CRYSTAL STRUCTURE OF $\mathrm{NaNd}_3[\mathrm{GeO}

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Abstract

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CRYSTAL STRUCTURE OF $\mathrm{NaNd_3[GeO_4]_2(OH)_2}$

The Na, Nd germanate (*E*-type according to (^{1})) was obtained by hydrothermal crystallization from the system $\mathrm{Na_2O—Nd_2O_3—GeO_2—H_2O}$ at 30-40% NaOH, $T = 450^\circ$ and $P = 1000$ atm (^{1}).

The parameters of the monoclinic centered cell (Å) are: $a = 5.260 \pm 0.001$, $b = 12.249 \pm 0.002$, $c = 13.931 \pm 0.003$; $\alpha = 90^\circ 15' \pm 1'$.

The diffraction symbol $2/mI—Ic$ corresponds to two Fedorov groups: $C_{2h}^6 = I2/c = I2/c(b)$ and $C_s^4 = Ic = Ic(b)$*.

The formula, based on chemical analysis with correction according to the results of the structural determination, is $\mathrm{NaNd_3[GeO_4]_2(OH)_2}$, $Z = 4$ at $\delta_{\mathrm{exp}} = 5.4$ g/cm^3.

A three-dimensional set of X-ray intensities from a spherical single crystal ($d = 0.134 \pm 0.005$ mm) with 566 pairs of reflections of the type $(\pm h)kl$, $c/l = 0, 1, 2, 3$ (Mo $K\alpha$ radiation, max $\sin\vartheta/\lambda$ taken as 1.0), was obtained on a DRON-1 by the variant of the nodal method (^{2}), with calculation of the setting angles according to (^{3}).

Table 1

$\mathrm{NaNd_3[GeO_4]_2(OH)_2}$. Coordinates of the basis atoms

Atoms	x/a	y/b	z/c
$\mathrm{Nd_I}$	0.041	0.000	0.250
$\mathrm{Nd_{II}}$	0.458	0.217	0.131
Ge	0.487	0.099	0.389
Na*	0.967	0.018	0.011
$\mathrm{O_1}$	0.340	0.031	0.102
$\mathrm{O_2}$	0.819	0.100	0.371
O	0.321	0.146	0.285
$\mathrm{O_3}$	0.367	0.193	0.475
$\mathrm{(OH)^-}$	0.864	0.151	0.165

Distances: Ge—O: 1.75; 1.77; 1.78; 1.77 Å. O—O (in the Ge tetrahedron): 2.67-2.96 Å.

* Coordinates of one of two equally probable positions related by a center of inversion.

The coordinates of the basis atoms (Table 1) were found from planar and three-dimensional syntheses—Patterson and electron-density syntheses. $R_{hkl} = 0.09$ (without taking absorption and the temperature factor into account).

Within the group $I2/c$ ($= C2/c$), one third of the Nd atoms ($\mathrm{Nd_I}$) occupy a special 4-fold position (on 2-fold rotation axes); two thirds ($\mathrm{Nd_{II}}$) and all Ge occupy general 8-fold positions. The four O atoms that tetrahedrally surround Ge are all crystallographically distinct, i.e., the cell contains 4 octets O_1—O_4. In the fifth octet, from the additional anions, the OH groups are assembled. The four Na atoms are displaced (slightly, but distinctly) from a 4-fold position (one system of inversion centers); their arrangement requires a formal abandonment of the center of symmetry in the structure as a whole, since the two positions for Na atoms near the inversion center that arise "automatically" mutually exclude one another (only one of them is needed!); nevertheless, each of these already 4-fold general positions within the groups Ic or $I2$ (either one) is equally probable, i.e., indistinguishable by X-rays.

Figure 2 gives a projection of the structure in a centrosymmetric aspect (with the symmetry elements of the group $I2/c$ shown). The mutual arrangement of the cations in the structure recalls a motif repeated in

* The piezoelectric effect is absent. The setting was chosen in accordance with that adopted for olivine (Fig. 1). At an angle α close to 90°, planes with nearly perpendicular slip directions alternate in the structure parallel to $\bar{A} = bc$.

of the whole series of "olivine-like" structures (1), but in essence represents a new variety of it.

Clearly distinguished are infinite serrated ribbons, located at two levels of the I-cell, made up of heterotypic cationic polyhedra joined by edges. In the cores of the ribbons, Na octahedra and $\mathrm{Nd_I}$-polyhedra alternate (twisted cubes with flattened square faces); in the teeth there are $\mathrm{Nd_{II}}$-polyhedra (trigonal prisms with a half-octahedron "attached" to one of the trapezoidal faces). The triplets of heterotypic polyhedra in the ribbon $(\mathrm{Na}, \mathrm{Nd_I}, \mathrm{Nd_{II}})$ are joined by edges in such a way that three-sided pockets are formed, to which Ge orthotetrahedra are "soldered" by their bases.

Fig. 1. Olivine ribbon with a core made up of distorted, but centrosymmetric octahedra, and noncentrosymmetric (but with a plane of symmetry) octahedra on the teeth. Along the ribbon axis, pockets with open gaps alternate with the apices of oppositely oriented pockets (triple points)

Fig. 3

Figure 1: Fig. 3

In the olivine structure the core of the ribbon consists exclusively of centrosymmetric octahedra, and therefore the two pockets adjoining each octahedron are opened by their gaps (Fig. 1) upward from the plane of the drawing and downward (open pockets and "triple points," to which the vertices of Ge tetrahedra of the opposite orientation are attached). In $NaNd_3[GeO_4]_2(OH)_2$, in the cores

Fig. 2. $NaNd_3[GeO_4]_2(OH)_2$. Projection of the structure on the yz plane. The black (dark) ribbon is at the 0 level, the white (light) ribbon at the $a/2$ level. Ge orthotetrahedra are schematically shown in circles.

of the ribbon and the "triple points" to which the apices of Ge tetrahedra of the opposite orientation are attached). In $NaNd_3[GeO_4]_2(OH)_2$, in the cores

(Fig. 2) centrosymmetric Na octahedra alternate with Nd_1-distorted cubes, through which twofold rotation axes pass, as a result of which pairs of open lunulae alternate with pairs of triple points along the axis of the rod, while the parameter c (along the axis of the rod) is doubled (somewhat more) in comparison with the same parameter in olivine (6.07–13.93 Å).

The Na cations in their octahedra are displaced from their centers (= centers of inversion). In Fig. 3 two positions are schematically shown inside the octahedra –

Fig. 3. Ribbons of three types of cation polyhedra with Ge orthotetrahedra in lunulae of two orientations. Paired circles in the octahedra indicate the equal probability of one of two positions for Na atoms within one octahedron

positions which, as noted, are equally probable, i.e., Na atoms occupy only one of two positions statistically (as do Li atoms in amblygonite[4]).

The interatomic distances in the structure $NaNd_3[GeO_4]_2(OH)_2$ do not exceed the permissible limits (Table 1). A quite satisfactory valence balance clearly distinguishes the OH group.

Owing to the centered group $I2/c(b)$, parallel to the plane bc the small cell period $a = 5.26$ Å is cut by two pairs of glide planes. One pair (planes c at levels 0 and 1/2) transforms one half of a cation ribbon with open lunulae into the second, with closed ones; the other pair (planes b at levels 1/4 and 3/4) connects the two ribbons per cell located at different heights.

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Note: Figure translations are in progress. See original paper for figures.