

Crystal Structure of $\text{Nd}_2\text{Te}_4\text{O}_{11}$: An Example of a Rare Earth Tellurium Oxide

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The preparation and growth of single crystals and crystal structure determination of $\text{Nd}_2\text{Te}_4\text{O}_{11}$ are reported. It crystallizes in the monoclinic system, space group $C2/c$, with parameters $a = 12.635(6)$ Å, $b = 5.204(1)$ Å, $c = 16.277(3)$ Å, $\beta = 106.02(8)^\circ$, and $Z = 4$. An agreement factor of $R = 2.3\%$ was obtained after refinement of positional and anisotropic thermal parameters. The structure is described as an interconnecting network of NdO_8 distorted square antiprisms, which link in two dimensions through edge sharing, with TeO_4 polyhedra which link in the same two dimensions through corner sharing. Sheets of $(\text{Nd}_2\text{O}_{10})_\infty$ join with those of $(\text{Te}_8\text{O}_{20})_\infty$ to form a three-dimensional network. The location and role of the lone pairs are discussed. The structure can also be described as a distorted hcp array of oxygen ions, neodymium ions, and lone pairs in which tellurium ions occupy selected trigonal bipyramidal sites. © 1990 Academic Press, Inc.

Introduction

The family of Te rare earth oxides, $\text{Ln}_2\text{Te}_4\text{O}_{11}$, with Ln being a rare earth element has been known for some time. Originally, the synthesis for all of the rare earth elements except Tb, Pr, and Ce was described (1), these members being isolated later (2). X-ray diffraction studies on polycrystalline samples have demonstrated that these materials have monoclinic symmetry with unit-cell parameters in the ranges $12.80 \geq$

$a \geq 12.26$ Å, $5.278 \geq b \geq 5.058$ Å, $16.42 \geq c \geq 15.90$ Å, and $105.92 \leq \beta \leq 106.18^\circ$ from $\text{Ln} = \text{La}$ to Lu . The structural determination has not been reported. The oxides of elements with a lone pair, for example Sn(II), Sb(III), or Te(IV), present interesting properties as luminescent activators (3).

This paper describes the synthesis and single crystal X-ray diffraction structural study for $\text{Nd}_2\text{Te}_4\text{O}_{11}$, the first for a rare earth tellurium oxide. The location of the lone pairs and the role they play in the coordination spheres of tellurium are discussed. An unusual function fulfilled by neodym-

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ium ions in atomic packing is also discussed.

Experimental

The $\text{Nd}_2\text{Te}_4\text{O}_{11}$ oxide was prepared as a microcrystalline powder by solid state reaction in air, from a stoichiometric mixture of Nd_2O_3 and TeO_2 heating for 24 h successively at 923, 973, 993 K. After each thermal treatment, the product was quenched, weighed, ground, and characterized by X-ray powder diffraction. The single crystals were obtained from a mixture of $\text{Nd}_2\text{Te}_4\text{O}_{11}$

previously synthesized and TeO_2 used as flux with molar ratio 1:10. This mixture was heated in air to 1123 K to obtain a melt, held at that temperature for 1 h and cooled at 5 K h^{-1} to room temperature.

The crystal quality, unit-cell dimensions, and space group were first investigated on a precession camera. The collection of the diffraction data was performed using an Enraf-Nonius CAD-4 diffractometer. Table I shows physical and crystallographic data of the selected crystal together with the experimental conditions of data collection.

TABLE I
PHYSICAL AND CRYSTALLOGRAPHIC DATA AND PARAMETERS
FOR DATA COLLECTION

Formula	$\text{Nd}_2\text{Te}_4\text{O}_{11}$
Molecular weight (g)	974.9
Color	Light violet
Morphology	Flat parallelepiped
Dimensions (mm)	$0.15 \times 0.075 \times 0.0063$
Crystal system	Monoclinic
Space group	$C2/c$ (No. 15)
a (Å)	12.635(6)
b (Å)	5.204(1)
c (Å)	16.277(3)
β (°)	106.02(8)
V (Å ³)	1028(3)
Z	4
D_x (g · cm ⁻³)	6.30
$F(000)$	1664
μ (MoK α) (cm ⁻¹)	212
Temperature (K)	293
Wavelength (MoK α) (Å)	0.71069
Monochromator	Oriented graphite
Take off (°)	5.0
Detector width (mm)	4×4
Scan type	$\bar{\omega}/2\theta$
Scan width (°)	$0.80 + 0.35 \tan \theta$
Prescan speed (°min ⁻¹)	10
Final scan $\sigma(I)/I$	0.018
Maximum time (sec)	100
Reflections for cell refinement	25, θ : 6–27°
Recorded reflections	3287, $\theta \leq 34^\circ$
hkl range	$0 \leq h \leq 19, 0 \leq k \leq 8, -25 \leq l \leq 25$
Intensity control reflections	3 -1 -3/-1 -3 -3/0 0 -12 every 3600 sec
Orientation control reflections	0 0 12/12 0 0 every 250 reflections

TABLE II
PARAMETERS OF REFINEMENTS AND RESULTS

Independent reflections	1573
Transmission coefficient range	0.51–1.00
Empirical absorption correction (23)	
Significant reflections	1291 $I > 3\sigma(I)$
Refined parameters	79
Extinction II (g) (24)	2.53×10^{-7}
Height in last difference-Fourier ($e \cdot \text{\AA}^{-3}$)	+0.87 at 1.03 \AA to Nd -0.66 at 0.50 \AA to Nd
$R = (\sum F_o - F_c) / (\sum F_o)$	0.023
$R_w = [\sum w(F_o - F_c)^2 / (\sum w F_o^2)]^{1/2}$ with $w = 4F_o^2 / (\sigma^2 + (0.03F_o^2)^2)$	0.028
$S = [\sum (F_o - F_c)^2 / (NO - NV)]^{1/2}$	1.16

The structure was determined by the Patterson method. The refinements were carried out by full-matrix least-squares calculations. Atomic scattering factors were corrected for anomalous dispersion (4). Calculations were performed with SDP (5) and illustrations with ORTEP (6) programs using a VAX 11/730 computer.

Results

Table II summarizes the refinement results. Table III lists fractional coordinates and equivalent isotropic thermal parameters, and Table IV gives bond lengths and angles.

TABLE III
POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL FACTORS, $B_{eq} = \frac{1}{3} \sum_i \sum_j (a_i \cdot a_j) \beta_{ij}$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Nd	0.11878(2)	0.25489(5)	0.03746(2)	0.570(4)
Te1	0.12955(2)	0.27912(6)	0.37194(2)	0.517(5)
Te2	0.11998(2)	0.72844(7)	0.20220(2)	0.693(5)
O1	0.2494(3)	0.0657(8)	0.3707(3)	0.89(6)
O2	0.2072(3)	0.5411(8)	0.4427(3)	0.83(6)
O3	0.0725(3)	0.1203(8)	0.4531(2)	0.78(6)
O4	0.4736(3)	0.0951(7)	0.3990(3)	0.81(6)
O5	0.3522(3)	0.5551(8)	0.3281(3)	0.94(7)
O6	0	0.850(1)	1/4	1.2(1)

Description of the Structure

1. Neodymium–Oxygen

There exists in the structure only one type of neodymium atom, coordinated to eight oxygen atoms. The Nd–O distances vary from 2.358 to 2.603 \AA (Table IV), the mean value of 2.46 \AA being in agreement with those found in neodymium phosphates, NdP₃O₉ (2.43 \AA) and NdP₅O₁₄ (2.44 \AA) (7). The oxygen atoms linked to that of neodymium occupy the corners of a distorted square antiprism (Fig. 1) in which the neodymium atom is situated approximately midway (1.34 and 1.25 \AA) between the two mean planes described, respectively, by atoms O1ⁱ, O2ⁱⁱ, O4ⁱ, O4^{vi} and O2ⁱⁱⁱ, O3^{iv}, O3^v,

TABLE IV
SELECTED BOND DISTANCES (\AA) AND ANGLES (°)

Nd–O1 ⁱ	2.500(4)		
Nd–O2 ⁱⁱ	2.389(4)		
Nd–O2 ⁱⁱⁱ	2.405(4)		
Nd–O3 ^{iv}	2.552(4)		
Nd–O3 ^v	2.365(4)		
Nd–O4 ⁱ	2.496(5)		
Nd–O4 ^{vi}	2.603(3)		
Nd–O5 ⁱⁱⁱ	2.358(4)		
Te1–O1	1.883(4)	Te2–O1 ⁱ	2.434(4)
Te1–O2	1.877(4)	Te2–O4 ⁱ	1.876(4)
Te1–O3	1.863(4)	Te2–O5 ⁱ	1.830(5)
Te1–O4 ^{vii}	2.694(4)	Te2–O6	1.989(3)
O1 ⁱ –Nd–O2 ⁱⁱ	75.3(1)	O2 ⁱⁱⁱ –Nd–O3 ^v	76.6(1)
O1 ⁱ –Nd–O2 ⁱⁱⁱ	77.7(1)	O2 ⁱⁱⁱ –Nd–O4 ⁱ	141.9(1)
O1 ⁱ –Nd–O3 ^{iv}	128.7(1)	O2 ⁱⁱⁱ –Nd–O4 ^{vi}	130.9(1)
O1 ⁱ –Nd–O3 ^v	153.9(1)	O2 ⁱⁱⁱ –Nd–O5 ⁱⁱⁱ	76.6(1)
O1 ⁱ –Nd–O4 ⁱ	66.7(1)	O3 ^{iv} –Nd–O3 ^v	73.9(1)
O1 ⁱ –Nd–O4 ^{vi}	121.3(1)	O3 ^{iv} –Nd–O4 ⁱ	67.2(1)
O1 ⁱ –Nd–O5 ⁱⁱⁱ	79.8(1)	O3 ^{iv} –Nd–O4 ^{vi}	71.5(1)
O2 ⁱⁱ –Nd–O2 ⁱⁱⁱ	73.7(1)	O3 ^{iv} –Nd–O5 ⁱⁱⁱ	74.4(1)
O2 ⁱⁱ –Nd–O3 ^{iv}	141.0(2)	O3 ^v –Nd–O4 ⁱ	139.2(1)
O2 ⁱⁱ –Nd–O3 ^v	94.4(1)	O3 ^v –Nd–O4 ^{vi}	75.1(1)
O2 ⁱⁱ –Nd–O4 ⁱ	108.0(1)	O3 ^v –Nd–O5 ⁱⁱⁱ	97.2(1)
O2 ⁱⁱ –Nd–O4 ^{vi}	69.6(1)	O4 ⁱ –Nd–O4 ^{vi}	81.2(1)
O2 ⁱⁱ –Nd–O5 ⁱⁱⁱ	144.5(1)	O4 ⁱ –Nd–O5 ⁱⁱⁱ	84.2(1)
O2 ⁱⁱⁱ –Nd–O3 ^{iv}	135.2(1)	O4 ^{vi} –Nd–O5 ⁱⁱⁱ	145.9(1)
O1–Te1–O2	98.6(2)	O1 ⁱ –Te2–O4 ⁱ	78.0(1)
O1–Te1–O3	102.5(2)	O1 ⁱ –Te2–O5 ⁱ	89.1(2)
O1–Te1–O4 ^{vii}	171.3(1)	O1 ⁱ –Te2–O6	173.53(9)
O2–Te1–O3	97.3(2)	O4 ⁱ –Te2–O5 ⁱ	103.2(2)
O2–Te1–O4 ^{vii}	74.9(1)	O4 ⁱ –Te2–O6	95.6(1)
O3–Te1–O4 ^{vii}	73.2(1)	O5 ⁱ –Te2–O6	92.0(2)

Note. Symmetry code i: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; ii: $x, 1 - y, -\frac{1}{2} + z$; iii: $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; iv: $-x, y, \frac{1}{2} - z$; v: $x, -y, -\frac{1}{2} + z$; vi: $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; vii: $-\frac{1}{2} + x, \frac{1}{2} + y, z$.

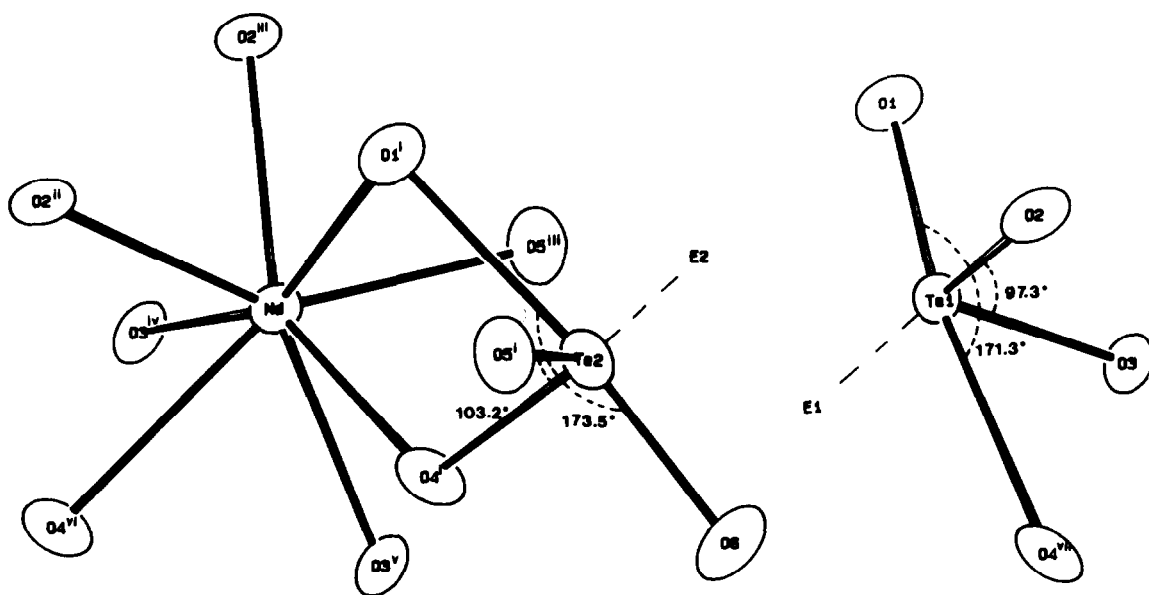


FIG. 1. Coordination polyhedra of the heavy atoms (with the calculated position of the Te atom lone pair E).

O5ⁱⁱⁱ. The displacements of oxygen atoms from the first mean plane are $\pm 0.09 \text{ \AA}$ while those from the second are $\pm 0.30 \text{ \AA}$. Only one oxygen atom, O6, is not coordinated to

Nd. The NdO_8 polyhedra share O3–O3, O2–O2, and O4–O4 edges to form net-like sheets of composition $(\text{Nd}_2\text{O}_{10})_\infty$ (Fig. 2) parallel to the (001) plane.

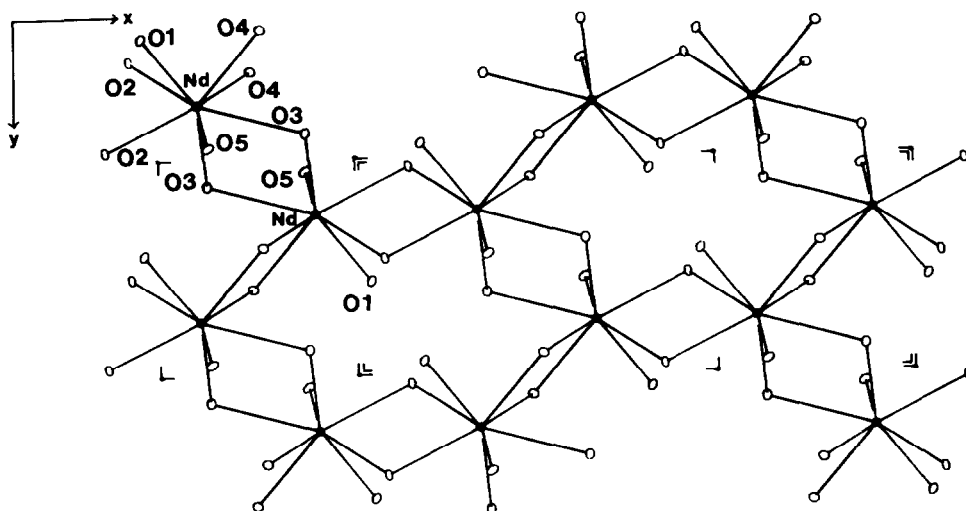


FIG. 2. Representation of the bidimensional Nd–O nets, projected on the (001) plane. \perp , origin of cell $z = 0$; \perp , origin of cell $z = 1$.

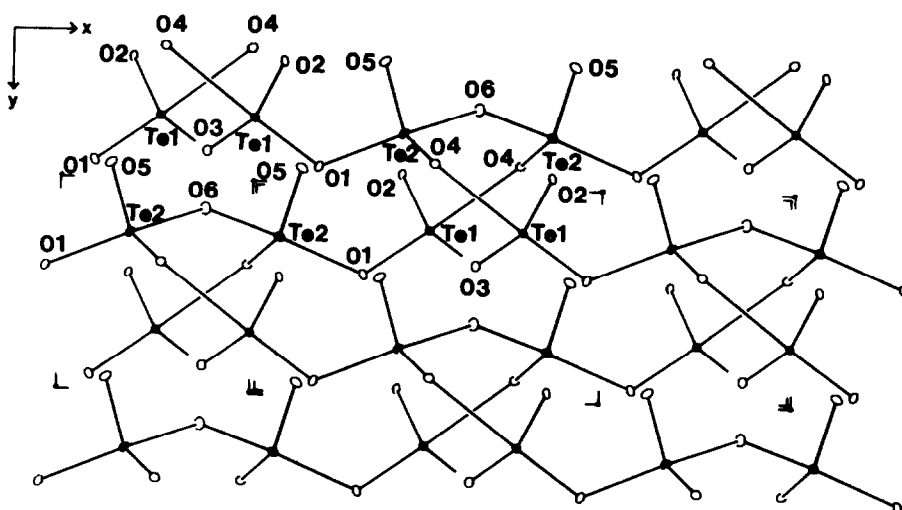


FIG. 3. Projection on the (001) plane of the twofold layers Te-O in $\text{Nd}_2\text{Te}_4\text{O}_{11}$. \blacksquare , origin of cell $z = 0$; \perp , origin of cell $z = 1$.

2. Tellurium-Oxygen

The two different tellurium atoms are coordinated to three oxygens at distances of less than 2 Å and a fourth at 2.694 Å for Te1 and 2.434 Å for Te2 (Table IV). If the bond-valence model (8, 9) is applied to interpret the Te coordination and only the three short Te-O interactions are considered, then the formula $S = 1.333 (d/1.854)^{-5.2}$, where d is the Te-O distance and S the valence for each liaison, gives the bond valence values of 3.78 for Te1 and 3.61 for Te2. In both cases, these valences are less than the theoretical +4 valence of tellurium. The interactions from the next more distant neighbors (Table IV) need to be taken into account in order to arrive at the values of 3.97 for Te1 and 3.92 for Te2 in good agreement with the theoretical value. This situation is similar to those found in a number of other tellurium oxides (10-13) when they are considered in this way.

Each Te1 is linked to two tellurium atoms and each Te2 is linked to three other tellurium atoms through oxygen atoms, thereby creating chains of Te1-O1-Te2-O6-Te2-

O1-Te1 in the [100] direction which in their turn are linked by Te1-O4-Te2 chains in the [010] direction (Fig. 3). The result is the formation of double layers of Te-O with the composition $(\text{Te}_8\text{O}_{20})_\infty$ parallel to the (001) plane.

3. Contribution of the Lone Pair, E

If the Te(IV) lone pair is considered as a sphere with a volume comparable with that of an oxygen ion (14), then the average volume for each anion for $\text{Nd}_2\text{Te}_4\text{O}_{11}\text{E}_4$ is 17.1 Å³, which is in good agreement with other values found for tellurium oxides (13, 15). Efforts have been made to identify meaningful positions for the lone pair on each tellurium atom. In a difference Fourier calculated after the last refinement, apart from maxima observed close to the neodymium atom (Table II), there appear residues of electron density of $0.5 e \cdot \text{Å}^{-3}$ at coordinates $x = 0.06, y = 0.39, z = 0.31$ and $x = 0.14, y = 0.64, z = 0.29$, at distances greater than 2 Å from oxygen atoms and situated, respectively, at 1.28 and 1.46 Å from Te1 and Te2. These peaks may represent lone

pair electron density: they are compatible with the definition of trigonal bipyramidal arrangements of anions around tellurium atoms, where the lone pairs occupy one of the equatorial apices. The distortion observed can be attributed to the repulsion between the lone pairs and the Te–O associations for each Te atom, the O_{ax} –Te– O_{ax} and O_{eq} –Te– O_{eq} angles being, respectively, less than 180 and 120°. These observations are not strongly significant in view of the nature of other remnants in the final difference Fourier calculation and we conclude that the positions of lone pairs have not been determined unequivocally. Nevertheless a consideration of the geometry of each tellurium atom, including the lone pair, is useful.

If the Te–O,E geometry is considered to be that of a distorted trigonal bipyramid, where E occupies an equatorial position, then a distortion coefficient can be calculated (using only the Te–O positions) with the empirical formula $D = (|180 - A|/180 + |120 - B|/120)10$, where A is the angle O_{ax} –Te– O_{ax} and B is the angle O_{eq} –Te– O_{eq} . For $Nd_2Te_4O_{11}$ the coefficients are, respectively, 2.4 and 1.8 for Te1 and Te2; values very near to those calculated for different "4" coordinated (i.e., excluding E) Te(IV) oxides: α -TeO₂ (16), $D = 2.1$; β -TeO₂ (17), $D = 2.3$; Zn₂Te₃O₈ (18), $D = 1.4$; Ta₂Te₂O₉ (13), $D = 2.5$; TiTe₃O₈ (19), $D = 2.7$; Te₃Nb₂O₁₁ (15), $D = 3.0$.

An idealized position for the lone pair on each tellurium atom has been calculated (14), the resultant positions being E1: $x = 0.0645$, $y = 0.3358$, $z = 0.2934$; and E2: $x = 0.1809$, $y = 0.5816$, $z = 0.2702$ (Fig. 1). These positions can then be used to calculate a distortion coefficient using the variations of dihedral angles from those for an ideal trigonal bipyramid (20). The coefficients for Te1 and Te2 are, respectively, $\Delta = 0.33$ and 0.29 (21) and the dihedral angles δa_1 111.0°, 111.5°; δa_2 107.7°, 110.5°; δa_3 108.9°, 104.1°; δa_4 111.7°, 110.2°; δa_5 109.5°,

105.4°; δa_6 107.9°, 108.0°; δe_1 34.7°, 33.2°; δe_2 66.6°, 64.4°; δe_3 35.4°, 39.8°.

An alternative description of the Te–O,E coordination polyhedra is possible using the interatomic/electronic distances and angles given in Table V. The values shown for $Nd_2Te_4O_{11}$ are in excellent agreement with those previously calculated (14) for a wide range of Te(IV) compounds.

4. Three-Dimensional Organization

Figure 4 represents a projection of the cell on (010) with only Te–O association (Fig. 4a) and Nd–O associations (Fig. 4b). The $(Te_8O_{21})_\infty$ and $(Nd_2O_{10})_\infty$ units are connected through oxygen atoms O1, O2, O3, O4, O5 to form a three-dimensional lattice. It can be seen that the complete structure is adequately described by superimposing the two Figs. 4a and 4b, and describing the corresponding sheets of polyhedra and the relationships between them.

When the structure is considered as being based on a close packed array of atoms it becomes clear that the neodymium ions occupy anion-like positions in the anion lattice. Some distortions within and on either side of each layer containing Nd occur as a result of its coordination requirements. A recalculation of the volume per "anion,"

TABLE V
COORDINATION POLYHEDRA DISTANCES (Å) AND ANGLES (°) ACCORDING TO REF. (14)

	Te1	Te2
a_1	2.81	2.90
a_2	2.86	2.84
d_1	1.87	1.85
d_2	2.29	2.21
l	4.56	4.42
Te-E	1.35	1.39
α	171.3	173.5
β	97.3	103.2
θ	39.3	48.3
φ	76.1	64.9

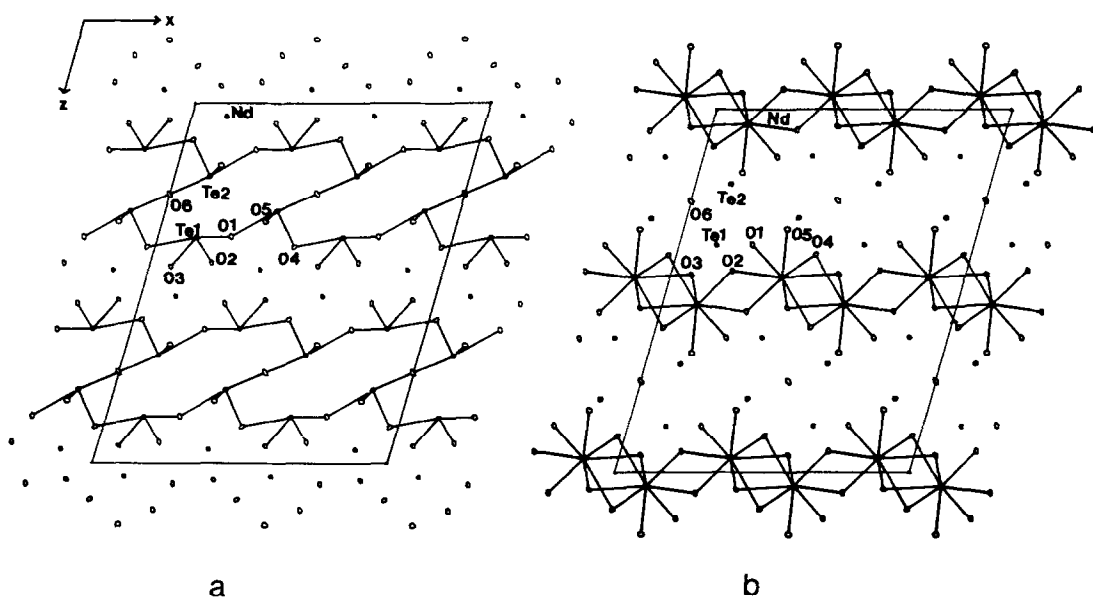


FIG. 4. Projection of the unit-cell of $\text{Nd}_2\text{Te}_4\text{O}_{11}$ (a) with Te-O bonds and (b) with Nd-O bonds represented (only the atoms with positions given in Table III are indicated).

this time including the lone pairs and neodymium atoms, gives a value of 15.1 \AA^3 per ion. This is towards the lower end of, but clearly within, the values previously tabulated suggesting that the packing is reasonably compact.

The structure can be alternatively described as a distorted hcp arrangement of oxygen ions, lone pairs, and neodymium atoms, in which tellurium ions occupy selected trigonal bipyramidal sites so as to form the Te-O,E systems already described.

There are three "unique" layers in the packing, each of which is displaced in successive layers (two of these layers are identical on inversion). One layer approximately $(-13 \ 0 \ 13)$, contains O1, O3, O4, O5, E2, and Nd. It is slightly distorted from an ideal close-packed layer and has Te2 in triangles formed by O4, O5, and E2. This layer and the second nominally include some of the O3 atoms even though in terms of the Te geometry and with ideal packing

geometry they would only be in the third layer. The second layer, approximately $(13 \ 0 \ -13)$, is the inversion of the first layer, and therefore necessarily contains O1, O3, O4, O5, E2, and Nd. The third layer, approximately $(-4 \ 0 \ 4)$, contains O2, O6, and E1 (and, if the geometry was ideal, would also contain O3). It has Te1 atoms in triangles defined by O2 and E1 (and O3) and is substantially distorted. If O3 is not considered as part of the layer, close packing geometry is not readily recognizable. Its inclusion results in a quite distorted net. In their calculated ideal (equatorial trigonal bipyramidal) positions the two lone pairs E1 appear too close to each other at 1.8 \AA (they are in fact equidistant on a line between two equivalent Te1 atoms).

The packing between these three layers and their equivalents is complex, repeating after 1.5 unit cells in a sequence that is $AB \ A^I B^I \ A^{II} B^{II} \ A^{III} B^{III} \ A^{IV} B^{IV} \ A^V B^V \ A^{VI} B^{VI} \ AB \ \dots$ in distorted hcp.

A significant feature of this description is

considered to be that Nd ions pack in the lattice of anions like Ba in BaNiO₃ (22). They occupy positions in approximately close-packed layers that are similar to positions occupied by oxygen ions.

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