SHORT COMMUNICATIONS

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Crystal structure refinement of matlockite

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MATLOCKITE is a lead halide with chemical formula PbFCl. First described from Matlock, Derbyshire, UK (Greg, 1851), its crystal structure was established using the crystal-chemical studies of Nieuwenkamp and Bijvoet (1932*a*). On the basis of a powder diffractogram obtained with synthetic PbFCl, they proposed a structural model in the space group *P*4/*nmm*, in which all atoms should lie on sites with low multiplicity. Such a model was successfully tested with a number of intensity data sets for natural matlockite collected with single crystal X-ray rotation photographs (Bannister, 1934), but never refined.

Recently matlockite was found, together with several other lead oxy- and hydroxyhalides, within the slags of Baratti beach, southern Tuscany, Italy (Franzini and Perchiazzi, 1992).

Since then, in studying various minerals from Baratti, concern with the crystal-chemistry of Pb has arisen. Therefore the authors thought it useful to carry out a structural refinement of matlockite, to have a better description of that structure and to allow comparisons with the coordination of Pb in other related minerals.

The chemical composition of matlockite from Baratti has been determined by electron microprobe analyses, and gave Pb 79.27, Cl 13.52 and F 7.24 (Σ 100.03%) (Franzini and Perchiazzi, 1992). These analytical data can be recalculated, on the basis Pb = 1, to the chemical formula $PbF_{0.996}Cl_{0.997}$, which is very close to ideal stoichiometry.

The intensity data were collected with a crystal of matlockite from Baratti (dimensions 0.3 × 0.15 × 0.02 mm) on an Ital Structures four-circle automatic diffractometer operating at 48 kV and 28 mA with graphite monochromated Mo-*K*α radiation (λ = 0.71069 Å). The operation was carried out in ω-2θ scan mode up to $2\theta = 70°$, scan width 1.4° + 0.3° tan θ, minimum scan speed 1.5°/min, proportionally raised on the basis of the intensity of a pre-scan of the peaks. The unit cell parameters *a* 4.110(1), *c* 7.246(1) Å were obtained from least-squares refinement of 2θ values of a set of 24 reflections ($15° < \theta < 23°$). The 636 intensity measurements ($\bar{6} \leqslant h \leqslant 6, 0 \leqslant k \leqslant 6, 0 \leqslant l \leqslant 11$) were reduced by Lorentz and polarization corrections to a set of 192 independent structure factors. The absorption correction was carried out by DIFABS (Walker and Stuart, 1983). The correction factors on *F* were in the range 0.565–2.174. The value of R_{int} from merging equivalents dropped from 0.219 (before the absorption correction) to 0.086 (after the absorption correction). The starting model was taken from Bannister (1934). The structure was refined using the SHELX package (Sheldrick, 1976) and converged to *R* 0.070, $R_w = 0.063$ [$w = 1/\sigma(F_0)^2$] for all 192 structure factors, using anisotropic displacement parameters. The U_{33} thermal parameter for F was held fixed to a reasonable positive value, as it refined to physically meaningless values, probably depending on minor inaccuracies in the absorption surface calculations. Scattering curves for neutral atoms and anomalous dispersion coefficients were taken from Cromer and Mann (1968) and from Cromer and Liberman (1970).

The final atomic coordinates and displacement parameters are given in Table 1. Bond lengths and the bond-valences computed according to Brese and O'Keeffe (1991) are given in Table 2. A listing of observed and calculated structure factors is available from one of the authors (MP), or from the editor, on request. A ball-and-stick drawing of the structure of matlockite as seen along [100] is shown in Fig. 1.

TABLE 1. Atomic coordinates and anisotropic displacement parameters (Å^2) for matlockite (U_{12} = U_{13} = U_{23} = 0)

Atom	x	y	z	$U_{11} = U_{22}$	U_{33}
Pb	0.25	0.25	0.2058(2)	0.0070(5)	0.0070(7)
F	0.25	0.75	0.0	0.005(5)	0.005
Cl	0.25	0.25	0.6497(16)	0.012(2)	0.008(4)

TABLE 2. Interatomic distances (Å) and bond valence balance calculations (v.u.) for matlockite

	Bond distance		Bond strength
Pb–F	2.539(1) (4 ×)		0.253
Pb–Cl	3.089(4) (4 ×)		0.221
Pb–Cl′	3.216(12)		0.157
Bond valence balance			
$\Sigma_{Pb}v$ = 2.053	$\Sigma_{F}v$ = 1.012		$\Sigma_{Cl}v$ = 1.041
Anion–anion contacts			
F–F	2.906(1)	F–Cl	3.266(9)
Cl–Cl′	3.626(14)	Cl–Cl	4.110(1)

All atoms in the structure of matlockite are in special positions. This results in highly regular coordinations. The bond valence balance for Pb, F and Cl gave sums very close to the theoretical values. Lead is nine-fold coordinated by 4 F and 5 Cl atoms in a monocapped square antiprism (Fig. 2). This is a quite unusual coordination for Pb, being reported in phosgenite only among related alteration minerals (Giuseppetti and Tadini, 1974). However, whereas in

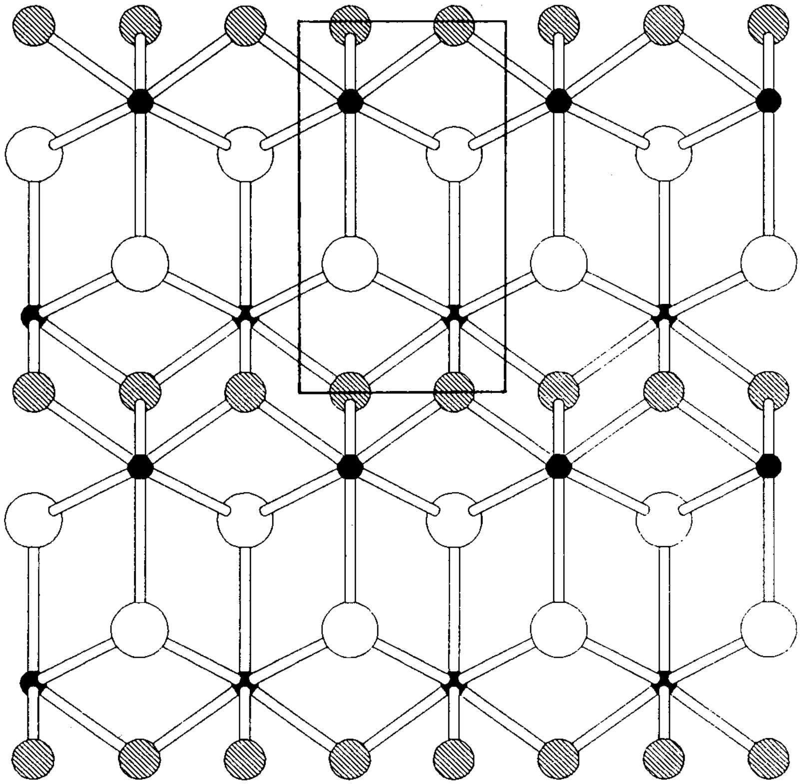

FIG. 1. The structure of matlockite as seen along [100]. Filled, hatched and open circles indicate Pb, F and Cl, respectively. The unit cell is outlined.

the present case the [PbX_9] polyhedra display $4mm$ symmetry, the corresponding polyhedra in phosgenite undergo significant distortions and their symmetry lowers to m. In matlockite the larger square has a side length (Cl–Cl contact) of 4.110 Å (a axis), the smaller square has a side length (F–F contact) of 2.906 Å ($a.\sqrt{2}/2$). The ninth coordinating Cl (hereafter indicated as Cl′) caps the polyhedron above the larger square.

A most common environment for Pb, which is displayed, for instance, in paralaurionite (Merlino *et al.*, 1993), fiedlerite-1*A* and fiedlerite-2*M* (Merlino *et al.*, 1994), penfieldite (Merlino *et al.*, 1995), is the eight-fold coordination in trigonal prism, or distorted square antiprism.

Chlorine atoms are connected to five Pb atoms in a square pyramidal configuration. The F atoms lie on (001) planes at $z = 0$, and are surrounded by four Pb atoms in a regular tetrahedral coordination. This rigidly closed coordination for F prevents any substitution of F by OH in matlockite.

The lead-centred polyhedra are strongly interconnected along a and b by sharing of (F–Cl–Cl) faces (cf. Fig. 2). The polyhedra are also connected along [001] by sharing of F–F and Cl–Cl′ edges.

Matlockite is isostructural with the synthetic compound PbFBr (Nieuwenkamp and Bijvoet, 1932*b*), which displays the same space group and comparable unit cell dimensions (a = 4.18, c = 7.59 Å). A different situation arises with the compound PbFI, whose unit cell parameter c is longer (a = 4.235, c = 8.81 Å; Rulmont, 1973). We carried out a structural simulation for PbFI with the DLS-76 program (Baerlocher *et al.*, 1977) using the matlockite model, and convergence was not attained. The lengthening of the c axis should remove the ninth, capping anion from the Pb coordination sphere in PbFI, and the coordination of Pb should reduce to a normal square antiprism, as happens for Bi in the related compound BiOBr (Ketterer and Krämer, 1986). The lack of interaction between the cation and the capping anion produces degeneration of PbFI and BiOBr into layered structures, in which double polyhedral layers parallel to (001) do not have any common element, and are held together by weak van der Waals interactions only.

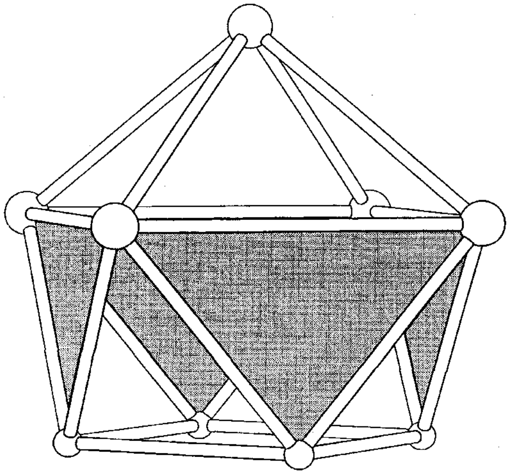

FIG. 2. The lead coordination polyhedron. Smaller and larger circles indicate F and Cl, respectively. The four F–Cl–Cl faces (shaded) are shared with neighbouring polyhedra.

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Stichtite [$Mg_6Cr_2(OH)_{16}CO_3\cdot 4H_2O$] in Nausahi ultramafites, Orissa, India – its transformation at elevated temperatures

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STICHTITE, the rare hydrated magnesian chrome carbonate, has been reported from only a few places in the world e.g. Dundas, Tasmania (Petterd, 1910); Barberton, Transvaal, South Africa (Hall, 1922); Cunningsburgh, Shetland Islands, Scotland (Read and Dixon, 1933) and the Black Lake area of Quebec, Canada (Poitevin and Graham, 1918). This is the first reported occurrence from India. The present work is mainly based on the physical (including optical) and chemical characteristics of stichtite and its transformation to other phases at elevated temperatures substantiated from XRD-peaks of the different mineralogical phases.

Geology

Stichtite occurs in the chromiferous ultramafites (mainly serpentinized dunite and peridotite) and chromite units of the Nausahi Ultramafic-mafic Complex (21°16′N, 86°20′E) in the Keonjhar district of Orissa, which belongs to a part of the Eastern Indian Shield. This ultramafic-mafic complex has intruded the Precambrian Iron Ore Group along a north–south tectonic lineament. The chromite ore bodies mainly occur as lenticular bands and *en échelon* pockets within the serpentinized dunite and peridotite host. The younger suite comprises enstatolite, lherzolite, fresh dunite, gabbro, norite, anorthosite and dolerite. The earlier ultramafites are metamorphosed under lower greenschist facies and a weak but persistent regional schistosity is very prominent in the serpentinized rocks. In places chromite ore bands are co-folded with meta-ultramafites and both have undergone post-crystallization shearing and faulting. Recently Das *et al.* (1994) reported the presence of platinum, gold and silver in the chromite-sulphide association of the ores, the sulphides being mainly of Fe, Cu and Ni.

Properties

Megascopically, stichtite in the present area occurs as purple or lilac massive aggregates or veinlets, mainly within chromitite and some within serpentinized ultramafites. In places it is weakly foliated or fibrous in character. Its hardness is $\leqslant 2$. Lustre is sub-pearly