBITE (2)

	wt.% oxide			cations	
	1	2		1	2
PbO	19.01	18.02	Pb	0.99	0.98
BaO	0.00	0.36	Ba	0.00	0.02
CaO	0.03		Ca	0.01	-
Sb_2O_5	0.25	7.66	Sb	0.02	0.58
ZnO	13.23	0.10	Zn	1.89	0.01
Fe_2O_3	41.96	61.40	Fe	6.11	9.34
MnO		5.35	Mn^{2+}	-	0.92
Mn_2O_3	7.13	5.73	Mn^{3+}	1.05	0.88
MnO_2	11.01		Mn^{4+}	1.47	-
TiO_2	2.84	0.10	Ti	0.41	0.02
Al_2O_3	4.52	0.00	Al	1.03	0.00
MgO	0.08	0.84	Mg	0.02	0.25
Total	100.06	99.56		13.00	13.00

Provenance of the samples: nežilovite is from Nežilovo, FYR Macedonia and magnetoplumbite is from Långban, Sweden.

TABLE 1B. REPRESENTATIVE RESULTS OF CHEMICAL ANALYSES OF HIBONITE

anal. no.	7	14	38	65	68	72	95	mean
				wt.% oxide				
CaO	7.12	7.03	6.67	7.00	6.87	6.82	6.07	6.80
MgO	2.79	2.74	2.92	3.24	3.24	3.29	2.71	2.99
La_2O_3	0.52	0.49	0.82	0.60	0.69	0.57	1.72	0.77
Ce_2O_3	0.90	1.04	1.43	1.02	1.14	1.17	2.41	1.30
Nd_2O_3	0.33	0.00	0.31	0.00	0.33	0.00	0.35	0.19
Fe_2O_3	3.27	3.40	3.36	3.29	3.30	3.31	3.07	3.29
Al_2O_3	78.01	78.45	77.40	75.97	76.88	76.66	78.32	77.38
TiO_2	5.04	5.16	5.37	6.61	6.51	6.72	4.24	5.66
SiO_2	0.59	0.57	0.48	0.43	0.40	0.40	0.49	0.48
ThO_2	1.21	1.20	1.11	0.93	0.78	0.97	0.72	0.99
Total	99.78	100.08	99.87	99.09	100.14	99.91	100.10	99.85
				formula proportions*				
Ca^{2+}	0.89	0.87	0.84	0.88	0.86	0.85	0.76	0.85
Mg^{2+}	0.49	0.47	0.51	0.57	0.56	0.57	0.47	0.52
La^{3+}	0.02	0.02	0.04	0.03	0.03	0.02	0.07	0.03
Ce^{3+}	0.04	0.04	0.06	0.04	0.05	0.05	0.10	0.06
Nd^{3+}	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.01
Fe^{3+}	0.29	0.30	0.30	0.29	0.29	0.29	0.27	0.29
Al^{3+}	10.72	10.74	10.69	10.53	10.56	10.55	10.85	10.66
Ti^{4+}	0.44	0.45	0.47	0.58	0.57	0.59	0.37	0.50
Si^{4+}	0.07	0.07	0.06	0.05	0.05	0.05	0.06	0.06
Th^{4+}	0.03	0.03	0.03	0.02	0.02	0.03	0.02	0.03

*based on 13 cations.

TABLE 2. CRYSTAL STRUCTURE ANALYTICAL DATA

	Nežilovite	Magnetoplumbite	Hibonite
a (Å)	5.849(1)	5.902(2)	5.613(1)
c (Å)	22.809(2)	23.185(8)	22.285(8)
V (Å^3)	675.8(2)	699.4(6)	608.0(5)
Z	2	2	2
Temperature (K)	100	298	298
Total no. of refl.	1375	1973	3747
Unique refl. $I > 3\sigma(I)$	268	453	391
Anisotropic thermal parameters for	Pb, M5, O1, O2, O3	Pb, M3, M4, M5, O1, O2	all atoms
Final *R*	0.045	0.069	0.053

RESULTS

General description of nežilovite

Nežilovite occurs in pink dolomitic marble from a Precambrian metamorphic complex of gneisses, schists and marbles in the Nežilovo area (the so-called "Mixed Series"), belonging to the Pelagonian massif. The mineral is associated with plagioclase, chlorite, phlogopite, cymrite, talc, piemontite, barite, hedyphane, braunite, gahnite, franklinite and hematite. It was discovered, together with the other phases listed, in the residue after acid-treatment (0.05 M HCl) of pieces of the marble. The paper of Bermanec *et al.* (1993) offers more details on the locality. The crystals are about 0.2 to 1 mm in size. They are thin tabular on {0001} and have subordinate hexagonal prism faces. The simple habit resembles that of hematite, but nežilovite has a dark brown or nearly black streak and is magnetic. Cleavage is prominent parallel to (0001). The microhardness (VHN_{25}) value is 735 (range 599–847).

Nežilovite is opaque, black, and without visible internal reflections. It is anisotropic, bireflectant and nonpleochroic. Reflectance values obtained on an isotropic section of the mineral are shown in Table 3. The overall reflectance is somewhat lower than that of magnetoplumbite (Criddle & Stanley 1993), a uniaxial, optically negative mineral, and there is also a slight difference in the dispersion (Fig. 1).

TABLE 3. REFLECTANCE DATA (R_O%) FOR NEŽILOVITE

λ (nm)	air	oil	λ (nm)	air	oil
400	25.7	11.6	560	22.2	8.7
420	25.1	11.1	580	21.8	8.5
440	24.7	10.7	589	21.7	8.3
460	24.1	10.2	600	21.5	8.2
470	23.8	10.0	620	21.1	8.0
480	23.5	9.7	640	20.8	7.8
500	23.1	9.5	650	20.7	7.7
520	22.8	9.2	660	20.6	7.6
540	22.5	8.9	680	20.3	7.5
546	22.4	8.8	700	20.2	7.4

Results of electron-microprobe analyses show that there is little intragranular variation in composition, which is significantly different from that of magnetoplumbite (Table 1A). A substantial amount of Mn^{4+} must be assumed to be present to charge-balance the formula. The weight loss experienced during thermal experiments, earlier erroneously interpreted as a dehydration reaction (Bermanec *et al.* 1993), possibly reflects a reduction of MnO_2.

The powder X-ray-diffraction pattern of nežilovite is given in Table 4. It is a hexagonal mineral, space-group symmetry $P6_3/mmc$, with the unit-cell parameters *a* 5.854(1), *c* 22.882(6) Å, *V* 679.1(5) Å^3

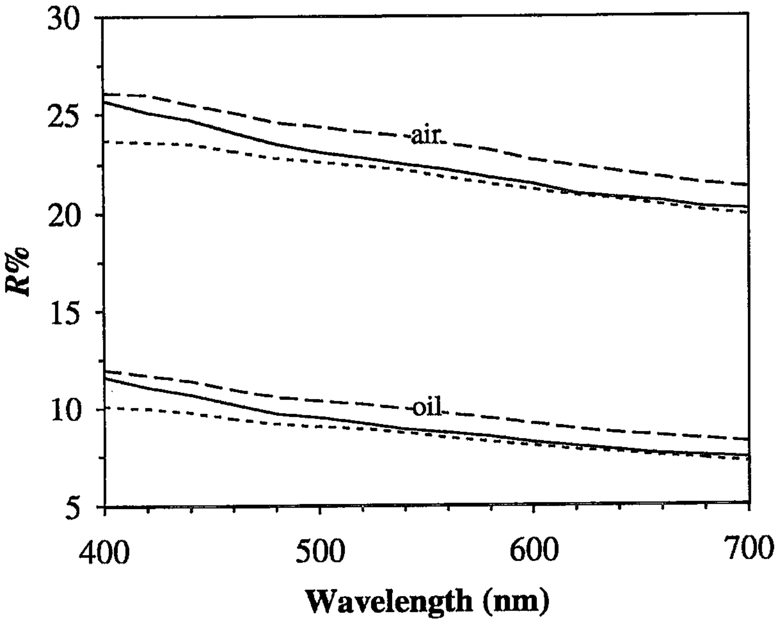

FIG. 1. Reflectance spectra of nežilovite (solid line) and magnetoplumbite (broken lines).

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR NEŽILOVITE

d_{obs} (Å)	I_{obs}	d_{calc} (Å)*	*h*	*k*	*l*
11.39	45	11.44	0	0	2
5.69	15	5.72	0	0	4
5.06	1	5.07	1	0	0
4.95	10	4.95	1	0	1
4.63	8	4.63	1	0	2
4.22	5	4.22	1	0	3
3.811	100	3.814	0	0	6
3.396	5	3.397	1	0	5
3.085	1	3.048	1	0	6
2.925	20	2.927	1	1	0
2.858	75	2.860	0	0	8
2.745	50	2.747	1	0	7
2.605	40	2.606	1	1	4
2.534	5	2.535	2	0	0
2.518	<1	2.519	2	0	1
2.491	1	2.491	1	0	8
2.473	1	2.475	2	0	2
2.407	25	2.406	2	0	3
2.287	5	2.288	0	0	10
2.275	<1	2.273	1	0	9
2.218	10	2.217	2	0	5
2.110	8	2.111	2	0	6
2.087	1	2.086	1	0	10
1.9240	8	1.9245	1	0	11
1.9058	5	1.9095	2	1	1
		1.9068	0	0	12
1.8561	1	1.8584	2	1	3
1.7999	5	1.8027	1	1	10
		1.7951	2	0	9
1.6940	2	1.6985	2	0	10
		1.6899	3	0	0
1.6545	10	1.6531	2	1	7
1.6361	30	1.6344	0	0	14
1.6208	5	1.6207	3	0	4
1.6089	10	1.6080	2	0	11
1.5535	1	1.5556	1	0	14
1.4633	10	1.4635	2	2	0

* calculated on the basis of the refined hexagonal unit-cell parameters a = 5.854(1) Å and c = 22.882(6) Å.

(refined from the powder data), and $Z = 2$. The calculated density, based on the above unit-cell volume and the empirical chemical formula (Table 1A), is 5.69(1) g/cm^3.

Data for hibonite and magnetoplumbite

About 100 electron-microprobe analyses were performed on hibonite (Table 1B) in order to study the pattern of chemical zoning. The more significant variations are found for the Mg, Ca, Ti and *REE* contents. There are no large differences between the present and earlier data for Madagascar hibonite (Maaskant *et al.* 1980, Rakotondrazafy *et al.* 1996), but the crystal-chemical details deserve more attention. Total iron is given as Fe_2O_3, although it is clear that a portion of the element is in the divalent state. This is evidenced by the stoichiometric relations (assuming full occupancy of O positions) and by recent spectroscopic measurements on similar material (Holtstam 1996). The magnetoplumbite sample (data based on nine point-analyses) is rich in Mn, Sb and Mg. To obtain electroneutrality in the formula, Mn must be partitioned between the tri- and divalent states.

The main chemical variations of the members of the magnetoplumbite group can be described by the general schemes of substitution $M'^{3+} = M^{3+}$ (*e.g.*, Fe = Al), $M^{2+} + M^{4+} = 2M^{3+}$ and $2M^{2+} + M^{5+} = 3M^{3+}$. For hibonite, there is also some replacement in the *A* position *via* coupled $REE^{3+} + M^{2+} = Ca^{2+} + Al^{3+}$ (*cf.* Rakotondrazafy *et al.* 1996). The chemical data also seem to indicate nonstoichiometry in the hibonite sample studied, manifested as a deficiency in *A*-type cations. Comparable results were recorded by Santosh *et al.* (1991) for *REE*-rich as well as *REE*-poor compositions of zoned, terrestrial hibonite. High-resolution transmission electron microscopy studies of meteoritic hibonite indicate that this kind of nonstoichiometry could be related to stacking disorder (Keller 1991), but the possibility of vacancies cannot be dismissed. In the present study, we have not been able to resolve this question. If, however, Th^{4+} is also assigned to *A*, which is justifiable on the basis of its ionic size and well-known preference for higher coordination geometries, the average deficiency is only 0.02 atoms per formula unit (*apfu*) and could not be expected to have a dramatic effect on the X-ray data.

Parts of the hibonite crystals show irregular optical zoning. In thin sections cut parallel to the **c** axis, there are in some cases twin-like lamellar structures, the different lamellae extinguishing in slightly different positions. Precession photographs of fragments with these features, however, indicated that they are single crystals. There is also no discernable chemical variation that correlates with this zonation.

Crystal-structure refinements

Cell parameters refined from the single-crystal diffraction data are given in Table 2, along with the final *R* values. The unit-cell volume of magnetoplumbite is slightly greater than that of nežilovite; the most important chemical differences that could explain this fact are the higher contents of Al and Zn and lower contents of Fe and Mn^{2+} in nežilovite. The relatively poor result of the refinement of magnetoplumbite is in part due to an imperfect crystal, with many minute solid inclusions present; the sample was selected on the basis of its composition rather than on the quality of the crystal.

TABLE 5. ATOM COORDINATES AND THERMAL PARAMETERS FOR THE REFINED STRUCTURES

	W	*S*	*x*	*y*	*z*	B_{eq}
Nežilovite						
Pb	2*d*		2/3	1/3	1/4	7.5
M1	2*a*	17.2	0	0	0	0.6
M2	4*e*	25.2	0	0	0.2590(4)	0.2
M3	4*f*	29.2	1/3	2/3	0.0272(1)	0.5
M4	4*f*	26.0	2/3	1/3	-0.1893(1)	0.5
M5	12*k*	23.8	0.1677(3)	0.3354(5)	-0.1063(1)	0.2
O1	4*e*		0	0	0.1512(8)	2.1
O2	4*f*		1/3	2/3	-0.0598(8)	0.6
O3	6*h*		0.361(4)	0.180(2)	3/4	3.1
O4	12*k*		0.145(1)	0.290(2)	0.0523(4)	0.8
O5	12*k*		0.5024	-0.5024(1)	0.3511(4)	1.1
Magnetoplumbite						
Pb	2*d*		2/3	1/3	1/4	7.4
M1	2*a*	29.7	0	0	0	0.3
M2	4*e*	28.3	0	0	0.2587(4)	0.6
M3	4*f*	28.0	1/3	2/3	0.0262(2)	0.7
M4	4*f*	38.3	2/3	1/3	-0.1895(2)	0.6
M5	12*k*	28.7	0.1667(3)	0.3335(6)	-0.1076(1)	0.6
O1	4*e*		0	0	0.1523(8)	1.6
O2	4*f*		1/3	2/3	-0.0585(8)	0.8
O3	6*h*		0.375(4)	0.188(2)	3/4	0.9
O4	12*k*		0.151(1)	0.301(2)	0.0532(4)	0.7
O5	12*k*		0.503(5)	-0.503(5)	0.3490(4)	0.9
Hibonite						
Ca	2*d*		2/3	1/3	1/4	2.8
M1	2*a*	13.0	0	0	0	0.5
M2	4*e*	12.9	0	0	0.2379(5)	1.1
M3	4*f*	13.7	1/3	2/3	0.0271(1)	0.7
M4	4*f*	14.7	2/3	1/3	-0.1889(1)	0.8
M5	12*k*	13.0	0.1679(2)	0.3358(4)	-0.1071(1)	0.4
O1	4*e*		0	0	0.1481(3)	0.7
O2	4*f*		1/3	2/3	-0.0565(3)	0.8
O3	6*h*		0.362(4)	0.181(2)	3/4	2.3
O4	12*k*		0.1531(4)	0.3063(8)	0.0520(4)	1.0
O5	12*k*		0.5043(5)	-0.5043(5)	0.3508(2)	0.9

W = Wyckoff notation of point position. *S* = refined site scattering power/site multiplicity (e^-). B_{eq} (Å^2) values are calculated according to Hamilton (1959).

TABLE 6. SELECTED BOND DISTANCES (Å) IN NEŽILOVITE, MAGNETOPLUMBITE AND HIBONITE

Nežilovite

	A	M1	M2	M3	M4	M5
O1			1 × 2.047(18)			1 × 1.983(10)
O1'			[1 × 2.46(2)]			
O2				1 × 1.985(8)		1 × 1.985(9)
O3	6 × 2.928(1)		3 × 1.840(18)		3 × 2.077(14)	
O4		6 × 1.894(9)		3 × 1.989(9)		2 × 2.018(9)
O5	6 × 2.845(7)				3 × 1.946(4)	2 × 1.932(9)
average:	2.886	1.894	1.892	1.988	2.012	1.978

Magnetoplumbite

	A	M1	M2	M3	M4	M5
O1			1 × 2.064(21)			1 × 1.994(10)
O1'			[1 × 2.47(2)]			
O2				1 × 1.964(9)		1 × 2.048(10)
O3	6 × 2.959(1)		3 × 1.932(18)		3 × 2.043(14)	
O4		6 × 1.976(11)		3 × 1.966(9)		2 × 2.061(10)
O5	6 × 2.840(12)				3 × 1.951(14)	2 × 1.966(10)
average:	2.900	1.976	1.965	1.966	1.997	2.016

Hibonite

	A	M1	M2	M3	M4	M5
O1			1 × 2.000(14)			1 × 1.871(4)
O1'			[1 × 2.54(2)]			
O2				1 × 1.864(4)		1 × 1.965(5)
O3	6 × 2.810(0)		3 × 1.779(8)		3 × 2.013(6)	
O4		6 × 1.886(4)		3 × 1.838(5)		2 × 1.990(5)
O5	6 × 2.745(5)				3 × 1.883(5)	2 × 1.850(4)
average:	2.778	1.886	1.834	1.844	1.948	1.919

A table of the observed and calculated structure-factors is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Table 5 shows the final atomic positional parameters for all three samples investigated, and in Table 6 the most relevant metal–O bond distances are given. The nežilovite data of Bermanec & Šćavničar (1993) are reproduced here for the sake of completeness. The refined scattering powers for each site (Table 5) show that the *M*3 and *M*4 sites have accommodated the comparatively heavier elements, *i.e.*, Zn (nežilovite), Sb (magnetoplumbite), Fe and Ti (hibonite).

The *A* site is almost completely occupied by Pb in magnetoplumbite and nežilovite; Ba and Ca are only minor substituents. The Ca–*REE* substitution in hibonite is reflected in a high site-scattering value (22.0 e^-).

Mössbauer data

The Mössbauer spectrum of nežilovite consists of two resolved pairs of lines, fitted to two doublets (Fig. 2). The χ^2 value converged at 1.9. The hyperfine parameters CS (centroid shift), QS (quadrupole splitting) and Γ (line width) obtained for the subspectra are given in Table 7. Uncertainties are probably less than ±0.02 mm/s. The intensities are given as the specific absorption-area relative to the total absorption-area.

TABLE 7. ^{57}Fe MÖSSBAUER PARAMETERS FOR NEŽILOVITE

Subspectrum	CS	QS	Γ	Intensity
I	0.29	1.73	0.36	11%
II	0.35	0.47	0.35	89%

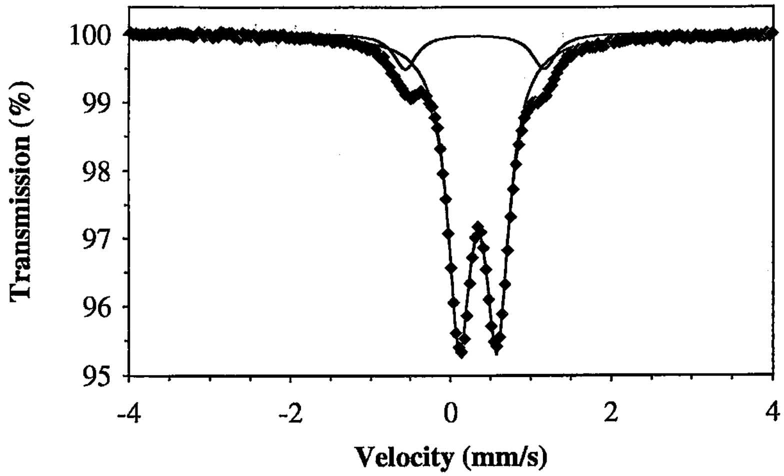

FIG. 2. Room-temperature Mössbauer spectrum of nežilovite.

DISCUSSION

Previously, only the contents of large cations (Ba, Pb, Ca, K) have been used to distinguish the different members of the magnetoplumbite group. There are, however, large variations in the concentrations of metal ions located at the *M* positions, which affect the properties of these compounds (cell dimensions, optical properties, magnetic behavior). The high concentration of Zn in the mineral from Nežilovo led us to divide the minerals of the group further. It was suspected that Zn^{2+} is confined to the tetrahedral sites; this has been confirmed by structural refinements (Bermanec & Šćavničar 1993; the present work). In the following, the general chemical-crystallographic properties and cation populations of the different sites are discussed. A table with average bond-distances in the refined structures and related synthetic compounds is given to facilitate the discussion (Table 8).

A site

The *A* site, located in the central part of the *R* blocks, has 12-fold coordination with oxygen, with two independent bond-distances. The average *A*–O contacts seem to be relatively independent of the actual species occupying the site; <*A*–O> is in the range of 2.89–2.91 Å and 2.75–2.78 Å for the ferrites and aluminates, respectively. This merely reflects the rigidity of the closest-packed array. As a consequence, relatively small cations located at this position become underbonded. For $CaAl_{12}O_{19}$, the bond-valence sum

TABLE 8. AVERAGE M–O DISTANCES IN MAGNETOPLUMBITE-TYPE COMPOUNDS

Site	CN	1	2	3	4	5	6	7	8
A	12	2.886	2.900	2.778	2.889	2.900	2.909	2.747	2.781
M1	6	1.894	1.976	1.886	1.968	1.998	2.000	1.879	1.879
M2	4+1*	1.892	1.965	1.834	1.967	1.942	1.932	1.824	1.839
M3	4	1.988	1.966	1.844	1.992	1.888	1.894	1.799	1.806
M4	6	2.012	1.997	1.948	1.986	2.007	2.021	1.906	1.923
M5	6	1.978	2.016	1.919	1.989	2.017	2.028	1.907	1.907

1. nežilovite 2. magnetoplumbite 3. hibonite (this work); 4. hawthorneite (Grey *et al.* 1987); 5. $PbFe_{12}O_{19}$ (Moore *et al.* 1989); 6. $BaFe_{12}O_{19}$ (Obradors *et al.* 1985); 7. $CaAl_{12}O_{19}$ (Utsunomiya *et al.* 1988); 8. $PbAl_{12}O_{19}$ (Iyi *et al.* 1990).

* only the four shortest distances are taken into account.

(Brown & Altermatt 1985) is 1.46 valence units (*vu*), whereas a value much closer to the expected formal charge of the ion is obtained for the Pb analogue (1.97 *vu*).

There is no evidence in any of three refined structures for displacement of the *A* cation from its special position at (⅓, ⅔, ¼), as has been observed in synthetic end-member magnetoplumbite (Moore *et al.* 1989). In fact, this feature, ascribed to lone-pair effects of Pb^{2+} by Moore *et al.* (1989), seems to be restricted to Pb ferrites with a low degree of substitution, such as plumboferrite (Holtstam *et al.* 1995).

M1 site

The *M*1 octahedra, belonging to the *S* blocks, are very regular ($\bar{3}m$ point symmetry). *M*1 is also the smallest six-coordinated site in terms of interatomic distances, with *M*1–O4 ranging from 1.88 Å (aluminate) to 2.00 Å (ferrite). The remarkably short distance (1.89 Å) in nežilovite indicates that this site hosts most of the Al contents of the mineral. The assumption is supported by the site-scattering value obtained (17 e^-). There is no indication of significant replacement of Al at this position in hibonite, either. This behavior of Al seems to be a general property of the group. The ordering of Al has been demonstrated, for example, by structure refinements of powder samples in the $Sr(Al,Fe)_{12}O_{19}$ solid-solution series (Sandiumenge *et al.* 1988) and by recent ^{57}Fe nuclear magnetic resonance studies of Al-substituted synthetic magnetoplumbite (Štěpánková *et al.* 1994). This preference is probably merely a function of ionic size. Note that the incorporation of comparatively large cations (see below) at the neighboring *M*3 site, which also coordinates to O4, is expected to reduce *M*1–O4 distances further. The relatively high scattering value for *M*1 in magnetoplumbite might indicate that a minor fraction of its Sb contents is located here.

M2 site

The *M*2 site is formally a five-coordinated site (trigonal bipyramid, site symmetry $\bar{6}m2$). The central atom, however, is displaced from its invariant position at (0, 0, ¼) and evenly split into two 4*e* sites, located slightly below and above the mirror plane at $z = \pm¼$. Keeping *M*2 fixed in the center of the bipyramid (2*b*) leads to significantly higher *R* values for the refined structures and extreme elongation of the U_{33} component of the anisotropic thermal-vibration parameter. The displacement from *m* is about 0.20 Å for magnetoplumbite and nežilovite, and 0.27 Å for hibonite. The phenomenon has in fact been encountered in all modern refinements of magnetoplumbite-type structures (*e.g.*, Obradors *et al.* 1985, Moore *et al.* 1989, Kimura *et al.* 1990). The interpretation of Mössbauer data for $BaFe_{12}O_{19}$ (Kreber *et al.* 1975; *cf.* Obradors *et al.* 1985) suggests that the disorder is of a dynamic kind, with the cation oscillating between two pseudotetrahedral sites, at least at higher temperatures. Although the Madelung part of the lattice energy (point charges) favors the central location, this is hindered by electronic repulsion between the cation and the equatorial O atoms (Graetsch & Gebert 1994).

The refined site-scattering values of magnetoplumbite, nežilovite and hibonite give little information about the metal contents at this site. However, Mössbauer data for hibonite from Madagascar and Fe^{3+}-doped synthetic compounds (Holtstam 1996) indicate that ferric iron is enriched here. Becket *et al.* (1988) found evidence for the location of Ti^{3+} at this site in meteoritic hibonite. The simplest explanation for this distribution of Fe^{3+} (ionic radius 0.64 Å) and Ti^{3+} (0.67 Å) is that *M*2 is a comparatively large site. The anomalously large displacement of the *M*2 atom in hibonite (the corresponding value for synthetic $CaAl_{12}O_{19}$ is only 0.17 Å) is probably related to the ordering of Fe^{3+}. In this case, the equatorial O3 atoms, located at the corners of a triangle on the mirror plane with a side of only 3.0 Å (compared to 3.3 Å for magnetoplumbite), interact more strongly with the cation. The relatively short *M*2–O distances encountered for nežilovite could suggest incorporation of some Mn^{4+} at this site.

M3 site

*M*3 is a nearly regular tetrahedral site situated at $z \approx 0$ and ½, *i.e.*, in the central section of the *S* blocks. In the natural samples, *M*3 is consistently larger than in the synthetic end-members. This is due to preferential ordering of larger, divalent species, *e.g.*, Zn^{2+} (nežilovite), Mn^{2+} (magnetoplumbite), Mg^{2+} and Fe^{2+} (hawthorneite, hibonite). In hibonite, Fe^{2+} is enriched at this site, as indicated by Mössbauer and optical spectroscopy (Holtstam 1994b, 1996). The marked preference of divalent cations for *M*3 has been confirmed for several synthetic compounds of the same structure type (Gasperin *et al.* 1984, Štěpánková *et al.* 1992, Cabañas *et al.* 1994, Graetsch & Gebert 1995). Such substitutions are electrostatically more favorable than incorporation of more highly charged ions, as could be demonstrated by consideration of Pauling bond-strength sums (Holtstam 1994a) or by calculation of Madelung factors for various hypothetical schemes of cation distribution (Graetsch & Gebert 1995). Note that this factor apparently predominates over the crystal-field effects of the divalent transition-metal cations; even Ni^{2+}, which possesses an exceptionally large octahedral crystal-field stabilization energy (CFSE), shows a marked preference for tetrahedral environment in this structure type (Laville *et al.* 1986).

About 95% of *M*3 (2 *apfu*) in nežilovite is occupied by Zn. The <*M*–O> bond length, 1.988 Å, is in good agreement with the common 0.60 Å radius of $^{[4]}Zn^{2+}$ (Shannon 1976). In magnetoplumbite, the interatomic distance is consistent with assignment of 90–100% of the divalent cations to this site. The Mn^{2+} contents of natural samples of magnetoplumbite, as calculated from the cell stoichiometries, have been found to range between 0.5 and 1.5 *apfu* (Holtstam 1994a). Clearly, some of these samples could have Mn dominant at *M*3. However, a further division of the group based on $^{[4]}Mn$ contents seems impractical at this time.

M4 site

The *M*4 sites are trigonally distorted (3*m*) octahedra that occur in pairs (dimers) with a common face, in an arrangement like in hematite. The *M*4 site scattering factors obtained for magnetoplumbite and hibonite indicate the presence of some heavy atoms at this site. Studies of substituted ferrites, using different experimental techniques, such as Mössbauer spectroscopy (Kreber & Gonser 1976), neutron diffraction (Cabañas *et al.* 1994) and X-ray diffraction (Graetsch & Gebert 1995), have demonstrated the strong preference of highly charged ions for this site. Accordingly, we have assigned Ti^{4+} (hibonite) and Sb^{5+} (magnetoplumbite) to *M*4. It can also be assumed that Mn^{4+}, which also has a large octahedral CFSE (Burns 1993), preferentially occupies this site in nežilovite. Hibonite shows some enrichment of Si^{4+}; by analogy with other tetravalent species, Si might be located at *M*4 as well.

Owing to cation-repulsion effects across the shared face at $z = \pm 1/4$ (*cf.* Pauling 1960), the O–O distance is reduced in the natural magnetoplumbite compared to the parent compound (2.57 *versus* 2.63 Å). There is also an increase in the intermetal *M*4–*M*4 distance for hibonite and magnetoplumbite. This is not observed for nežilovite, which could be due to the small ionic radius of Mn^{4+} (similar to that of Al^{3+}; Shannon 1976).

M5 site

The *M*5 site, located at the interface between the *S* and *R* blocks, is a distorted (*m* point symmetry) octahedral site. In natural minerals, however, the degree of distortion in terms of bond distances is less important than in the synthetic compounds. The shortening of the *M*5–O2 and *M*5–O4 bonds (2.09 and 2.10 Å in $PbFe_{12}O_{19}$, respectively; Moore *et al.* 1989) is a consequence of the incorporation of larger M^{2+} ions at the tetrahedral sites, where the polyhedral expansion occurs at the expense of both *M*1 and *M*5. In hibonite, Al occupies *M*5, and there appears to be little, if any, substitution of the transition elements for Al. For magnetoplumbite and nežilovite, the site population is expected to be more complex. On the basis of average interatomic distances and the site-scattering value, one could expect that a fraction of the Al contents of nežilovite (1.03 *apfu*) is located here. Mn^{3+} possesses a relatively large octahedral CFSE (Burns 1993) and, owing to the Jahn–Teller effect, it should become enriched at a distorted octahedral site like *M*5. Although this cannot be proven directly by the X-ray-diffraction experiments, the bulk of Mn^{3+}, which is a major component in nežilovite and most samples of magnetoplumbite (Holtstam 1994a), is assigned to *M*5. Above a certain concentration, Mn^{3+} will probably force a symmetry change of the sample or lead to breakdown of the crystal.

Trivalent chromium, at most a minor species in magnetoplumbite (Holtstam 1994a) and hibonite (Burns & Burns 1984), is an important constituent of hawthorneite and yimengite. By virtue of its electron configuration (d^3), it is expected to order in the octahedral sites only; it has been confirmed in Mössbauer spectroscopic studies of the $Sr(Fe,Cr)_{12}O_{19}$ series that Cr^{3+} preferentially occupies *M*5 and *M*1 (Rao *et al.* 1979).

Mössbauer characteristics of nežilovite

The relatively small centroid-shift values of the two doublets in nežilovite are characteristic for high-spin Fe^{3+} coordinated by oxygen ligands (*e.g.*, Coey 1984). In agreement with the chemical data (Table 1A), there is no evidence for the presence of Fe^{2+}. The large quadrupole splitting for subspectrum I clearly links it to Fe^{3+} residing at the trigonal bipyramidal *M*2 site. Although regular in terms of angles, the large difference between long axial (*M*–O1) and short equatorial (*M*–O3) bond distances for this coordination polyhedron is expected to create an irregular distribution of charges around the central Fe atom. The X-ray crystallographic data show that the octahedral *M*1 and tetrahedral *M*3 sites are almost filled with Al and Zn, respectively. Thus, our subspectrum II is attributed to Fe^{3+} distributed over the remaining cation positions, *M*4 and *M*5. The fact that they are both distorted octahedral sites, with similar average *M*–O distances, explains why they are unresolved in the Mössbauer spectrum. The anticipated ordering of Fe^{3+} in *M*2 does not seem to be wholly substantiated by the present data (complete ordering would correspond to 1 Fe *apfu*, or 16% of total iron). However, site-occupancy refinements from Mössbauer spectra require that the effective recoil-free fraction (*f*) is essentially the same for all Fe atoms, giving equal probabilities for absorption. This is probably not the case here, where the *M*2 atom is expected to be mobile along [0001], which would give rise to a marked anisotropy of *f*. Such anisotropy has been verified experimentally on single crystals of barium ferrite (Kreber *et al.* 1975), where the Mössbauer effect vanishes for $^{[M2]}Fe$ when the γ-ray propagation direction is collinear with **c**. A conventional interpretation of intensity data would thus lead to an underestimation of the Fe contents at this site. As stated, it is of course possible that *M*2 is partly also occupied by some other cation.

Nežilovite is paramagnetic. The pure ferrites of this structure type (*e.g.*, BaFe$_{12}$O$_{19}$) are normally ferrimagnetic, and their Mössbauer spectra at room temperature are decomposed into a number of sextets (*e.g.*, Kojima 1982). Preliminary data for natural magnetoplumbite (Långban) also indicate an ordered magnetic structure. It is known from studies of synthetic ferrites (*e.g.*, Kreber & Gonser 1976), however, that the Curie temperature is lowered by replacement of Fe^{3+} by other cations. In nežilovite, ferric iron is heavily diluted by species like Zn^{2+}, Mn^{4+}, Al^{3+} and Ti^{4+}, and hence its paramagnetic character. Both magnetoplumbite and nežilovite crystals are attracted by a permanent magnet, but the effect is noticeably weaker for the latter mineral.

CONCLUSIONS

(i) As previously demonstrated for synthetic material, interstitial divalent cations are strongly ordered at the tetrahedral sites of the spinel-like layer in magnetoplumbite-group minerals.
(ii) Nežilovite is the Pb- and $^{[4]}$Zn-dominant ferrite member of the group.
(iii) The introduction of divalent ions is achieved by coupled incorporation of tetravalent and pentavalent cations that are mainly ordered over the octahedral sites in the face-sharing interlayer doublet.
(iv) Tetravalent manganese, a previously unrecognized component of magnetoplumbites *sensu lato,* is present in nežilovite.
(v) The ions with different charges (Zn^{2+}, Mn^{2+}, Ti^{4+}, Sb^{5+}, *etc.*) tend to improve the local charge-balance in the crystal structure, and their absence would make the formation of magnetoplumbite-group minerals in geological environments a less likely event.

ACKNOWLEDGEMENTS

We are grateful to S. Prugovečki, Zagreb, for help with collecting X-ray-diffraction data. We thank R.F. Martin and P.B. Leavens for helpful suggestions on ways to improve the text. The work was supported by the Swedish Natural Science Research Council (NFR).

REFERENCES

ADELSKÖLD, V. (1938): X-ray studies on magneto-plumbite, PbO·6Fe$_2$O$_3$, and other substances resembling "beta-alumina", Na$_2$O·11Al$_2$O$_3$. *Ark. Kem. Mineral. Geol.* **12A**-29, 1-9.

ALLEN, J.M., GROSSMAN, L., LEE, TYPHOON & WASSERBURG, G.J. (1980): Mineralogy and petrography of HAL, an isotopically unusual Allende inclusion. *Geochim. Cosmochim. Acta* **44**, 685-699.

BECKET, J.R., LIVE, D., TSAY FUN-DOW, GROSSMAN, L. & STOLPER, E. (1988): Ti^{3+} in meteoritic and synthetic hibonite. *Geochim. Cosmochim. Acta* **52**, 1479-1495.

BERMANEC, V., BALEN, D., ŠĆAVNIČAR, S. & TIBLJAŠ, D. (1993): Zn-rich magnetoplumbite from Nežilovo, Macedonia. *Eur. J. Mineral.* **5**, 957-960.

________ & ŠĆAVNIČAR, S. (1993): Magnetoplumbite from Nežilovo, Macedonia: crystal structure refinement of zinc-rich magnetoplumbite. *Neues Jahrb. Mineral. Monatsh.*, 481-486.

BROWN, I.D. & ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.

BURKE, E.A.J. (1980): New data on magnetoplumbite from Långban, Sweden. *Neues Jahrb. Mineral. Monatsh.*, 141-148.

BURNS, R.G. (1993): *Mineralogical Applications of Crystal Field Theory.* Cambridge University Press, Cambridge, U.K.

________ & BURNS, V.M. (1984): Crystal chemistry of meteoritic hibonites. *Proc. Lunar Planet. Sci. Conf. 15th, J. Geophys. Res.* **89**, C313-321.

CABAÑAS, M.V., GONZÁLEZ-CALBET, J.M., RODRÍGUEZ-CARVAJAL, J. & VALLET-REGÍ, M. (1994): The solid solution BaFe$_{12-2x}$Co$_x$Ti$_x$O$_{19}$ ($0 \leq x \leq 6$): cationic distribution by neutron diffraction. *J. Solid State Chem.* **111**, 229-237.

COEY, J.M.D. (1984): Mössbauer spectroscopy of silicate minerals. *In* Mössbauer Spectroscopy Applied to Inorganic Chemistry **1** (G.J. Long, ed.). Plenum Press, New York, N.Y. (443-509).

CRIDDLE, A.J. & STANLEY, C.J. (1993): *Quantitative Data File for Ore Minerals* (3rd ed.). Chapman and Hall, London, U.K.

DONG ZHENXIN, ZHOU JIANXIONG, LU QI & PENG ZHIZONG (1983): Yimengite, K(Cr,Ti,Fe,Mg)$_{12}$O$_{19}$, a new mineral from China. *Am. Mineral.* **70**, 218 (abstr.).

ENRAF-NONIUS (1983): *Structure Determination Package (SDP).* Enraf-Nonius, Delft, The Netherlands.

GASPERIN, M., SAINE, M.C., KAHN, A., LAVILLE, F. & LEJUS, A.M. (1984): Influence of *M*$^{2+}$ ions substitution on the structure of lanthanum hexaaluminates with magnetoplumbite structure. *J. Solid State Chem.* **54**, 61-69.

GRAETSCH, H. & GEBERT, W. (1994): Positional and thermal disorder in the trigonal bipyramid of magnetoplumbite structure type SrGa$_{12}$O$_{19}$. *Z. Kristallogr.* **209**, 338-342.

________ & ________ (1995): Cation distribution in magnetoplumbite type SrTi$_6$Co$_6$O$_{19}$. *Z. Kristallogr.* **210**, 9-18.

GREY, I.E., MADSEN, I.C. & HAGGERTY, S.E. (1987): Structure of a new upper-mantle, magnetoplumbite-type phase, Ba[Ti$_3$Cr$_4$Fe$_4$Mg]O$_{19}$. *Am. Mineral.* **72**, 633-636.

HAGGERTY, S.E., GREY, I.E., MADSEN, I.C., CRIDDLE, A.J., STANLEY, C.J. & ERLANK, A.J. (1989): Hawthorneite, $Ba[Ti_3Cr_4Fe_4Mg]O_{19}$: a new metasomatic magnetoplumbite-type mineral from the upper mantle. *Am. Mineral.* **74**, 668-675.

HAMILTON, W.C. (1959): On the isotropic temperature factor equivalent to a given anisotropic temperature factor. *Acta Crystallogr.* **12**, 609-610.

HOLTSTAM, D. (1994a): Mineral chemistry and parageneses of magnetoplumbite from the Filipstad district, Sweden. *Eur. J. Mineral.* **6**, 711-724.

——— (1994b): Optical absorption study of terrestrial hibonite. *Int. Mineral. Assoc., 16th Gen. Meeting (Pisa), Program Abstr.*, 178.

——— (1996): Iron in hibonite: a spectroscopic study. *Phys. Chem. Minerals* **23**, 452-460.

———, NORRESTAM, R. & SJÖDIN, A. (1995): Plumboferrite: new mineralogical data and atomic arrangement. *Am. Mineral.* **80**, 1065-1072.

IBERS, J.A. & HAMILTON, W.C. (1974): *International Tables for X-Ray Crystallography* **IV**. Kynoch Press, Birmingham, U.K.

IYI, N., TAKEKAWA, S. & KIMURA, S. (1990): Refinement of the structure of lead hexaaluminate ($PbAl_{12}O_{19}$). *J. Solid State Chem.* **85**, 318-320.

JERNBERG P. & SUNDQVIST, T. (1983): A versatile Mössbauer analysis program. *Univ. of Uppsala, Inst. of Physics Rep.*, **UUIP-1090**.

KELLER, L.P. (1991): Stacking disorder and non-stoichiometry in meteoritic hibonite. *Eos, Trans. Am. Geophys. Union* **72**, 141 (abstr.).

KIMURA, K., OHGAKI, M., TANAKA, K., MORIKAWA, H. & MARUMO, F. (1990): Study of the bipyramidal site in magnetoplumbite-like compounds. *J. Solid State Chem.* **87**, 186-194.

KOHN, J.A., ECKART, D.W. & COOK, C.F., JR. (1971): Crystallography of the hexagonal ferrites. *Science* **172**, 519-525.

KOJIMA, H. (1982): Fundamental properties of hexagonal ferrites with magnetoplumbite structure. *In* Ferromagnetic Materials **3** (E.P. Wohlfahrt, ed.). North-Holland, Amsterdam, The Netherlands (305-391).

KREBER, E. & GONSER, U. (1976): Determination of cation distribution in Ti^{4+} and Co^{2+} substituted barium ferrite by Mössbauer spectroscopy. *Appl. Phys.* **10**, 175-180.

———, ———, TRAUTWEIN, A. & HARRIS, F.E. (1975): Mössbauer measurements of the bipyramidal lattice site in $BaFe_{12}O_{19}$. *J. Phys. Chem. Solids* **36**, 263-265.

LAVILLE, F., PERRIN, M., LEJUS, A.M., GASPERIN, M., MONCORGE, R. & VIVIEN, D. (1986): Synthesis, crystal growth, structural determination and optical absorption spectroscopy of the magnetoplumbite type compound $LaNiAl_{11}O_{19}$. *J. Solid State Chem.* **65**, 301-308.

MAASKANT, P., COLEN, J.J.M.M.M. & BURKE E.A.J. (1980): Hibonite and coexisting zoisite and clinozoisite in a calc-silicate granulite from southern Tanzania. *Mineral. Mag.* **43**, 995-1003.

MOORE, P.B., SEN GUPTA, P.K. & LE PAGE, Y. (1989): Magnetoplumbite $Pb^{2+}Fe^{3+}{}_{12}O_{19}$: refinement and lone-pair splitting. *Am. Mineral.* **74**, 1186-1194.

OBRADORS, X., COLLOMB, A., PERNET, M., SAMARAS, D. & JOUBERT, J.C. (1985): X-ray analysis of the structural and dynamic properties of $BaFe_{12}O_{19}$ hexagonal ferrite at room temperature. *J. Solid State Chem.* **56**, 171-181.

PAULING, L. (1960): *The Nature of the Chemical Bond.* Cornell Univ. Press, Ithaca, N.Y.

RAKOTONDRAZAFY, M.A.F., MOINE, B. & CUNEY, M. (1996): Mode of formation of hibonite ($CaAl_{12}O_{19}$) within the U–Th skarns from the granulites of S–E Madagascar. *Contrib. Mineral. Petrol.* **123**, 190-201.

RAO, P.M., GÉRARD, A. & GRANDJEAN, F. (1979): A Mössbauer study of the effects of the substitution of Fe by Cr in $SrFe_{12}O_{19}$. *Phys. Status Solidi* **A54**, 529-536.

SANDIUMENGE, F., GALI, S. & RODRÍGUEZ, J. (1988): X-ray profile analysis of cation distribution in $SrAl_xFe_{12-x}O_{19}$ solid solutions. *Mater. Res. Bull.* **23**, 685-692.

SANTOSH, M., SANDIFORD, M. & REED, S.J.B. (1991): Zoned hibonites from Punalur, South India. *Mineral. Mag.* **55**, 159-162.

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

SHELDRICK, G.M. (1976): *SHELX-76: Program for Crystal Structure Determination.* Univ. of Göttingen, Göttingen, Germany.

ŠTĚPÁNKOVÁ, H., ENGLICH, J. & LÜTGEMEIER, H. (1994): NMR study of Ga and Al substituted hexagonal ferrites with magnetoplumbite structure. *IEEE Trans. on Magnetics* **30**, 988-990.

———, KOHOUT, J. & ŠIMŠA, Z. (1992): NMR study of Ti–Co, Ti–Mg and Ti substituted hexagonal ferrites with magnetoplumbite structure. *J. Magn. Magnet. Mat.* **104-107**, 411-412.

UTSUNOMIYA A., TANAKA, K., MORIKAWA, H., MARUMO, F. & KOJIMA, H. (1988): Structure refinement of $CaO{\cdot}6Al_2O_3$. *J. Solid State Chem.* **75**, 197-200.

Received May 3, 1996, revised manuscript accepted July 26, 1996.