

ZENZÉNITE: $Pb_3(Fe^{3+}, Mn^{3+})_4Mn^{4+}_3O_{15}$, A NEW MINERAL SPECIES FROM LÅNGBAN, FILIPSTAD, SWEDEN, AND ITS CRYSTAL STRUCTURE

DAN HOLTSTAM AND BENGT LINDQVIST

Department of Mineralogy, Swedish Museum of Natural History, Box 50007, S-104 05 Stockholm, Sweden

MATS JOHNSON AND ROLF NORRESTAM

Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

ABSTRACT

Zenzénite, ideally $Pb_3(Fe^{3+}, Mn^{3+})_4Mn^{4+}_3O_{15}$, is a new mineral species from Långban, Filipstad, Sweden. It is hexagonal holosymmetric, space group $P6_3/mcm$, with a 10.008(4), c 13.672(8) Å, V 1186(1) Å³ and $Z = 4$. The strongest five observed reflections of the X-ray powder pattern [d in Å(I_{obs})(hkl)] are: 3.18(8)(211), 2.828(7)(114), 2.663(10)(213), 2.366(6)(222) and 1.687(8)(226). Zenzénite is black and opaque, and in polished section it appears white with a weak bireflectance (in oil). The anisotropy is strong. Calculated luminance values ($Y\%$) based on reflectance measurements (10 nm steps) in the visible spectrum (relative to the C illuminant) are 24.8–29.2 (air) and 10.8–14.5 (oil). Cleavage parallel to {001} is prominent. $VHN_{50} = 764$. D_x equals 6.83 g/cm³ for an empirical formula and 6.97 g/cm³ for the ideal with an Fe/Mn³⁺ ratio of 1.6. The structure has been determined and refined with the 372 most significant X-ray reflections with $\sin(\theta)/\lambda \leq 0.65$ Å⁻¹ to $R = 2.8\%$ and shown to be isostructural with synthetic $Pb_3Mn_7O_{15}$. The structure consists of, *inter alia*, layers perpendicular to the [001] direction of edge-sharing coordination octahedra around the Mn(Fe) positions. The Pb positions are located between the layers. Empirical bond-valences estimated from the observed bond-distances suggest that those metal ion positions containing major amounts of tetravalent Mn are located within the layers. The name of this new mineral honors Dr. Nils Zenzén (1883–1959).

Keywords: zenzénite, new mineral species, composition, crystal structure, lead manganese oxide, Långban, Sweden.

SOMMAIRE

La zenzénite, nouvelle espèce minérale découverte à Långban (Filipstad, en Suède), possède la formule idéale $Pb_3(Fe^{3+}, Mn^{3+})_4Mn^{4+}_3O_{15}$. Elle est holosymétrique hexagonale, groupe spatial $P6_3/mcm$, avec a 10.008(4), c 13.672(8) Å, V 1186(1) Å³ et $Z = 4$. Les cinq raies les plus intenses du cliché de poudre [d en Å(I)(hkl)] sont 3.18(8)(211), 2.828(7)(114), 2.663(10)(213), 2.366(6)(222) et 1.687(8)(226). C'est un minéral noir et opaque; en lumière réfléchie, la zenzénite est blanche et montre une faible biréflexance (dans l'huile). L'anisotropie est prononcée. Les valeurs calculées de sa luminance (Y , en %), fondées sur les mesures de sa réflectance (en intervalles de 10 nm) dans la partie visible du spectre (en relation avec l'illuminant C), sont 24.8–29.2 (dans l'air) et 10.8–14.5 (dans l'huile).

Un clivage dans le plan {001} est prominent. $VHN_{50} = 764$; la densité est égale à 6.83 pour une formule empirique et 6.97 pour la formule idéale et un rapport Fe/Mn³⁺ de 1.6. Nous en avons déterminé la structure en utilisant 372 des réflexions les plus intenses ayant $\sin(\theta)/\lambda \leq 0.65$ Å⁻¹, jusqu'à un résidu R de 2.8%. La zenzénite est isostructurale avec le composé synthétique $Pb_3Mn_7O_{15}$. La structure est faite, entre autres, de feuillets perpendiculaires à [001] d'octaèdres qui contiennent les sites Mn(Fe). Les atomes de Pb sont situées entre ces feuillets. Les valeurs empiriques des valences de liaison, déterminées à partir des distances interatomiques, font penser que les positions cationiques où loge le Mn tétravalent se trouvent dans les feuillets. Le nom honore Nils Zenzén (1883–1959).

(Traduit par la Rédaction)

Mots-clés: zenzénite, nouvelle espèce minérale, composition, structure cristalline, oxyde de plomb et de manganèse, Långban, Suède.

INTRODUCTION

The Långban mines, Filipstad, in south-central Sweden, have been a true horn of plenty of new mineral species during the last century (Magnusson 1930, Moore 1970). During the course of an investigation of oxide minerals from the locality, grains of a phase with properties not corresponding to any known mineral were discovered. The new mineral species, zenzénite, was subsequently recognized by the IMA Commission on New Minerals and Mineral Names. The name was selected to honor Dr. Nils Zenzén (1883–1959), mineralogist, geologist and historian of science, who acted as senior curator at the Department of Mineralogy of the Swedish Museum of Natural History (NRM) over the period 1926–1950. Holotype material is preserved at NRM, Stockholm (catalogue no. 401841).

APPEARANCE AND PHYSICAL PROPERTIES

Zenzénite is found in a sample of a carbonate-phyllosilicate skarn rock of a rare kind, collected when the mining operations were still going on, but of unknown original position within the mines. Granular dolomite is the dominant carbonate

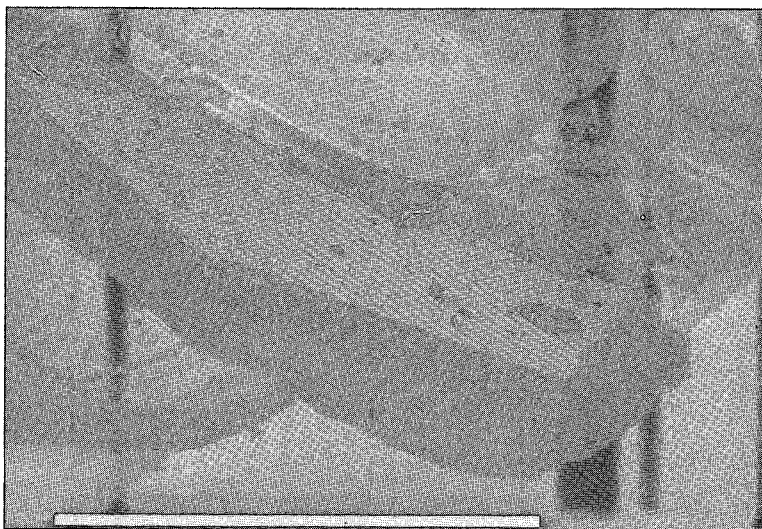


FIG. 1. Scanning electron micrograph of a zenzénite grain attached to jacobsite (upper left) and dolomite (right). Length of bar = 100 μm .

mineral, but minor amounts of calcite, barytocalcite and norsethite also are present. The silicate fraction consists of a manganese-bearing chlorite, which forms translucent grains of a faint orange color, and reddish brown kinoshitalite. Occasional black, tabular crystals of pinakiolite up to 5 mm in size also are present. Evenly distributed throughout the rock are hausmannite and jacobsite, the latter with a large proportion of magnesioferrite in solid solution; both form grains less than 1 mm across. Macedonite, PbTiO_3 , has been identified in polished sections.

Zenzénite is black and opaque. It appears as subhedral to euhedral grains up to 150 μm in longest dimension, always in contact with larger grains of the spinel-type oxides. Most crystals are tabular on {001} (Fig. 1). In a single case, zenzénite has been observed as a 50- μm -wide rim surrounding jacobsite. The mineral exhibits distinct cleavage parallel to {001}. Microhardness measurements gave a VHN_{50} of 764 (average of six readings, range 739–795), corresponding to a calculated Mohs hardness of 5.7. The indentations were close to perfect and accompanied by radial fractures. The density could not be measured owing to the small grain-size and paucity of the new mineral, but the calculated density based on the unit-cell content is 6.83 g/cm^3 . Zenzénite grains are weakly attracted by a hand magnet.

OPTICAL PROPERTIES

In reflected, plane-polarized light, zenzénite is bright white, and resembles galena. There is no

reflection pleochroism, and a weak bireflectance is barely visible in oil immersion. Under crossed polars, it is distinctly anisotropic, with rotation tints in shades of gray and pale brown. Neither internal reflections nor twinning have been observed.

Reflectance measurements within the visible spectrum have been performed on several grains of zenzénite, using a microphotometer system equipped with a plane-glass reflector and $\times 16$ objective, adjusted to give a field of measurement with a diameter of 15 μm . Carborundum (Zeiss no. 472) was used as a standard throughout, with an oil with $N_D = 1.515$ for measurements on immersed grains. Reflectance values obtained on a maximum-bireflectance grain, together with the calculated values of color, are given in Table 1. The spectral reflectance curves of zenzénite (Fig. 2) are uncomplicated and without prominent features. The deviations from straight-line behavior encountered in the 400–440 nm interval should probably be attributed to instrumental error. The scatter of R_0 values in this region has been found to lie within $\pm 1\%$ absolute. The results of the measurements above this region were more consistent ($\pm 0.2\%$).

The difference in luminance ($Y\%$) for the two vibration directions R_0 and R_c can be taken as a measure of the bireflectance. It has been found to vary between 1.2% and 4.2% for the grains measured. Zenzénite has its dominant wavelength around 492 nm in both media (*i.e.*, in the blue-green part of the spectrum) relative to the A illuminant, but the excitation purity (saturation) is too low to cause a hue discernible by the eye.

MINERAL CHEMISTRY

TABLE 1. REFLECTANCE DATA FOR ZENZÉNITE

λ /nm	R_o	R_e	imR_o	imR_e
400	32.0	25.9	17.4	12.5
420	31.7	26.2	17.2	12.4
440	31.6	26.5	16.8	12.2
460	31.2	26.2	16.4	12.0
480	30.8	25.9	16.0	11.7
500	30.4	25.6	15.6	11.5
520	30.0	25.4	15.2	11.2
540	29.6	25.1	14.8	11.0
560	29.2	24.8	14.4	10.8
580	28.7	24.5	14.0	10.5
600	28.3	24.2	13.6	10.3
620	27.8	23.9	13.3	10.0
640	27.4	23.6	13.0	9.81
660	27.1	23.3	12.7	9.56
680	26.8	22.9	12.5	9.36
700	26.5	22.6	12.3	9.18
COLOR VALUES - C illuminant				
x	0.301	0.302	0.293	0.296
y	0.309	0.311	0.301	0.304
Y%	29.2	24.8	14.5	10.8
$P_e\%$	4.2	3.4	7.9	6.7
λ_d	481	481	479	480
- A illuminant				
x	0.438	0.440	0.430	0.433
y	0.406	0.407	0.404	0.405
Y%	28.8	24.6	14.2	10.6
$P_e\%$	2.3	1.9	4.2	3.6
λ_d	493	494	492	492

X-RAY CRYSTALLOGRAPHY

Preliminary investigations indicated that zenzénite is isostructural with synthetic $Pb_3Mn_7O_{15}$, whose structure was initially (Darriet *et al.* 1978) described in terms of an orthorhombic noncentrosymmetric space-group $Cmc2_1$ and the unit-cell parameters a 17.28(1), b 9.98(1), c 13.55(1) Å. Later it was sug-

Reconnaissance analyses of the new mineral with an energy-dispersion detection unit with beryllium window removed indicated that no elements heavier than boron, besides those listed below, are present. Several grains of zenzénite also have been checked for intragranular as well as intergranular compositional homogeneity by means of EDS microanalysis. The variation was found to be restricted to $\pm 0.7\%$ absolute of the mean amount present for the major oxides. Wavelength-dispersion analysis of the new mineral was performed using an ARL-SEM-Q microprobe with an accelerating voltage of 15 kV. The following standards were used: galena (Pb), barite (Ba), rhodonite (Mn), hematite (Fe), sphalerite (Zn), rutile (Ti) and glass (Mg, Al, Si). The average results (in wt.%) obtained from five measurements are: PbO 53.68, BaO 0.06, TiO_2 0.19, Mn_2O_3 8.88, MnO_2 23.63, Fe_2O_3 15.36, ZnO 0.00, MgO 0.12, Al_2O_3 0.19, SiO_2 0.03, total 102.15, yielding an empirical structural formula $Pb_{2.87}Ba_{0.01}(Fe^{3+}_{2.30}Mn^{3+}_{1.35}Mg_{0.04}Al_{0.04})(Mn^{4+}_{3.24}Ti^{4+}_{0.03}Si_{0.01})O_{15}$ based on 7 cations exclusive of Pb and Ba. A simplified formula would be $Pb_3(Fe^{3+}_{2.46}Mn^{3+}_{1.54})Mn^{4+}_3O_{15}$, which gives a higher value of the calculated density, 6.97 g/cm³, than that given above.

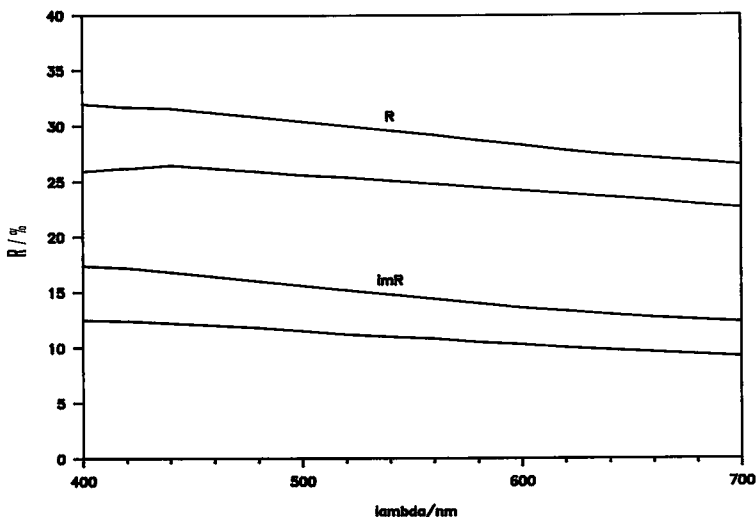


FIG. 2. Spectral reflectance curves of zenzénite, measured in air (R) and in oil (ImR).

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR ZENZÉNITE

I_{obs}	d_{meas} (Å)	d_{calc} (Å)	$h k l$
		6.837*	0 0 2
		5.019*	1 1 0
		4.046*	1 1 2
5	3.42	3.418	0 0 4
8	3.18	3.194	2 1 1
1	2.947	2.961	2 1 2
2	2.900	2.898	3 0 0
7	2.828	2.825	1 1 4
10	2.663	2.665	2 1 3
6	2.366	2.356, 2.374	2 2 2, 3 1 1
1	2.279	2.279	0 0 6
1	2.202	2.198	2 2 3
2	2.125	2.131	3 1 3
4	2.104	2.102	2 1 5
3	2.074	2.075	1 1 6
1	1.971	1.973	3 2 1
1	1.831	1.827, 1.834	3 2 3, 4 0 4
2	1.811	1.809	3 1 5
1	1.789	1.791	3 0 6
1	1.711	1.709	0 0 8
8	1.687	1.687	2 2 6
3	1.552	1.551, 1.550	5 1 1, 5 0 4
2	1.516	1.518	3 1 7
2	1.476	1.477	5 1 3

57.3 mm Gandolfi camera, CuK α radiation

* reflection expected to be present from the single-crystal study.

TABLE 3. EXPERIMENTAL CONDITIONS FOR THE CRYSTAL STRUCTURE DETERMINATION OF ZENZÉNITE

Space group	$P6_3/mcm$
Unit cell dimensions	$a=10.008(4)$ Å, $c=13.672(8)$ Å
Unit cell volume, V	$1186(1)$ Å ³
Formula units per unit cell, Z	4
Radiation	MoK α
Wavelength, λ	0.71073 Å
Temperature, T	293(1) K
Crystal shape	prismatic
Crystal size	0.114x0.056x0.028 mm
Diffractometer	Stoe 4-circle
Determination of unit cell	
number of reflections	14
2 θ -range	12.8 to 24.4°
Intensity data collection	ω -2 θ scan technique
maximum $\sin(\theta)/\lambda$	0.704 Å ⁻¹
range of h, k, l	0-14, 0-14, 0-19
internal R	0.060
number of collected refls.	2953
" " unique	650
" " observed	372
criterion for significance	$I > 5 \cdot \sigma(I)$
Absorption correction	numerical integration
linear absorption coefficient	501 cm ⁻¹
transmission factor range	0.07 to 0.26
Structure refinement	full-matrix least squares
minimization of	$\sum w \Delta F^2$
anisotropic thermal parameters	Pb and Mn(Fe) atoms
isotropic " "	O atoms
number of refined parameters	36
weighting scheme	$(\sigma^2(F) + 0.0002 F ^2)^{-1}$
final R for observed refls.	0.028
" wR " " "	0.029
" wR " all 650 refls.	0.038
" $(\Delta/\sigma)_{max}$	0.06
" $\Delta\rho_{min}$ and $\Delta\rho_{max}$	-4.1 and 2.1 e ⁻ /Å ³

gested by Marsh & Herbstein (1983) that the structure was better described with the related centrosymmetric space-group $Cmcm$. With the identical intensity data set as initially used by Darriet *et al.* (1978), Le Page & Calvert (1984) eventually found

TABLE 4. FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS ($\times 10^4$ Å²) FOR THE ZENZÉNITE STRUCTURE

Atom	x	y	z	U_{iso}
Pb(1)	0.6136(1)	0.6136(1)	3/4	154(4)
Pb(2)	0.2678(1)	0.2678(1)	3/4	123(4)
M(1)	0.8318(1)	0.1683(1)	1/2	88(10)
M(2)	1/3	2/3	0.1462(2)	61(6)
M(3)	1/2	1/2	1/2	84(14)
M(4)	0	0	0	106(16)
O(1)	0.4882(9)	0.3271(9)	0.0802(7)	125(17)
O(2)	0.5254(13)	0.1727(12)	1/4	86(22)
O(3)	0.1645(11)	0.1645(11)	0.0730(10)	122(24)
O(4)	0.6709(11)	0.6709(11)	0.0734(10)	102(23)

TABLE 5. THE SHORTEST METAL - O DISTANCES (Å) WITH E.S.D. FOR THE COORDINATION POLYHEDRA

Atoms	Distance	Distance
Pb(1) - O(2)	2.301(11) ×2	2.323(25) ×2
- O(1)	2.718(10) ×4	2.693(18) ×4
Mean	2.579	2.570
Pb(2) - O(2)	2.276(11) ×2	2.239(25) ×2
O(4)	2.492(12) ×2	2.588(29) ×2
Mean	2.384	2.414
M(1) - O(1)	1.904(10) ×2	1.891(29) ×2
- O(4)	1.930(12) ×2	1.935(18) ×2
- O(3)	1.974(12) ×2	1.975(22) ×2
Mean	1.936	1.934
M(2) - O(1)	1.974(10) ×3	1.983(18) ×3
- O(2)	2.080(11) ×3	2.075(25) ×3
Mean	2.027	2.029
M(3) - O(4)	1.983(12) ×2	1.883(29) ×2
- O(1)	2.002(10) ×4	1.938(18) ×4
Mean	1.996	1.920
M(4) - O(3)	1.926(12) ×6	1.926(22) ×6
Mean	1.926	1.926

The left column shows the results obtained in the present study of zenzénite and the right column those of Le Page & Calvert (1984) for synthetic Pb₃Mn₇O₁₅.

that a description in terms of the hexagonal space-group $P6_3/mcm$ could significantly improve the structural model. The distributions of distances, angles and the thermal parameters obtained with hexagonal symmetry were found to be more regular, and no indication of disorder was observed. Le Page & Calvert (1984) also suggested that the compound be re-examined with a new data-set by future investigators to confirm their structure description.

The structure determination was undertaken in order to test the structural similarity of zenzénite to synthetic Pb₃Mn₇O₁₅, to verify the $P6_3/mcm$ space-group symmetry for this structure type, and to obtain an improved structural characterization in terms of degree of order of the metal atoms.

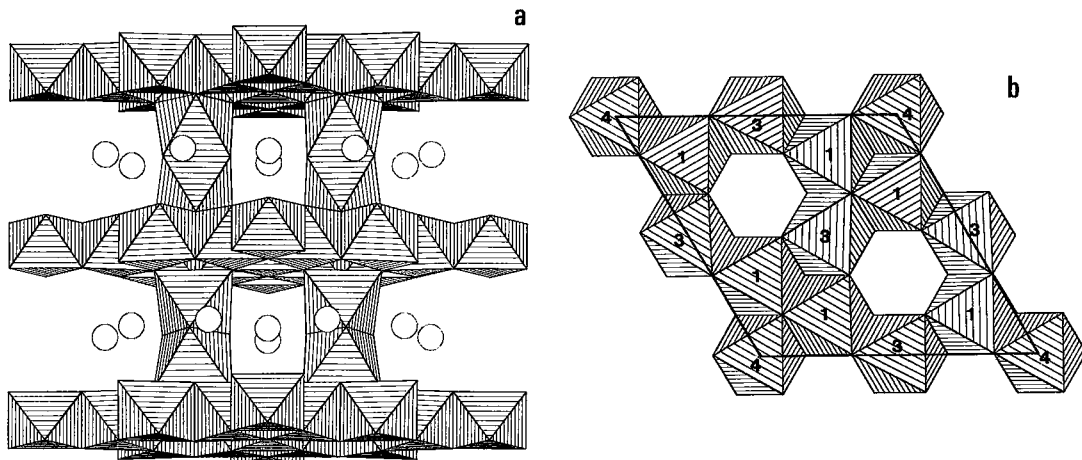


FIG. 3. a) The zenzénite structure viewed approximately perpendicular to [001]. The positions of the lead atoms are shown as spheres; the coordination octahedra are those around the Mn(Fe) positions. b) Unit-cell content of layers (at $z \approx 0$) of edge-sharing octahedra around the metal positions $M(1)$, $M(2)$ and $M(4)$. The origin of the unit cell is at the lower left corner, and the numbers given are the labels of the M positions (cf. Table 4).

X-ray powder data

An X-ray powder-diffraction pattern was obtained using a 57.3 mm Gandolfi camera with Ni-filtered $\text{CuK}\alpha$ radiation. Measured as well as calculated d values are given in Table 2 together with estimated intensities. Refinement of the parameters of the hexagonal cell by least-squares methods from the powder data yielded a 10.037 Å, c 13.67, V 1193 Å³, with $Z = 4$. They should be compared to the more precise cell obtained from the single-crystal measurements (Table 3).

Crystal-structure analysis

The X-ray-diffraction data collected with a single-crystal diffractometer were corrected for background, Lorentz, polarization and absorption effects. Further relevant experimental conditions are listed in Table 3. Final unit-cell parameters were obtained by least-squares analysis of accurately determined reflection-positions (cf. Table 3). As discussed above, a simplified chemical formula $\text{Pb}_{3.00}\text{Mn}_{4.54}\text{Fe}_{2.46}\text{O}_{15}$ was given by microprobe analysis. As the X-ray scattering powers of Mn and Fe are very similar, no determination of the proportion of Mn and Fe can be obtained from the X-ray investigation.

A refinement of the structural model, allowing all metal ions to vibrate anisotropically and the oxygen atoms, isotropically (36 parameters and the 372 most significant reflections), gave a weighted wR value of 0.029 (unweighted linear R of 0.028). The choice of the space-group symmetry, $P6_3/mcm$, is fully supported by the outcome of the structural refinements.

The final atomic coordinates and thermal parameters are given in Table 4. Lists of observed and calculated structure-factor amplitudes have been

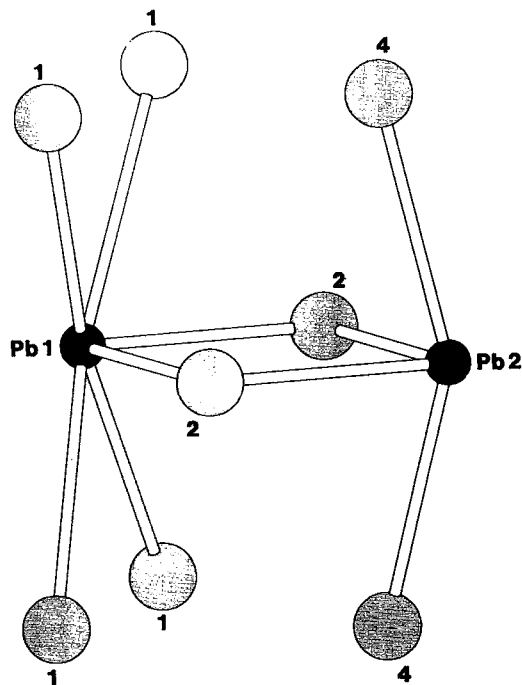


FIG. 4. The oxygen coordination around the lead atoms Pb(1) and Pb(2) in the zenzénite structure. The distance between Pb(1) and Pb(2) is 3.461(1) Å. The numbers given are the labels of the oxygen atoms (cf. Table 4).

submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2. The most relevant interatomic distances are listed in Table 5. The structural refinements were performed by means of the SHELX-76 program package (Sheldrick 1976), using atomic X-ray scattering factors for neutral atoms from the International Tables for Crystallography (1974). The polyhedral packing diagrams were obtained with the program STRUPLO84 (Fischer 1985).

Description of the structure

The structural model (Fig. 3) obtained in the present study agrees in general with that obtained by Darriet *et al.* (1978) for the synthetic compound $\text{Pb}_3\text{Mn}_7\text{O}_{15}$, although they used an orthorhombic instead of a hexagonal symmetry to describe their structure. Thus, all the Mn(Fe) atoms are octahedrally coordinated by oxygen atoms; the two crystallographically independent lead atoms (Fig. 4) can be described as being coordinated to four and six nearest oxygen atoms, respectively. As expected, the lead atoms are off-center in the coordination polyhedra owing to the presence of stereo-active lone-pairs of $6s^2$ electrons (see, *e.g.*, Hyde & Andersson 1989). Repulsion between the lone-pair and neighboring oxygen atoms displaces the Pb atom toward the lone-pair vertex, an effect also met in, for example, the structure of quenselite, $\text{PbMn}^{3+}\text{O}_2(\text{OH})$, (Rouse 1971).

The crystal structure can be considered as composed of layers (Fig. 3b) perpendicular to the [001] direction, consisting of edge-sharing coordination octahedra around the Mn(Fe) positions $M(1)$, $M(3)$ and $M(4)$. Within these layers, there are voids arranged as shown in Figures 3b and 5. Two octahedra around $M(2)$ are linked together by face-sharing to form hematite-like entities that link the layers together by sharing corners with the octahedra surrounding the voids. The lead atoms are located half-way between the layers, and share coordinating oxygen atoms with the Mn(Fe) atoms.

The structure can be looked upon as a six-layer close-packing (*hcp*) of anions in the unit cell, with lead ions replacing six of the anions in every third layer. The stacking sequence [$\bullet h h h h h \bullet$] distinguishes zenzénite from most other related oxide minerals, which are based on alternating sequences of cubic and hexagonal close-packing. Compare, for example, magnetoplumbite, $\text{Pb}(\text{Fe}^{3+}, \text{Mn}^{3+})_{12}\text{O}_{19}$ (Moore *et al.* 1989), with [$\bullet c h h c h h c \bullet$], and senaite, $\text{Pb}(\text{Ti}, \text{Fe}, \text{Mn})_{21}\text{O}_{38}$ (Grey & Lloyd 1976) with [$\bullet h c h c h c h c \bullet$] as the *c*-axis repeat. The distribution of metal - O bond distances in the present structure agrees within 4σ from those obtained by Le Page & Calvert (1984) for the revised structure of $\text{Pb}_3\text{Mn}_7\text{O}_{15}$ (Table 5). The present study has given considerably improved accuracies (*esd* of 0.01 Å) in the observed lengths compared to earlier studies.

The X-ray-diffraction study indicates full occupancy of all the metal positions; with the assumption of divalent lead, the formal charge of

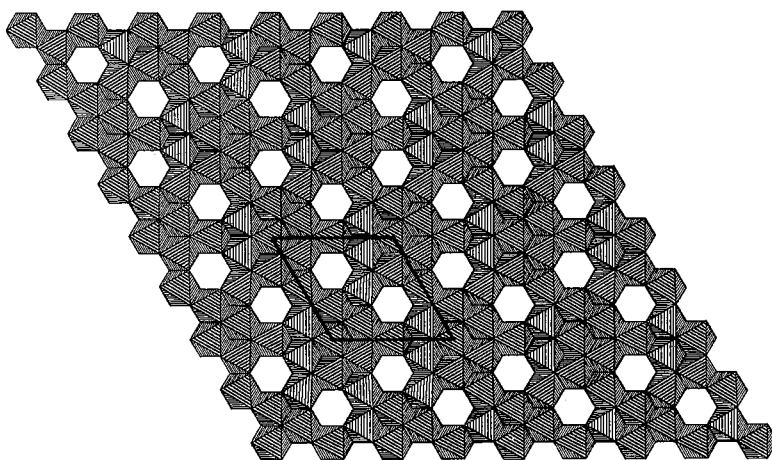


FIG. 5. Extended representation of the layers (*cf.* Fig. 3b) of edge-sharing coordination octahedra, viewed along [001]. The translation-symmetry-related entities formed by one $M(4)$ octahedron (at the origin) surrounded by six $M(1)$ octahedra are linked to each other by the $M(3)$ octahedra. The estimated formal charges at these positions (+4, +3.8 and +3) decrease in the sequence $M(4)$, $M(1)$ to $M(3)$.

the Mn(Fe) content must be +3.43 in order to obtain electroneutrality. To extract a reasonable distribution of the tri- and tetravalent metal ions at the M positions, calculations of empirical bond-valences have been performed, using the parameter values (r_0) for the bond valence - bond distance correlation-functions, $s = \exp [r_0 - r] / 0.37$, given by Brown & Altermatt (1985). Fortunately, the parameter values for Mn^{3+} , Fe^{3+} and Mn^{4+} are very similar [1.760(5), 1.759(3) and 1.753(6) Å, respectively]. Thus, one single r_0 value (1.76 Å) may be used as an estimate for all three ion types. Summations of the estimated bond-valences at each M position give the values 3.73, 2.94, 3.18 and 3.84 for the M positions number 1, 2, 3 and 4, respectively. The values obtained for the lead positions Pb(1) and Pb(2), 1.98 and 2.00, agree well with the expected formal valence +2 for Pb. The estimated bond-valences for the M positions indicate that the $M(4)$ and also the $M(1)$ positions contain major amounts of tetravalent metal ions. The $M(3)$ positions seem to contain only minor amounts of tetravalent ions, and the $M(2)$ positions, to contain only trivalent ions. A simple model giving electroneutrality, which is in reasonable accord with the estimated bond-valences, would suggest that the $M(2)$ and $M(3)$ positions are occupied by trivalent ions, the $M(4)$ position by a tetravalent ion, whereas the $M(1)$ position is occupied both by tetravalent and trivalent ions in the proportions 5:1. In accordance with the estimated bond-valences, the trivalent Fe content can be expected to be found mostly in the $M(2)$ or $M(3)$ positions. As the difference in X-ray scattering powers, slightly higher for Fe^{3+} than Mn^{3+} , could yield somewhat smaller thermal parameters for a position with a higher Fe content, it seems possible that $M(2)$ contains a major fraction of the Fe. The average metal-oxygen bond distances [2.027 and 1.996 Å for $M(2)$ and $M(3)$, respectively] are also slightly longer for this position. An assumption of full Fe occupancy at the $M(2)$ position and limited occupancy at other metal positions would give a chemical formula in good agreement with the results of the microprobe analyses.

As discussed above, the $M(1)$, $M(3)$ and $M(4)$ positions are located in layers (Figs. 3b, 5) through the structure. Thus, the metal ions expected to have higher formal charges are located within the layers, and those with lower charges [Pb and $M(2)$], between the layers. Within the layers, each $M(4)$ position (at the origin), with a formal charge of +4, according to the simple model suggested above, is surrounded by six $M(1)$ positions with formal charge +3.83. The coordination octahedra around these metal ions with high formal charges, repeated by unit translation along a_1 and a_2 , are well separated by octahedra around the metal ions $M(3)$, which have a lower formal charge (cf. Fig. 5).

ORIGIN OF THE MINERAL

The apparent paucity of zenzénite in the Långban deposit appears to be somewhat enigmatic. The skarns of Långban are generally rich in the elements that constitute the mineral, often combined in minerals like magnetoplumbite and members of the kentrolite-melanotekite series, $\text{Pb}_2\text{Mn}_2\text{Si}_2\text{O}_9$ - $\text{Pb}_2\text{Fe}_2\text{Si}_2\text{O}_9$. The limiting factor should probably be looked for in the physical conditions. It is clear that the appearance of tetravalent manganese would require an exceptionally high fugacity of oxygen as compared to the bulk of the skarn rocks. Zenzénite formation, as a result of transformation and replacement of other manganese-iron bearing oxides, is most likely a late event, yet at conditions far different from those responsible for the genesis of the well-known mineral associations, characterized by highly reduced phases like native lead, that are found in late veins, cutting ores and skarns.

ACKNOWLEDGEMENTS

We thank A.J. Criddle and C.J. Stanley (The Natural History Museum, London) for their help with the reflectance measurements and Riksmusei Vänner for a travel grant.

REFERENCES

- 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.
- DARRIET, B., DEVALETTE, M. & LATOURRETTE, B. (1978): Structure cristalline de $\text{Pb}_3\text{Mn}_7\text{O}_{15}$. *Acta Crystallogr.* **B34**, 3528-3532.
- FISCHER, R.X. (1985): STRUPLO84, a Fortran plot program for crystal structure illustrations in polyhedral representation. *J. Appl. Crystallogr.* **18**, 258-262.
- GREY, I.E. & LLOYD, D.J. (1976): The crystal structure of senaite. *Acta Crystallogr.* **B32**, 1509-1513.
- HYDE, B.G. & ANDERSSON, S. (1989): *Inorganic Crystal Structures*. John Wiley & Sons, New York.
- INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY (1974): Vol. IV. Kynoch Press, Birmingham, England.
- LE PAGE, Y. & CALVERT, L.D. (1984): $\text{Pb}_3\text{Mn}_7\text{O}_{15}$: a further change in the space group of a published crystal structure. *Acta Crystallogr.* **C40**, 1787-1789.
- MAGNUSSON, N.H. (1930): Långbans malmtrakt. *Sver. Geol. Undersök. Ca* **23**, 1-111.

- MARSH, R.E. & HERBSTEIN, F.H. (1983): Some additional changes in space groups of published crystal structures. *Acta Crystallogr.* **B39**, 280-287.
- MOORE, P.B. (1970): Mineralogy & chemistry of Långban-type deposits in Bergslagen, Sweden. *Mineral. Rec.* **1**, 154-172.
- _____, SEN GUPTA, P.K. & LE PAGE, Y. (1989): Magnetoplumbite, $Pb^{2+}Fe_{12}^{3+}O_{19}$: refinement and lone-pair splitting. *Am. Mineral.* **74**, 1186-1194.
- ROUSE, R.C. (1971): The crystal structure of quenselite. *Z. Kristallogr.* **134**, 321-332.
- SHELDRIK, G.M. (1976): SHELX-76: *Program for Crystal Structure Determination*. University of Göttingen, Germany.

Received October 2, 1990, revised manuscript accepted January 9, 1991.