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CRYSTALLOGRAPHY

1970

SovietRxiv

Abstract

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UDC 548.736.5

CRYSTALLOGRAPHY

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A NEW MODIFICATION OF THE SCHEELITE STRUCTURAL TYPE–THE CRYSTAL STRUCTURE OF Nd_2WO_6

The structure of a number of tungstates and molybdates has proved to be closely related to the widespread type $CaWO_4$ (scheelite) (^{1}). These are, above all, $Eu_2(WO_4)_3$ (^{2}), $Bi_2(WO_4)_3$ (^{3}), both with a tripled scheelite cell, and α-$Nd_2(MoO_4)_3$ with an 11-fold cell by volume (^{4}). In all cases a and b of the initial (tetragonal) cell change while the parameter along the principal direction c remains constant ($a_{\text{sh}} = b_{\text{sh}} = 5.24$, $c_{\text{sh}} = 11.385$ Å).

Crystals of Nd_2WO_6 were obtained under hydrothermal conditions from systems with Nd_2O_3, WO_3—aqueous LiCl solution, and also from KCl and NaCl melts.

Table 1

Atom	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$	B
W	0.1531	0.0001	0.3526	0.0002	0.2145	0.0005	0.2
Nd_1	0	–	0.6314	0.0004	0.250	–	0.4
Nd_2	0.1731	0.0002	0.8845	0.0003	0.2859	0.0006	0.4
Nd_3	0	–	0.1110	0.0004	0.250	–	0.3
O_1	0.407	0.003	0.519	0.005	0.485	0.010	0.3
O_2	0.420	0.003	0.261	0.005	0.493	0.011	0.3
O_3	0.422	0.003	0.035	0.005	0.396	0.011	0.7
O_4	0.272	0.003	0.053	0.004	0.117	0.011	0.4
O_5	0.270	0.003	0.205	0.005	0.487	0.011	0.1
O_6	0.390	0.003	0.222	0.005	0.036	0.010	0.7

The cell is simply related to the scheelite one: $a = 15.92$ ($\approx 3a_{\text{sh}}$), $b = 11.39$ ($\approx c_{\text{sh}}$); $c = 5.508$ Å ($\approx b_{\text{sh}}$); $\beta = 92°$. $Z = 8$. The diffraction symmetry is $I-/c$ (space groups $I2/c$ and Ic)*. Thin crystalline plates of Nd_2WO_6 are formed by the pinacoid (100) and are elongated along c. All the samples investigated by x-ray diffraction were twins on (100), but in one crystal $0.26 \times 0.33 \times 0.02$ mm^3 the dimensions of the second individual were minimal, which significantly reduced the distortion of the intensities of the main component and made it possible to have, for deciphering the structure, a satisfactory initial array: $\sim$ 2400 reflections $hk0 \div hk6$, $h0l$ (Mo radiation). In estimating the intensities on the γ^2 blackening scale, one of the $hk0$ reflections served as the initial standard. After correction for LP factors, a very nonuniform modulation of intensities remained unaccounted for, caused both by the plate-like shape of the sample ($\mu_{\text{lin}} = 477.2$ cm^{-1}) and by the presence of the twin.

Owing to insufficient difference in the scattering powers of Nd and W and to the superperiodicity of the structure along a, the Patterson projections $P(uv)$ and $P(uw)$, as well as that weighted by F^2_{h1l}, did not give a concrete distribution of the cations.

* The authors of ([6]) indicated the "tabular" setting ($C2/c$), but the setting is more complicated: $a = 16.92$ ($\approx 3a_{\text{sh}} - b_{\text{sh}}$), $b = 11.36$ ($\approx c_{\text{sh}}$), $c = 5.506$ Å ($\approx b_{\text{sh}}$); $\beta = 110°39'$ (Fig. 1A).

Analysis of possible distributions of cations in Nd_2WO_6 over the planes showed that the only ordered distribution satisfying the I-cell and the glide plane c is obtained when pairs of adjacent (scheelite) planes with alternating Nd and W are separated by single purely neodymium planes (Fig. 1B). The ideal coordinates of the basis cations corresponding to this distribution are: (4) Nd_1: $x = 0$, $y = 5/8$, $z = 1/4$; (8) Nd_2: 1/6, 3/8, 1/4; (4) Nd_3: 0, 1/8, 1/4; (8) W: 1/6, 3/8, 1/4. Refinement of the scheme by the least-squares method (l.s.m.) ([7]), first using 1000 F^2_{hkl} ($hk0$, $hk1$, $hk2$ and $h0l$; $\sin\vartheta/\lambda \leq 1.0$), and then using 940 reflections $hk0$–$hk6$ ($\sin\vartheta/\lambda \leq 0.7$), gave $R_{hkl} = 20\%$.

Refinement of isotropic temperature corrections did not lead to convergence. The quoted coefficients R_{W} and B_{Nd} are the result of selection and minimization of the R-factor; they were fixed during the l.s.m. refinement of the B values for O.

As was to be expected ([2,7]), localization of the light atoms was not accessible by direct methods. On Patterson projections the cation–oxygen vectors are merged into a diffuse maximum, indicating that all anions are located inside quartets (tetrahedra) of cations. More precise positions of the 6 basis O atoms in their "tetrahedra" were calculated on the basis of the assumed interatomic distances; it was taken into account that, at the shortest W–W distance of 3.88 Å, the coordination of W should not exceed 5 ([8]).

Table 2

Interatomic distances (Å)

Pair	Distances
Nd–Nd	3.74; 3.78; 3.81; 3.83; 3.94; 3.97; 3.99; 4.02; 4.07
W–Nd	3.48; 3.61; 3.69; 3.85; 3.89; 3.99; 4.08; 4.15
W–W	3.88; 4.35

W-tetrahedron	Distance
W–O_3	1.84
–O_4	1.83
–O_5	1.81
–O_6	1.71
–O_2	2.06
O–O	2.47; 2.58; 2.63; 2.67; 2.74; 2.80; 2.95; 3.16; 3.19

Nd_1-octahedron	Distance
Nd_1–O_2	2.38 (×2)
–O_3	2.42 (×2)
–O'_3	2.53 (×2)
–O_6	2.61 (×2)
O–O	2.63; 2.81; 2.86; 3.01; 3.07 (×2); 3.08; 3.69; 3.74; 4.17

Nd_2-octahedron	Distance
Nd_2–O_1	2.22
–O'_1	2.39
–O_2	2.41
–O_4	2.47
–O_5	2.51
–O'_5	2.54
–O'_4	2.67
–O_6	2.73
O–O	2.47; 2.68; 2.79; 2.89; 2.95; 2.98; 3.00 (×2); 3.01; 3.03; 3.08; 3.16; 3.53 (×2); 3.68; 3.70; 3.75; 3.88

Nd_3-octahedron	Distance
Nd_3–O_1	2.30 (×2)
–O_2	2.38 (×2)
–O'_1	2.49 (×2)
–O_6	2.82 (×2)
O–O	2.58; 2.79; 2.95; 2.98; 2.99; 3.07; 3.72; 4.00; 4.15; 4.19

The coordinates of the oxygen atoms were stably refined by l.s.m. to $R_{hkl} = 16.9\%$. The final values of all coordinate parameters (within the group $I2/c$)

and standard deviations are collected in Table 1, and the interatomic distances in Table 2.

The structure of Nd_2WO_6 is an interesting illustration of the tendency of heavy multicharged cations to preserve their relative arrangement (“cationic framework”) under variations in the cation distribution and in the positions of anions. For the first time, such an “energetic” function of cation packings (analogous to closest anion packings) was noted by one of the authors (^{9}) for the “generalized” CaF_2 type.

We start from the fluorite cation framework with Ca atoms at the nodes of a cubic (face-centered) lattice (a = 5.46 Å, Fedorov group $Fm3m$). In the derivative framework of tetragonal scheelite, translationally identical cations along one of the axes are replaced by alternating unlike ones; doubling of the translation lowers the symmetry to $I4_1/a$. Another group consists of tetragonal $La_2(MoO_6)$ and Bi_2NbO_5F ($a' = a\sqrt{2}$ = 5.77 and 5.41 Å, c = 16.00 and 16.63 Å$^{(10,11)}$) and rhombic Bi_2WO_6 (a = 5.436, b = 5.456, c = 16.415 Å) and Bi_2MoO_6 (a = 5.50, b = 16.24, c = 5.49 Å$^{(12,13)}$). The changed stoichiometry corresponds to redistribution in a geometrically unchanged framework: pairs of adjacent planes with large cations (Bi, La) are interleaved by single planes with medium cations (Nd, W, and Mo), with an evident tripling of the perpendicular translation (Fig. 1).

The synthesis of these distributions gives the cation framework of Nd_2WO_6: tripling of one period combined with scheelite doubling of the second makes possible (at identical stoichiometry La_2MoO_6–Nd_2WO_6) alternation of a “pure” neodymium layer with two mixed layers of the scheelite type (Nd : W = 1 : 1) (Fig. 1).

In the starting CaF_2 each anion is among 4 cations. In Nd_2WO_6 the anion shifts toward one of the faces of the tetrahedron, and in the first coordination sphere three cations remain (W + 2Nd). In Nd_2WO_6, of the 6 basis atoms only one, O_1, falls into a purely neodymium tetrahedron; the rest are in mixed ones: O_2 and O_6 in (W + 2Nd), O_3, O_4, and O_5, as in scheelite, move onto the face of the tetrahedron 2W + 2Nd and lower the coordination number to 3 (W + 2Nd). O_1 and O_2, having an elongated W–O distance (2.06 Å), remain almost at the centers of the tetrahedra, while O_6, for which one O–W distance is the shortest (1.77 Å) and the distances to the other cations are increased (2.61; 2.73; 2.82 Å), occupies an intermediate position.

Fig. 1. **A**–relationship between the scheelite lattice (square lining) and the lattices of α-$Nd_2(MoO_4)_3$–a_1, c_1; $Bi_2(WO_4)_3$–a_2, c_2; $Eu_2(WO_4)_3$–a_2, c_2, and a_3, c_3; (3)-type setting according to (2)); Nd_2WO_6–a_4, c_4 (6) and a_5, c_5 (5). –distribution of cations in the cell of α-$Nd(MoO_4)_3$; the elementary cell of $Eu_2(WO_4)_3$ with ordered cation arrangement is outlined. –scheme of the distribution of cations in the cell of Nd_2WO_6. –scheme of the distribution of cations in the cells of Bi_2MoO_6, La_2MoO_6, Bi_2NbO_5F.

In Nd_2WO_6 the coordination number 5 for W is not connected with polymerization of the W-oxygen radical. As in $NdWO_4OH$(9), inclusion of O_2 in the coordination polyhedron of W shortens the distances O_2–O_5 = 2.47, O_2–O_6 = 2.58, and O_2–O_3 = 2.63 Å, which become common edges of the W and Nd polyhedra (W–Nd = 3.61; 3.69; 3.48 Å). The fifth O centers the enlarged face O_3–O_5–O_6 of the W tetrahedron (O–O = 2.95; 3.16; 3.19 Å), completing it to a trigonal bipyramid.

For 3 basis Nd atoms the coordination is eightfold with an average distance Nd –O = 2.49 Å. The Nd_1 and Nd_3 polyhedra filling one cation plane are distorted cubes; the Nd_2 polyhedron is deformed to a significant extent.

to a greater extent. The Nd polyhedra are joined by common edges; the W tetrahedra are incorporated into the framework only through vertices.

The tendency of the crystals to twin on (100) can be associated with parallel (100) corrugated layers of O atoms, which are arranged according to the well-known tetragonal motif with an alternation of squares and rhombi (Fig. 3).

Fig. 2. Projection of a layer–one half of the elementary cell of Nd_2WO_6 ($0 < z < 1/2$)–onto the (001) plane

Fig. 3. Pseudotetragonal pattern of oxygen atoms in a layer of Nd_2WO_6 parallel to (100), with $x \approx 5/12$

The solution and description of the structure of Nd_2WO_6 were carried out within the space group $I2/c$. However, among approximately 2500 reflections, about 30 very weak ones violate the I extinction rule. Their formal consideration requires the symmetry $P2_1/c$, assigned by P. V. Klevtsov et al. (unpublished) to Nd_2WO_6, but within the accuracy of the experiment this in fact changes nothing.

The authors thank P. V. Klevtsov and L. Yu. Kharchenko for the samples provided for the study.

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Received
20 II 1970

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