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Grandreefite, $Pb_2F_2SO_4$: Crystal structure and relationship to the lanthanide oxide sulfates, $Ln_2O_2SO_4$

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ABSTRACT

Grandreefite, $Pb_2F_2SO_4$, has been determined to be monoclinic rather than orthorhombic as reported in its original description. Its cell parameters are $a = 8.667(1)$, $b = 4.4419(6)$, $c = 14.242(2)$ Å, $\beta = 107.418(2)°$ ($Z = 4$) and the space group is $A2/a$. The crystal structure, refined to $R = 0.032$ for 399 observed reflections, consists of layer fragments of the β-PbF_2 structure parallel to (100) alternating with layers of isolated sulfate tetrahedra. The layer sequence in the unit cell is SO_4-PbF_2Pb-SO_4-PbF_2Pb-SO_4. Pb is coordinated to four F and four O forming a distorted bicapped trigonal prism. The structure of grandreefite is closely related to that of the lanthanide oxide sulfates, $Ln_2O_2SO_4$. Electrostatic bond strength and empirical bond-valence considerations suggest that the topologies of the structures differ with respect to the ligation of the sulfate oxygen atoms to the large cations.

INTRODUCTION

Grandreefite, $Pb_2F_2SO_4$, is a recently described lead fluoride sulfate from the oxidized zone of the Grand Reef mine, a small epithermal Pb-Cu-Ag deposit in Graham County, Arizona. The mineral was found in an isolated vug with three other new minerals containing Pb and F: pseudograndreefite, laurelite, and aravaipaite (Kampf et al., 1988).

The powder pattern of grandreefite is very similar to those of the lanthanide oxide sulfates, $Ln_2O_2SO_4$ (Ln = La, Pr, Nd, etc.), and single-crystal study provided cell dimensions and systematic extinctions similar to those of the lanthanide phases. It was therefore inferred that grandreefite was isostructural with these compounds.

The lanthanide oxide sulfates have been the subjects of numerous studies because of their unusual physical and chemical properties. They are of interest in luminescent screen technology because they can be formed by the oxidation of lanthanide oxide sulfide luminophores during the thermal treatment of luminescent screens (Laptev et al., 1987). It is remarkable that the lanthanide oxide sulfates exhibit a common structure type across the entire lanthanide series despite a marked variation in lanthanide ionic radii (Ballestracci and Mareschal, 1967). The crystal structure of $La_2O_2SO_4$ was solved by Fahey (1976) using powder-diffraction methods. His refinement in space group *I*222 yielded an *R* value of 0.091; however, the location of the four equivalent sulfate oxygen atoms must be considered suspect because of their very large isotropic temperature factor ($B = 15$ Å^2). Haschke (1988) reported on a single-crystal study of $Pr_2O_2SO_4$ by D. R. Peacor in which similar metal, O, and S positions were found, but the positions of the sulfate oxygen atoms could not be determined. The latter refinement in space group *Immm* yielded electron density maps which suggested rotational disorder of the sulfate group. The *R* value for this refinement was 0.11 (Peacor, personal communication, 1989). It was hoped that the complete solution of the grandreefite structure would be possible and that it might shed light on the orientation of the sulfate group in the $Ln_2O_2SO_4$ structure.

STRUCTURE DETERMINATION

Intensity data were measured using a Huber automated diffractometer with monochromatized Mo*Kα* radiation and the $\theta/2\theta$ scan method. Data were corrected for Lorentz and polarization factors. All computations were carried out with the University of California, Los Angeles crystallographic computing package. Scattering factors for neutral atoms and anomalous dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974).

The grandreefite used in this study was from the type specimen, catalog number 33608, although this was formerly incorrectly designated as specimen 25414 of the Natural History Museum of Los Angeles County (Kampf et al., 1988). The initial crystal studied was an irregular fragment measuring 0.15 × 0.26 × 0.32 mm. The orthorhombic cell parameters reported in the original description, $a = 4.439(4)$, $b = 13.575(13)$, and $c = 4.333(4)$ Å, were obtained by least-squares refinement of four-circle diffractometer data. A total of 268 independent reflections were measured. An absorption correction based upon hypothetical crystal faces to approximate the shape of the crystal was applied. The structure refined in space group *I*222 to $R = 0.076$ and $R_w = 0.113$; however, the O atoms could not be located. Refinements using the other possible space groups, $I2_12_12_1$, *Imm*2, and *Immm*, were unsuccessful.

It was suspected that the absorption correction was not

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entirely adequate because of the irregular shape of the crystal and the high linear absorption coefficient ($\mu_l = 641$ cm^{-1}). Consequently, a 0.1 mm diameter sphere was ground from another crystal fragment. During orientation it was found that one cell angle deviated from orthogonality by 0.3°. Least-squares refinement of the monoclinic cell parameters using the setting angles of 18 strong reflections in the range $17.8° < 2\theta < 26.5°$ yielded a = 4.3334(9), b = 4.4400(9), c = 13.580(3) Å, and β = 90.301(3)°.

Omega peak-scans for the first crystal were reexamined and several were found to be split, suggesting that the crystal might be twinned. Twinning would also account for the apparent orthorhombic cell determined for the first crystal. Optical examination of this crystal for twinning was not attempted because its high refractive indices require that such examination be made in immersion oils in which the mineral is unstable; however, other grandreefite crystal fragments were found to exhibit coarse polysynthetic twinning. Scans of ten peaks in various quadrants for the second crystal exhibited no splitting and this crystal is, therefore, assumed to be untwinned.

A total of 768 reflections were measured at a scan rate of 3.0°/min from a hemisphere of reciprocal space to a 2θ limit of 60°. Three standard reflections measured every hour showed no significant intensity variation during the period of data collection. A total of 83 reflections had $I < 3\sigma(I)$ and were considered unobserved. To allow for any deviation from spherical shape an empirical ψ-scan absorption correction was applied. Equivalent reflections were averaged to obtain 392 independent reflections. The agreement index for symmetry-equivalent reflections was 0.019.

Refinement in space group $I2$ was seemingly successful. O atoms were located by difference Fourier synthesis. Refinement with anisotropic temperature factors for Pb and isotropic temperature factors for all other atoms yielded $R = 0.029$ and $R_w = 0.039$. However an unusually short distance (1.91 Å) between equivalent O atoms in adjacent sulfate tetrahedra emerged. Subsequent refinement in space group $I1$ using the same cell yielded virtually identical O positions.

Although a difference Fourier synthesis did not show any significant unassigned electron density (all $\Delta F < 1.6$ e/Å^3), further refinement in space group $I2$ was attempted with O sites split and assigned half occupancy so as to correspond to adjacent sulfate groups that were related by inversion. The coordinates of the O sites did not converge well and the isotropic temperature factors of O attained the unreasonable values of 0.8, 2.7, 0.1, and −0.6 Å^2. Other explanations based upon twinning, disorder, etc. to account for the short O-O distance were carefully considered and ultimately dismissed.

It was noted that a doubled cell (supercell) with space group $A2/a$ would accommodate the same arrangement of atoms except that alternate sulfate groups could be inverted (Fig. 1a), thus eliminating the very short O-O distance. The lattice parameters, based upon the same 18 (reindexed) reflections, are a = 8.667(1), b = 4.4419(6), c = 14.242(2) Å, and β = 107.418(2)° (Z = 4). Calculations indicated that reflections corresponding to this superstructure would generally be of very low intensity; nevertheless, it was disconcerting that none were observable on long exposure precession films. The choice of this supercell is supported principally by good convergence of all parameters during subsequent refinements, by reasonable values for all temperature factors, and by atomic distances and angles consistent with with those in similar compounds.

A new data set was obtained following the procedures outlined above. A total of 1442 reflections were measured, of which 689 were considered observed. Averaging of equivalent reflections resulted in 399 independent reflections with an agreement index of 0.025. Only five superstructure reflections met the criterion of $I > 3\sigma(I)$ for observed reflections.

Refinement with an anisotropic temperature factor assigned only to Pb gave $R = 0.032$ and $R_w = 0.043$. The shortest O-O distance is 2.38 Å, between symmetry-equivalent O atoms in the same sulfate tetrahedron.

The coordinates and temperature factors are listed in Table 1, the observed and calculated structure factors in Table 2,[1] and the interatomic distances and angles in Table 3.

STRUCTURE DESCRIPTION

The structure of grandreefite (Fig. 1a) consists of layers of PbF_2Pb parallel to (001) alternating with layers of isolated sulfate tetrahedra. The layer sequence in one unit cell is SO_4-PbF_2Pb-SO_4-PbF_2Pb-SO_4. The PbF_2Pb layer can be considered to be a fragment of the β-PbF_2 (fluorite) structure, with Pb alternately above and below the interstices in a square planar sheet of F atoms. Similar layers are found in tetragonal PbO and in numerous Pb, Bi, and lanthanide oxyhalides and related structures [e.g., thorikosite (Rouse and Dunn, 1985) and asisite (Rouse et al., 1988)].

Pb is eight coordinated to four F, forming a PbF_4 square pyramid with Pb at its apex, and to four O, each from a different sulfate group. The Pb-F distances are 2.39, 2.52, 2.57, and 2.71 Å (average 2.55 Å) and the Pb-O distances are 2.54, 2.60, 2.82, and 2.84 Å (average 2.70 Å) (Table 3 and Fig. 2). The coordination polyhedron can best be described as a distorted bicapped trigonal prism, with two F and one O(1) located at the corners of each prism base and O(2) located at the point of each cap. Each Pb polyhedron shares each of its four F-F edges and two of its F-O(2) edges with other Pb polyhedra in the PbF_2Pb layer and its O(1)-O(1) edge with a Pb polyhedron across the sulfate layer. The Pb polyhedra share only corners with the sulfate tetrahedra.

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[1] A copy of Table 2 may be ordered as Document AM-91-446 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

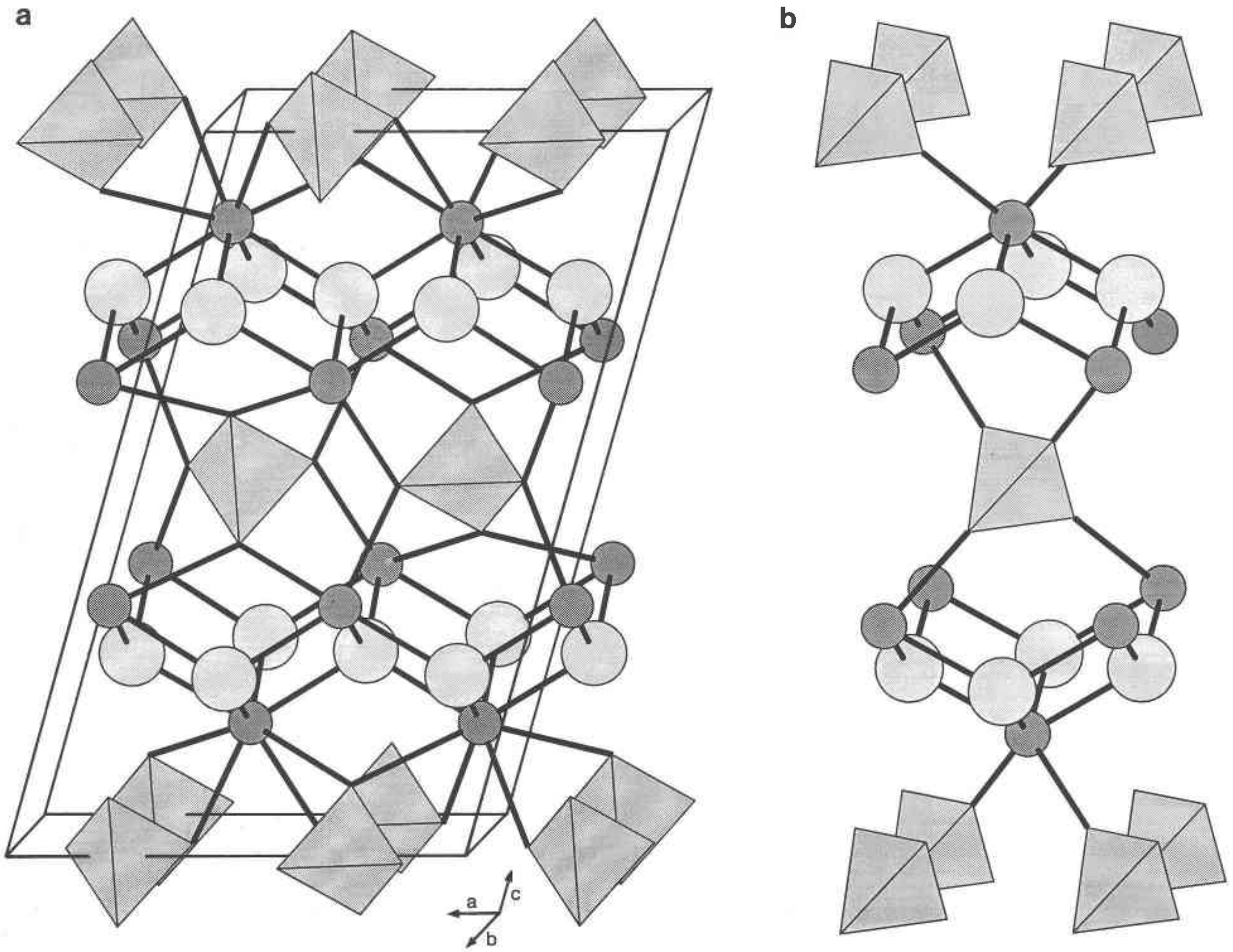

Fig. 1. (**a**) Crystal structure of grandreefite. Pb atoms are darkly shaded and F atoms are lightly shaded. Sulfate groups are shown as shaded tetrahedra. (**b**) Crystal structure of lanthanum oxide sulfate based upon Fahey (1976). La atoms are darkly shaded and nonsulfate O atoms are lightly shaded.

The sulfate groups have S-O distances of 1.49 Å and O-S-O angles between 105.8° and 110.7° (average 109.45°) (Table 3). F atoms have tetrahedral coordination by four Pb. Both O(1) and O(2) are coordinated to one S and two Pb. Pauling electrostatic bond-strength sums indicate that all anions are exactly saturated: $p_F = 4 \times 2/8 = 1.00$, $p_O = (2 \times 2/8) + 6/4 = 2.00$. Empirical bond-valence sums (in v.u.) are 1.83 for Pb, 5.71 for S, 0.95 for F, 2.02 for O(1), and 1.71 for O(2) (Brown and Altermatt, 1985).

The Pb^{2+} lone electron pair, which often strongly affects crystal structures containing this cation, is not stereoactive in the structure of grandreefite. The Pb coordination polyhedron does not display any obvious distortion attributable to a lone pair.

RELATIONSHIP TO $Ln_2O_2SO_4$

The relative positions of all atoms except the sulfate O atoms in the structure of grandreefite are essentially the same as those of the corresponding atoms in the structure of the lanthanide oxide sulfates, with Pb and F playing the same roles as Ln and O, respectively (compare Figs. 1a and 1b). Because the O atoms of the sulfate group contribute relatively little to the structure factor amplitudes, the powder patterns of these compounds are vir-

TABLE 1. Positional and thermal parameters in grandreefite

Atom	*x*	*y*	*z*	*B* (Å²)
Pb	0.0785(1)	0.5089(8)	0.1548(1)	0.58(2)*
S	¼	0.050(2)	0	0.2(1)
F	0.127(1)	0.967(5)	0.247(1)	1.0(2)
O(1)	0.115(2)	0.252(4)	0.003(1)	1.1(3)
O(2)	0.299(2)	0.858(5)	0.090(1)	1.1(3)

Note: Estimated standard deviations are in parentheses.

* This value is equivalent to the anisotropic temperature factors $\beta_{11} = 0.0024(1)$, $\beta_{22} = 0.0075(5)$, $\beta_{33} = 0.00052(3)$, $\beta_{12} = 0.0024(6)$, $\beta_{13} = 0.00062(4)$, and $\beta_{23} = 0.0003(4)$.

TABLE 3. Selected interatomic distances (Å) and angles (°) in grandreefite

		Pb bicapped trigonal prism		
Pb-F	2.39(2)	F-F	2.95(3)	72.7(6)
-F	2.52(1)	F-F	3.07(2)	71.5(4)
-F	2.57(1)	F-F	3.07(2)	77.1(4)
-F	2.71(2)	F-F	3.35(4)	78.7(6)
-O(1)	2.54(2)	F-O(1)	3.67(2)	88.5(5)
-O(1)	2.60(2)	F-O(1)	3.69(2)	95.2(6)
-O(2)	2.82(2)	F-O(1)	3.71(2)	94.2(5)
-O(2)	2.84(2)	F-O(1)	3.80(2)	94.7(5)
Average	2.62	F-O(2)	2.81(3)	62.3(5)
		F-O(2)	2.81(3)	63.1(5)
		F-O(2)	3.07(2)	71.7(5)
		F-O(2)	3.15(2)	68.9(5)
		O(1)-O(1)	2.95(4)	70.1(7)
		O(1)-O(2)	3.19(3)	72.8(6)
		O(1)-O(2)	3.20(3)	71.8(5)
		O(1)-O(2)	3.36(2)	77.2(5)
		O(1)-O(2)	3.46(2)	79.4(5)
		Average	3.25	77.1
		Sulfate tetrahedron		
S-O(1)	1.49(2) × 2	O(1)-O(1)	2.38(3)	105.8(1.5)
-O(2)	1.49(2) × 2	O(1)-O(2)	2.44(3)	109.6(0.9) × 2
Average	1.49	O(1)-O(2)	2.45(3)	110.5(0.9) × 2
		O(2)-O(2)	2.46(3)	110.7(1.5)
		Average	2.44	109.45

Note: Estimated standard deviations are in parentheses.

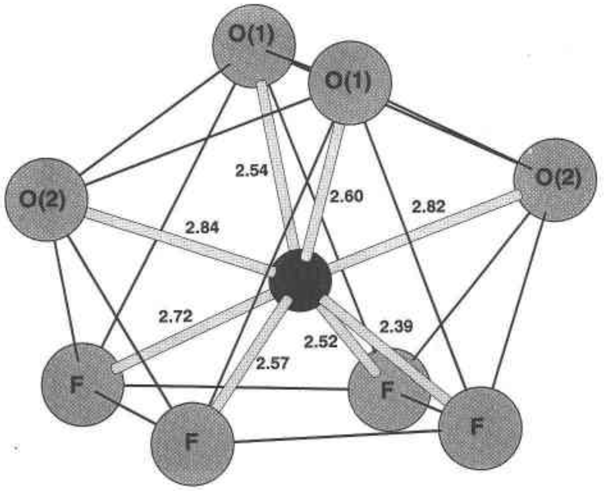

Fig. 2. The coordination polyhedron around Pb in grandreefite represented as a bicapped trigonal prism, with two O(2) atoms as the capping ligands.

tually identical. Neglecting the sulfate O atoms, these compounds are essentially tetragonal ($a \approx 4.0$ Å) as are many of the lead oxyhalides and related compounds.

If the sulfate oxygen atoms in $Pr_2O_2SO_4$ were completely disordered, being distributed in spherical shells as suggested by the refinement of Peacor in space group *Immm* (Haschke, 1988), a tetragonal cell might well be expected for this compound. Refinements in the other possible orthorhombic space groups, *I*222, *Imm*2, and $I2_12_12_1$ were similarly unsuccessful in locating the sulfate oxygen atoms, but refinements were not attempted in corresponding monoclinic space groups (Peacor, personal communication, 1989). It is of note that the *R* value obtained by Peacor, 0.11, is similar to that obtained for grandreefite using an orthorhombic cell and prior to the determination of the positions of the sulfate oxygen atoms.

The $La_2O_2SO_4$ structure determination by Fahey (1976) using powder data yielded atomic positions of low precision and a sulfate oxygen position which must be considered suspect. Nevertheless, it is of interest to examine the Pauling electrostatic bond-strength sums and empirical bond-valence sums for this structure. Notably, the position that Fahey determined for O of the sulfate group is consistent with this atom being coordinated to only one La atom and also with La being six coordinated (Fig. 1b). Electrostatic bond-strength sums corresponding to this arrangement show all O atoms to be saturated: $p_{O(oxide)} = 4 \times 3/6 = 2.0$ and $p_{O(sulfate)} = 3/6 + 6/4 = 2.0$. Empirical bond-valence sums (in v.u.) are 3.34 for La, 6.96 for S, 2.14 for O(1), and 2.34 for O(2). The high sum for S corresponds to very short S-O(2) bonds of 1.42 Å. A relatively small shift in the position of O(2), yielding bond distances of La-O(2) = 2.45 Å and S-O(2) = 1.47 Å, would bring the bond-valence sums for S, La, and O(2) into close accord with ideal values.

If sulfate oxygen atoms in the $La_2O_2SO_4$ structure were positioned as in the grandreefite structure so as to be coordinated to two La atoms ($CN_{La} = 8$), electrostatic bond-strength sums indicate that the oxide oxygen atoms would be significantly undersaturated ($p_O = 4 \times 3/8 = 1.5$) and the sulfate oxygen atoms would be oversaturated [$p_O = (2 \times 3/8) + 6/4 = 2.25$]. Furthermore, if it is assumed that the La, S, and O(1) locations determined by Fahey are correct, an abnormally long La-O(2) distance of 2.74 Å would be required to obtain an ideal empirical bond-valence sum for La in eightfold coordination.

Based upon electrostatic bond strength and empirical bond-valence considerations, it is likely that Fahey's structure determination is essentially correct and that the topologies of the $La_2O_2SO_4$ and $Pb_2F_2SO_4$ (grandreefite) structures differ with respect to the sulfate oxygen linkage and large cation coordination. Because La^{3+} is the largest of the trivalent lanthanide atoms, it is highly unlikely that any of the lanthanide oxide sulfates have the grandreefite structure.

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