THE CRYSTAL STRUCTURE OF LANDAUITE \

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Abstract

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THE CRYSTAL STRUCTURE OF LANDAUITE *

Samples of landauite from the Burpala massif (Northern Baikal region) were kindly provided by A. M. Portnov. In the X-ray part of the first report on landauite (1), its monoclinic symmetry, space group $A2/a$, was established. The grouping of the chemically distinct components of the mineral was given in the form:

$$[\mathrm{Zn}_{0.39}\ \mathrm{Mn}_{0.15}\mathrm{Fe}^{2+}_{0.09}\ \mathrm{Fe}^{3+}_{0.29}]_{0.92}[\mathrm{Ti}_{2.87}\mathrm{Fe}^{3+}_{0.10}]_{2.97}.$$

Taking into account the repeatedly noted (2) transition, in the presence of Mn, of part of Ti into the trivalent state** leads to the formula of the diorthotype $\mathrm{Ti}_2\mathrm{R}^{3+}_2\mathrm{O}_7$,

where

$$\mathrm{R} = \mathrm{Ti}^{3+}_{0.87}\mathrm{Zn}^{2+}_{0.39}\mathrm{Fe}^{2+}_{0.09}\mathrm{Mn}^{3+}_{0.15}\mathrm{Fe}^{3+}_{0.39}.$$

At a density of 4.42 g/cm^3, the cell contains 4 units of the indicated composition. The cell parameters were refined: $a = 5.225 \pm 0.005$ Å, $b = 8.955 \pm 0.07$ Å, $c = 9.783 \pm 0.007$ Å; $\beta = 107°$.

The experimental material consisted of layer-line patterns $0kl$—$4kl$; $h0l$, $h1l$ (Mo radiation, Weissenberg goniometer). The intensities of the reflections were estimated on a $\sqrt[4]{2}$-blackening scale and were recalculated into amplitudes F_{hkl} with the standard exclusion of the LP-factor. Because of the small size of the crystal fragment and its irregular shape, the absorption factor was not taken into account. The statistics of the $1kl$ intensities and the analysis of the Patterson projections confirmed the presence of a center of symmetry.

By means of the minimization function M_4, from two Patterson projections $P(xz)$, $P(yz)$, the positions of the heavier Ti, R were established. Further investigation proceeded in two directions.

1. On the assumption of the formula $Ti_2^{4+}R_2^{3+}O_7$, $\sim 1/3(0.87)$ of the Ti atoms (Ti^{3+}) become principal atoms in the R group and only statistically replace Zn, Fe, Mn atoms in the general 8-fold complex of positions of the group $A2/a$. A three-dimensional Patterson function and an electron-density distribution by signs determined from the coordinates of the Ti and R atoms were constructed. In the corresponding sections it proved possible to localize four independent O atoms. The fixed atomic positions were refined by the least-squares method and also by a series of successive approximations. For the averaged R, the atomic scattering factor f_j was calculated in accordance with the formula written above. Upon refinement over 547 nonzero reflections, a discrepancy factor $R_{hkl} = 15.6\%$ was obtained.

2. The possibility of the chemical formula $Ti_3^{4+}R^{2+}O_7$ was taken into account, and then, within the group $A2/a$, 1/3 of the Ti cations, the entire group R, and even one of the O atoms must occupy special 4-fold complexes, i.e. all of them are located on twofold axes or at centers of symmetry. Neither the sections of the three-dimensional Patterson function nor the projections of electron density $\sigma(xz)$, $\sigma(yz)$ of such a centrosymmetric variant showed noticeable peaks in the corresponding positions. From the analysis of interatomic distances it likewise followed that it was impossible to place Ti and R^{3+} either on twofold axes or at centers of symmetry. Thus, the second variant of the formula required for the crys-

became the symmetry Aa with all atoms in fourfold positions. In successive approximations the cations Ti and R, localized according to the first variant, were slightly displaced from the centrosymmetric arrangement, and then several cycles of coordinate refinement were carried out with a varying percentage content of different atoms in the split positions. It turned out that the amount of Ti in the two subgroups Ti_1 and Ti_2 is close to 4, while the quality of the atoms in the subgroups Ti_3 and R (recalculated to f_j) excluded any difference between them. After refinement of this variant the atomic coordinates differed almost not at all from the centrosymmetric ones, and the R-factor, equal to 16.5% for the second variant, showed the incorrectness of rejecting centrosymmetry. The coordinates of all atoms within the Fedorov group $A2/a$ and the temperature corrections are given in Table 1. Two projections of the structure are shown in Figs. 1 and 2.

Table 1

Coordinates of the basis atoms of landauite

Atom	x/a	y/b	z/c	u_j
R	0	0.100	0.141	1.36

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* In honor of Academician L. D. Landau in connection with the award to him of the Nobel Prize.

** More details in the concluding lines of this report.

Fig. 1. Structure of landauite (axonometry) of elongated octahedra around the larger Ti3+ (statistically replaced by Mn, Fe, Zn) and half-octahedra around Ti4+.

Figure 1: Fig. 1. Structure of landauite (axonometry) of elongated octahedra around the larger Ti3+ (statistically replaced by Mn, Fe, Zn) and half-octahedra around Ti4+.

Atom	x/a	y/b	z/c	u_j
Ti	0.250	0.375	0.143	1.58
O_1	0.000	0.482	0.182	2.35
O_2	0.250	0	0	2.64
O_3	0	0.231	0	2.85
O_4	0.250	0.725	0.235	1.89

The structure of landauite is characterized by cation polyhedra of two types: five-vertex polyhedra and slightly elongated octahedra. In the tetragonal pyramids—half-octahedra—there are half-valent Ti atoms, while in the octahedra the larger Ti^{3+} atoms are statistically replaced by Zn, Fe^{3+}, Fe^{2+}, Mn^{3+} atoms. The interatomic distances in the tetragonal pyramids (half-octahedra) are: four 1.75; 1.78; 1.80; 2.06; mean 1.98, and the fifth 2.53 Å. Interatomic distances in the R-octahedra: 1.81; 1.83; 1.87; 1.88; 2.34; 2.39; mean 2.02 Å.

Fig. 1. Structure of landauite (axonometry) of elongated octahedra around the larger Ti^{3+} (statistically replaced by Mn, Fe, Zn) and half-octahedra around Ti^{4+}.

Half-octahedra around Ti^{4+}, i.e., its fivefold coordination, have already been demonstrated in the structure of synthetic Na_2TiSiO_5 (^{3}), and also in the structure of lamprophyllite (^{4}); half-octahedra around Mn have been found in one of the modifications of MnF_2, but the most interesting are Mn half-octahedra in the structure of the synthetic phosphor $K_2Zn_4Mn_2 \cdot Si_4O_{15} = K_2Zn_4Mn[Si_2O_7][SiO_4]_2$ *. Here (^{5}) the Mn half-octahedra, along a common (one of the equatorial) edge (lying in the mirror plane), are paired into groups $[Mn_2O_8]$, and neighboring Mn approach to 3.0 Å. In landauite the Ti half-octahedra are also paired along a common edge (the center of symmetry lies on it) with a Ti—Ti distance of 2.83 Å, but then these bivalent groups become links of a chain (connected by the glide plane a) (Fig. 2) with the formula of the metatype $[Ti_2O_6]_\infty$ and even with a metasilicate (pyroxene) repeat period of 5.23 Å. The other cell dimensions are also close to the pyroxene ones, but in the formula of landauite there is one more O, and therefore each O atom occupies a volume $V_O = 15.6$ Å^3, considerably smaller than in the pyroxene—diopside ($V'_O = 18.8$), but still larger than in ideal close packing (V''_O

* Fivefold coordination of Ti underlies the crystal-chemical interpretation of the peculiarities of the behavior of Ba titanate $BaTiO_3$.

Fig. 2

Figure 2: Fig. 2

$= 13$ Å^3). The reason is the use by landauite cations of more spacious polyhedra in comparison with Si in tetrahedra and Ca in a distorted octahedron; both positions are associated with a considerable "unpacking" of the packing.

The leveling, at first glance unexpected, in one crystallographic position of cations with very different radii: Ti^{4+} (0.64–0.68), Mn^{2+} (0.91–0.80)* had already been noted by one of the authors of this paper (^{2}) in Khibiny minerals (seidozerite, lorenzenite), in which both Ti and Mn take part together, with the possibility of the homogenizing equilibrium
$Ti^{4+} + Mn^{2+} \rightleftarrows Ti^{3+} + Mn^{3+}$. The cations in the right-hand side already have almost identical radii (0.69–0.70). In the structure of neptunite (^{6}), Mn and Ti in a single chain of octahedra alternate over independent crystallographic positions, but not in a strictly stoichiometric ratio.

Fig. 2. Landauite. Chains elongated along $c = 5.23$ Å, consisting of Ti^{4+} semi-octahedra with metaformula $[Ti_2O_6]_\infty$, due to two shared edges of each semi-octahedron with neighboring ones

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* The first figures are from Goldschmidt's tables, the second according to Ahrens.

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