SOVIET PHYSICS–CRYSTALLOGRAPHY VOL. 10, NO. 5 MAR.-APR., 1966

THE STRUCTURE OF CALCIUM SEIDOZERITE

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Translated from Kristallografiya, Vol. 10, No. 5,
pp. 591-595, September-October, 1965
Original article submitted February 23, 1965

The structure of a new calcic variety of seidozerite from the Baikal area has been analyzed. The atomic coordinates were refined by the method of least squares. A comparison is drawn between the structure analysis results for the Khibiny and Baikal minerals.

In 1958 E. I. Semenov found and described seidozerite, a new Zr, Ti silicate from the Lovozero Massif (Kol'skii Peninsula) [1]. A structure analysis of this mineral [2] showed the presence of something which was unusual from the crystallochemical point of view, the isomorphous replacement of titanium by 25% zirconium. Not long ago, Portnov discovered a new variety of seidozerite in the northern Baikal area [3]. The basic difference between the chemical compositions of the Kol'skii and Baikal minerals was that the latter had a considerably higher Ca content, with a corresponding reduction in Ti. It would be difficult to class this as isomorphic replacement, because of the great difference between the ionic radii. The purpose of the present investigation was to resolve the question of isomorphic replacement in calcium seidozerite, and to refine its structure. This last appeared desirable, since the structure of seidozerite had been interpreted from two projections containing overlapping atoms.

The unit cell constants for Ca seidozerite were $a = 5.54 \pm 0.02$, $b = 7.10 \pm 0.03$, $c = 18.36 \pm 0.10$ A, and $\beta = 102°40'$, calculated from rotation photographs (RKV-86 camera, Mo radiation), which is in good agreement with the constants of Khibiny seidozerite, $a = 5.53 \pm 0.02$, $b = 7.10 \pm 0.03$, $c = 18.30 \pm 0.10$ A, and $\beta = 102°43'$. The experimental material for the reflection intensity studies, collected on six Weissenberg layer line photographs (equi-inclination x-ray goniometer, Mo radiation), consisted of 135 independent, nonzero reflections of type $h0l$, $160-h1l$, $157-h2l$, $101-0kl$, $184-1kl$, $248-2kl$. The symmetry of the x-ray photographs, and the systematic absence rule obeyed confirmed that Ca seidozerite had the x-ray group $2/mP-/c$. From a comparison of the Patterson projections of the Khibiny and Baikal specimens, which confirmed the closeness of their structures, it was decided to assign the Ca seidozerite the centrosymmetric space group $P2/c$, and to take its initial atomic coordinates in the structure analysis to be the same as those of the Khibiny seidozerite [2]. As already pointed out, we considered that the most important question was the distribution of the cations among the independent crystallographic positions. The cationic compositions of the seidozerite samples, calculated on two Si atoms, were $Na_{1.79}Ca_{0.19}Mg_{0.17} \cdot Mn_{0.23}Fe_{0.19}Al_{0.10}Zr_{0.72}Ti_{0.63}Nb_{0.02}$ for the Khibiny specimen (Semenov [1]), and $Na_{1.81}Ca_{0.64}Mn_{0.28} \cdot Fe_{0.21}Zr_{0.70}Ti_{0.39}$ for the Baikal specimen (Portnov [3]).

These atoms were distributed among six crystallographic positions, of which two were general, and four were multiple, on the twofold rotation axis. Working from the chemical analysis, the peak heights on the electron density maps, and the interatomic distances, successive approximations led to the following groups of cations for the Khibiny seidozerite (note that a change in the distribution of cations affected the coordinates of the atoms): $(0.72Zr + 0.28Ti)$, $(0.23Mn + 0.17Mg + 0.10Fe)$, $(0.35Ti + 0.02Nb + 0.09Fe + 0.04Al)$, and $(0.90Na + 0.10Ca)$ for one general and two special positions. This arrangement of cations gave good agreement for the peak heights and satisfactory interatomic distances for the lowest value of the reliability factor. Particular attention was paid to the determination of the kinds of cations which randomly occupied the same crystallographic position as the zirconium. Because of the marked difference between the ionic radii of Zr^{+4} (r = 0.82 A) and Ti^{+4} (r = 0.64 A), there was little a priori probability of isomorphous introduction of Ti into positions occupied by Zr. However, the experimental evidence (the R-factor, the peak heights, and the interatomic distances) meant that the above association of cations had to be accepted. A crystallochemical interpretation of these results has been provided by Belov [4], who put forward the idea of the governing role of the manganese in the replacement of zirconium by titanium.

The structure of the calcium seidozerite was refined by the least-squares method. The particular features of the computing program used [5] meant that the coefficients for bringing different layer lines to a common scale could only be refined for one system of layer lines. We were therefore unable to relate the $0kl$, $1kl$, $2kl$ reflections with the $h0l$, $h1l$, $h2l$ reflections, these layer lines being recorded on rotating the crystal about the axes *a* and b respectively. We first refined the y- and z-coordinates of the basic atoms (keeping the x-coordinates "frozen"), using 533 independent nonzero reflections of the types $0kl$, $1kl$, $2kl$. The y-coordinates obtained in this manner were then fixed during the refining of the x- and z-coordinates, from 452 reflections of the types $h0l$, $h1l$, $h2l$. These two cycles were repeated alternately several times. The procedure used enabled us to compare the refined z-coordinates obtained from two different sets of layer lines, and to estimate the real accuracy of the results. The maximum spread of the z-coordinates of the cations was found to be 0.005 A. The corresponding average value for the anion z-coordinates was 0.013 A, with a maximum difference of 0.038 A. The linear x-ray absorption coefficient (λ = 0.71 A) in the seidozerite was $\mu = 35\ cm^{-1}$. When F^2_{hkl} was calculated from the experimental intensities without taking the absorption into account, an error was introduced into the structure amplitudes which was greatest for reflections of type $0kl$, $1kl$, $2kl$, since the crystal fragment used, with roughly equal dimensions along *a* and c, was elongated along b. This was reflected in the final reliability factors, which had the values of 14.6 and 9.97% for all nonzero reflections of the $0kl$, $1kl$, $2kl$ and $h0l$, $h1l$, $h2l$ groups respectively. In the last stages of the structure refinement, the least-squares method was used to obtain the individual isotopic temperature corrections, which are listed in Table 1 together with the final coordinates of the principal atoms. These corrections carry within themselves the systematic errors through neglecting absorption, and the chance errors arising in the visual estimation of intensities.

TABLE 1. Coordinates and Individual Isotropic Temperature Factors for the Principal Atoms in Calcium Seidozerite

Atom	x/a	y/b	z/c	B, A^2
Zr	0.198(2)	0.118(9)	0.0739	1.4
Ti	0.0000	0.109(3)	0.2500	1.0
Ca (Mn)	0.5000	0.348(8)	0.2500	1.0
Na_I (Ca)	0.202(1)	0.611(6)	0.0693	1.6
Na_{II}	0.0000	0.609(6)	0.2500	1.1
Na_{III}	0.5000	0.850(0)	0.2500	1.5
Si_I	0.723(1)	0.385(3)	0.1042	0.7
Si_{II}	0.722(1)	0.839(8)	0.1053	0.9
O_I	0.736	0.611	0.108	1.5
O_{II}	0.440	0.318	0.065	1.4
O_{III}	0.440	0.903	0.076	0.9
O_{IV}	0.919	0.314	0.056	0.9
O_V	0.900	0.909	0.051	1.0
O_{VI}	0.787	0.306	0.188	0.9
O_{VII}	0.816	0.919	0.187	1.2
O_{VIII}	0.241	0.127	0.183	1.6
(F, OH)	0.302	0.570	0.191	0.7

The reliability factors were about one percent higher if calculated without taking the individual temperature factors into account (15.6 and 11.0%).

The most probable distribution of cations, based on the chemical analysis [3], which was in accord with the peaks found on the electron density maps and which gave the reliability factors mentioned above, had the form Zr(0.70Zr + 0.20Mn + 0.10Fe), ½Ti(0.39Ti + 0.11Fe), ½Ca(0.42Ca + 0.08Mn), Na_I(0.78Na + 0.22Ca), ½Na_{II}(0.50Na), ½Na_{III}(0.50Na). The Baikal seidozerite lacked the titanium which was isomorphously present in the zirconium positions in the Khibiny seidozerite. The amount of titanium present in octahedral coordination, on the twofold axes, was practically the same in the Khibiny and Baikal minerals. The relatively small amount of Fe and Mn present, and the closeness of these elements in the periodic table, made it difficult to decide their distribution unambiguously, among the crystallographic positions in Ca seidozerite. A further difficulty arose through the variety of valence states typically shown by Fe and Mn. Table 2 lists cation–anion interatomic distances in the Ca seidozerite structure. These distances support the distribution of cations suggested above, and are not abnormal [6]. The only discrepancy involves the Ca(Mn) octahedron, which will be discussed further below. The edges of the Si_I- and Si_{II}-tetrahedra have lengths of 2.59-2.69 A and 2.57-2.68 A. The distances between oxygens in the Ti octahedra are 2.72-2.89 A. The $O_V - O_V{}^*$ edge shared between two Zr octahedra is shortened, down to 2.70 A. The other

TABLE 2. Interatomic Distances in the Calcium Seidozerite Structure, in A

Si_I-tetrahedron		Si_{II}-tetrahedron		Ti-tetrahedron	
$Si_I - O_I$	1.61	$Si_{II} - O_I$	1 63	Ti $2O_{VI}$	2.01
O_{II}	1.64	O_{III}	1.60	$2O_{VII}$	1.92
O_{IV}	1.62	O_V	1.62	$2O_{VIII}$	2.00
O_{VI}	1.60	O_{VII}	1 57		

Ca(Mn)- octahedron		Na_{II}-polyhedron		Na_{III}-octahedron	
Ca(Mn)— $2O_{VI}$	2.17	$Na_{II} - 2O_I$	2.68	$Na_{III} - 2O_{VII}$	2.35
$2O_{VIII}$	2.29	$2O_{VI}$	2.59	$2O_{VIII}$	2.58
2(F, OH)	2.08	$2O_{VII}$	2.58	2(F, OH)	2.41
		2(F, OH)	2.20		

Zr-octahedron		Na_I (Ca)-polyhedron	
Zr—O_{II}	1.98	Na_I (Ca)—O_I	2.82
O_{III}	2.03	O_I^*	2.88
O_{IV}	2.05	O_{II}	2.47
O_V	2.19	O_{III}	2.44
O_{V*}	2.24	O_{IV}^*	2.61
O_{VIII}	1.96	O_{IV}	2.31
		O_V	2.67
		(F, OH)	2.19

edges of the Zr octahedra have lengths of from 2.85 to 3.12 A. The average cation—anion distance in the Na_{III} octahedron, 2.45 A, is exactly equal to the corresponding standard value [6]. Six of the anions surrounding the Na_{II} atom are 2.20-2.59 A away, with another two oxygens 2.68 A distant, making a total coordination of eight for Na_{II}. The electron density peak corresponding to the Na_I atom was higher than those for Na_{II} and Na_{III}. This point, and the behavior of the R-factor, forced us to the conclusion that a proportion of the Na in the Na_I position are randomly replaced by Ca. The corners of this anion octahedron are 2.19-2.67 A away from the Na_I (Ca) atom. The O_I bridge atoms of the two translationally-identical $[Si_2O_7]$ diortho groups are 2.82 and 2.88 A away from Na_I(Ca), and lie at the centers of two opposite and greatly elongated octahedron edges, raising the coordination of the Na_I(Ca) to eight. The geometry of the connections between the $[Si_2O_7]$ groups, the Zr octahedra, and the Na_I(Ca) eight-cornered polyhedra is shown in Fig. 1 (in a projection along the c-axis).

The average cation—anion distance in the Ca(Mn) octahedron is 2.18 A, which is 0.12 A lower than the accepted standard value for Ca octahedra, and which is close to the corresponding values for the Mn and Fe octahedra. The average cation—anion distances in the octahedra of calcium seidozerite (averaging the six shortest distances only in the eight-cornered polyhedra) are 1.98 A for Ti octahedra, 2.08 A for Zr octahedra, 2.18 A for Ca(Mn) octahedra, 2.45 A for Na_I(Ca) "octahedra," 2.46 A for Na_{II} "octahedra," and 2.45 A for Na_{III} octahedra. Of the last three polyhedra, only the first lies in a general position, the other two being on twofold rotation axes, or in other words, these three polyhedra have only two principal cations distributed among them. The total quantity of Na and Ca in the Baikal seidozerite, which must be distributed among these six polyhedra, is 2.45 atoms, i. e., we must allocate 0.45 of the large cat-

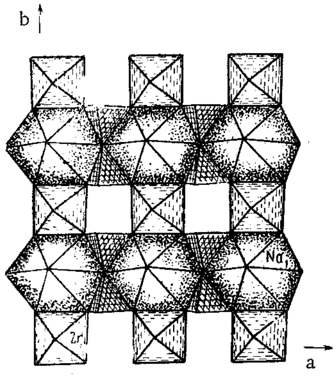

Fig. 1. Method of connecting the $[Si_2O_7]$ groups with the Zr octahedra and the Na_I(Ca) eight-cornered polyhedra. Projection along the c-axis.

ions to the octahedron with an average cation–anion distance of 2.18 A.

We will not stop to describe the structural arrangement in Baikal seidozerite, since it has the same architectural features as the Khibiny mineral [2]. The transformation of the octahedra into eight-cornered polyhedra (inclusion of a seventh and eighth atom in the Na_I and Na_{II} spheres of coordination) is shown in Fig. 2. The left-hand side of the drawing (Fig. 2A) shows the projection, along b, of the diorthogroups and a layer of $Na_I(Ca)$- and Na_{II}-polyhedra, each of which has four edges shared with Si tetrahedra (see Fig. 1).

The seventh and eighth atoms around the Na_I and Na_{II} cations are the bridge oxygen atoms of the $[Si_2O_7]$ group. If the layer of Na_I and Na_{II}-polyhedra is removed, the customary seidozerite arrangement of octahedra is seen (Fig. 2B).

As noted above, the Ca seidozerite structure has six crystallographically different positions in which to accommodate cations. The least reliable data obtained from the x-ray diffraction study of seidozerite are those on the distribution of Mn and Fe, since these two are similar not only in their atomic numbers, but also in their ionic radii. The other cations were located comparatively reliably. The most likely formula for Ca seidozerite is as follows: $Na(Na_{0.78}Ca_{0.22})(Ca_{0.42}Mn_{0.08})(Zr_{0.70}Mn_{0.20}\cdot Fe_{0.10})(Ti_{0.39}Fe_{0.11})O[Si_2O_7](F, OH)$. It will be appreciated that the values of the fractional coefficients are derived from the chemical analysis [3], and are not calculated from the electron density values. A comparison of the generalized formulas for Khibiny seidozerite, $Na_4MnTi(Zr, Ti)_2O_2[Si_2O_7]_2\cdot(F, OH)_2$, and Baikal seidozerite, $Na_2(Na, Ca)_2(Ca, Mn)Ti\,Zr_2O_2[Si_2O_7]_2(F, OH)_2$, shows that the parallel increase in Ca and decrease in Ti in the latter specimen takes place within the framework of ordinary crystallochemical concepts. The Baikal mineral lacks the Ti which randomly replaced Zr in the Khibiny seidozerite. The Zr octahedron has Mn and Fe present instead of Ti, and Ca is randomly introduced into one of the three independent Na positions, and into the former Mn octahedron of Khibiny seidozerite.

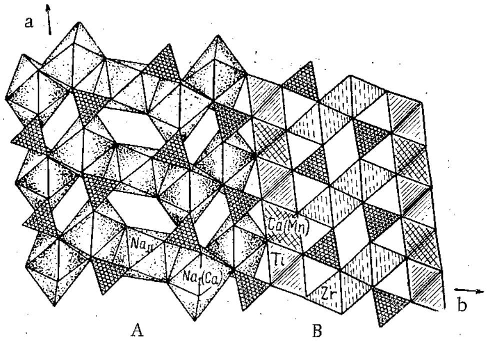

Fig. 2. Projection of the structure of calcium seidozerite along the b-axis. A) Layer of eight-cornered polyhedra; B) layer of octahedra.

It is the authors' pleasant duty to thank A. M. Portnov for the kind gift of specimens of calcium seidozerite, and to thank Academician N. V. Belov for his interest in the work and for some valuable comments.

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