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STRUCTURE OF INORGANIC COMPOUNDS

Crystal Structure of Zirconium-Rich Seidozerite

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Abstract—The crystal structure of seidozerite was refined (a Siemens P4 diffractometer, MoK_α radiation, 1180 independent reflections, anisotropic refinement, $R = 0.053$). The monoclinic unit-cell parameters are $a = 5.627(1)$ Å, $b = 7.134(1)$ Å, $c = 18.590(4)$ Å, $\beta = 102.68(1)°$, sp. gr. $P2/c$, $Z = 4$. The structural formula, $Na_{1.6}Ca_{0.275}Mn_{0.425}Ti_{0.575}Zr_{0.925}[Si_2O_7]OF$, agrees well with the results of the electron probe analysis. Seidozerite is demonstrated to belong to the meroplesiotype polysomatic series including the structures of more than 30 titano- and zirconosilicates. *© 2002 MAIK "Nauka/Interperiodica".*

INTRODUCTION

The zirconosilicate seidozerite was discovered by E.I. Semenov in 1958 in the Lovozero alkaline massif [1]. This mineral belongs to a rather large group of (Zr,Ti)-silicates, whose structures contain three-layer heteropolyhedral stacks denoted by *HOH*, where *O* is the central layer consisting of octahedra, and *H* are the outer layers formed by Si-tetrahedra and octahedra of highly charged Zr or Ti cations. In 1964, A.M. Portnov described the second specimen of seidozerite from North Baikal [2]. The crystal structures of the specimens from both deposits were studied by the photographic method [3, 4]. However, the high *R* factors (0.166 and 0.207 for the *h*0*l* and 0*kl* reflections, respectively) obtained in the pioneering study [3] and the high, although slightly improved, *R* factors (0.146 for the non-zero 0*kl*, 1*kl*, and 2*kl* reflections and 0.100 for the non-zero *h*0*l*, *h*1*l*, and *h*2*l* reflections) obtained in the more recent investigation [4] cast some doubt upon the characteristics of the cation distribution in the seidozerite structure.

Recently, seidozerite crystals were also discovered in another region of the Burpala massif (North Baikal). They are characterized by an higher ZrO_2 content (28.18–30.17 wt %) compared to those in the specimens from the Burpala and Lovozero massifs studied earlier (19.6–23.15 and 23.14 wt %, respectively). The high ZrO_2 content in the new seidozerite specimen, the availability of single crystals suitable for X-ray diffraction analysis, and the present-day possibilities of the instruments have stimulated interest in the refinement of the seidozerite structure.

EXPERIMENTAL

The seidozerite crystals were found in an alkaline pegmatitic body 1 m in thickness and 10 m in length located in the southwestern region of the Burpala alkaline massif, whose area and age were evaluated at 150 km^2 and 330 Ma, respectively. Seidozerite occurs as elongated crystals crosscutting earlier catapleiite isolations and intergrowing with grains of nepheline and feldspar.

According to the results of the electron probe analysis performed for three crystals, the average chemical compositions of the major components of seidozerite are as follows (wt %): SiO_2, 29.39; ZrO_2, 29.20; TiO_2, 13.03; Al_2O_3, 0.26; MnO, 5.76; CaO, 3.81; FeO, 1.90; MgO, 0.32; Na_2O, 12.26; K_2O, 0.05; Nb_2O_5, 0.68; La_2O_3, 0.11; Ce_2O_3, 0.15; and F, 3.06; the sum is 99.98. This composition corresponds to the following chemical formula of seidozerite describing the cation contents (with respect to 36 anions, namely, O^{2-} and F^-):

$$(Na_{6.29}Ca_{1.08}K_{0.02}La_{0.01}Ce_{0.01})$$

$$\cdot (Zr_{3.77}Ti_{2.59}Mn_{1.29}Fe_{0.42}Mg_{0.13}Nb_{0.08})(Si_{7.78}Al_{0.08}).$$

A crystal of dimensions 0.08 × 0.08 × 0.1 mm^3 was selected under a microscope and was used for the qualitative electron probe analysis (a Philips PW 515 *xl* 30 microprobe, the accelerating voltage was 20 kV; the current intensity was 9 nA; and the diameter of the electron beam was 5 μm). The results of the analysis confirmed the presence of the above-mentioned cations in the mineral. The X-ray diffraction data were collected from the same crystal on an automated Siemens P4 diffractometer. The crystallographic characteristics and the details of the X-ray diffraction study and structure refinement are given in Table 1.

Table 1. Crystallographic characteristics and details of X-ray diffraction study

Formula	$Na_{1.6}Ca_{0.275}Mn_{0.425}Zr_{0.925}Ti_{0.575}[Si_2O_7]OF$
Unit-cell parameters, Å	$a = 5.627(1)$, $b = 7.134(1)$, $c = 18.590(4)$ $\beta = 102.68(1)°$
Sp. gr.; Z	$P2/c$; 4
Unit-cell volume V, Å^3	728.06(3)
Calculated density ρ, g/cm^3	3.574
Absorption coefficient μ, mm^{-1}	3.34
Molecular weight	391.8
F_{000}	746.0
Diffractometer	Siemens P4
Wavelength, Å	0.71069
Maximum value of the 2θ angle, deg	60.01
Total number of reflections	3291
Total number of independent reflections	2122
Number of independent reflections with $\|F\| > 4\sigma(F)$	1180
R_{int}, %	7.81
Number of parameters in the refinement	138
R_F upon isotropic refinement	0.081
R_F upon anisotropic refinement	0.053
$wR(F^2)$	0.145
GOF	0.990
$\Delta\rho_{max}$, e/Å^3	1.09
$\Delta\rho_{min}$, e/Å^3	−1.27

Table 2. Distribution of the cations over the positions in the seidozerite structure

Position	Content according to study [3]	Content according to study [4]	The present study	Electron content	Electron content taking into account the real occupancy	Average cation–anion distance	Sum of ionic radii
Zr	$Zr_{0.75}Ti_{0.25}$	$Zr_{0.7}(Mn, Fe)_{0.3}$	$Zr_{0.8}Ti_{0.2}$	36.24	36.40	2.127	2.057
Ti	Ti	$Ti_{0.39}Fe_{0.11}$	$Ti_{0.35}Zr_{0.125}$	24.86	25.40	1.994	1.928
Mn	Mn(Mg)	$Ca_{0.42}Mn_{0.08}$	$Mn_{0.29}Na_{0.125}Ti_{0.025}$	18.35	18.35	2.265	2.153
Na(1)	Na	$Na_{0.78}Ca_{0.22}$	$Na_{0.965}Ca_{0.035}$	11	11.31	2.568	2.540
Na(2)	Na	Na	$Na_{0.43}Ca_{0.07}$	12.28	12.28	2.498	2.534
Ca	Na	Na	$Ca_{0.170}Mn_{0.135}Na_{0.080}$	15.28	15.31	2.394	2.300

Note: The cation content in the unit cell is $Na_{6.3}Ca_{1.1}(Mn, Fe)_{1.7}Zr_{3.8}Ti_{2.6}$ according to the data of the electron probe analysis and $Na_{6.4}Ca_{1.1}(Mn, Fe)_{1.7}Zr_{3.7}Ti_{2.3}$, according to the results of X-ray diffraction study.

The unit-cell parameters were determined by the least-squares method based on the angular parameters of 40 reflections in the range $8° \le 2\theta \le 27°$. The absorption correction was applied using the ψ scanning procedure. The structure was refined within the space group $P2/c$ starting from the atomic coordinates determined earlier [4]. Initially, the structure was refined isotropically to $R = 0.081$ for 1180 reflections with $|F| > 4\sigma(F)$ using the SHELX97 program package [5]. At subsequent stages, the electron contents of six cationic positions were refined, and the anisotropic thermal parameters were included, which made it possible to reduce the $R(F)$ factor to 0.053. The distribution of the cations over six nonequivalent positions was established based on the refinement of their electron contents, the correspondence between the structural formula and the data of electron probe analysis, the electroneutrality of the chemical formula, the valence

Table 3. Coordinates, thermal parameters, multiplicities (Q), and occupancies (q) for the basis atoms

Atom*	x/a	y/b	z/c	Q	q	U_{eq}^{**}, Å^2 × 100
Zr	0.2004(1)	0.1193 (1)	0.07342(4)	1	1	0.97(2)
Ti	0.0	0.1153(3)	0.25	0.5	0.475	1.14(3)
Mn	0.5	0.3566(4)	0.25	0.5	0.440	1.74(6)
Na(1)	0.2051(6)	0.6157(5)	0.0695(1)	1	1	1.13(5)
Na(2)	0.0	0.6149(8)	0.25	0.5	0.5	2.18(9)
Ca	0.5	0.8656(7)	0.25	0.5	0.385	3.32(8)
Si(1)	0.7273(4)	0.3872(4)	0.1046(1)	1	1	1.00(4)
Si(2)	0.7217(4)	0.8422(3)	0.1049(1)	1	1	0.99(4)
O(1)	0.738(1)	0.6135(8)	0.1096(3)	1	1	2.3(1)
O(2)	0.451(1)	0.3264(9)	0.0680(3)	1	1	2.1(1)
O(3)	0.440(1)	0.9015(9)	0.0763(3)	1	1	2.0(1)
O(4)	0.927(1)	0.3267(9)	0.0586(3)	1	1	1.6(1)
O(5)	0.904(1)	0.9073(8)	0.0518(3)	1	1	1.4(1)
O(6)	0.797(1)	0.3154(8)	0.1900(3)	1	1	1.6(1)
O(7)	0.817(1)	0.9141(9)	0.1888(3)	1	1	1.7(1)
O(8)	0.240(1)	0.124(1)	0.1849(3)	1	1	1.9(1)
F	0.301(1)	0.600(1)	0.1922(3)	1	1	3.9(2)

* The cation contents of the positions correspond to those presented in Table 2.

** The U_{eq} values are calculated based on anisotropic thermal displacements of the atoms.

balance, and the fact that the average interatomic distances should be approximately equal to the sum of the ionic radii of the cations and anions in the corresponding polyhedra. The resulting distribution (Table 2) differs from the distributions found earlier [3, 4] and is supported by the lowest R factor. The structural formula 2(Na,Ca){(Na,Ca)(Ca,Mn,Na,□)(Mn,Na,Ti,□)(Ti,Zr,□) [(Zr,Ti)Si_2O_7]OF} (the content of the *H* layer is enclosed in brackets, and the content of the *HOH* stack is enclosed in braces; $Z = 4$) agrees well with the results of electron probe analysis. The distribution of the cations presented in Table 2 should be considered as the optimum compromise between the experimental results of chemical and X-ray analysis. Conceivably, there are insignificant variations in the cation contents in particular polyhedra, which are, apparently, responsible for the higher values of U_{eq} for the cations located in the Ca position compared to U_{eq} for the Na(1) and Na(2) positions.

Table 4. Interatomic distances (Å)

Zr–O(8) 2.035(5)	Na(1)–F 2.229(6)	Ca–F 2.340(8)
–O(3) 2.051(6)	–O(4) 2.370(6)	–F' 2.340(8)
–O(2) 2.061(6)	–O(3) 2.419(7)	–O(7) 2.345(6)
–O(4)' 2.110(6)	–O(2) 2.488(7)	–O(7)' 2.345(6)
–O(5) 2.223(6)	–O(4)' 2.570(7)	–O(8) 2.497(7)
–O(5)' 2.281(5)	–O(5)' 2.659(7)	–O(8)' 2.497(7)
Average, 2.127	–O(1) 2.886(7)	Average, 2.394
	–O(1)' 2.925(7)	
Mn–F 2.209(8)	Average, 2.568	Ti–O(7) 1.974(6)
–F' 2.209(8)		–O(7)' 1.974(6)
–O(6) 2.225(6)	Na(2)–F 2.200(5)	–O(8) 2.002(5)
–O(6)' 2.225(6)	–F' 2.200(5)	–O(8)' 2.002(5)
–O(8) 2.361(7)	–O(7) 2.529(8)	–O(6) 2.007(6)
–O(8)' 2.361(7)	–O(7)' 2.529(8)	–O(6)' 2.007(6)
Average, 2.265	–O(6) 2.560(8)	Average, 1.994
	–O(6)' 2.560(8)	
	–O(1) 2.702(6)	
	–O(1)' 2.702(6)	
	Average, 2.498	

The final coordinates of the basis atoms and their thermal parameters are given in Table 3. The interatomic distances are listed in Table 4. The valence balance was calculated according to Brese and O'Keeffe [6], and the results are presented in Table 5. The Si(1)–O and Si(2)–O bond lengths are (1.610(6)–1.632(6) and 1.612(6)–1.637(6) Å, respectively with average values 1.618 and 1.626 Å, respectively) close to the standard values and are therefore not given in Table 4. The projection of the structure (the ATOMS program [7]) is shown in the figure.

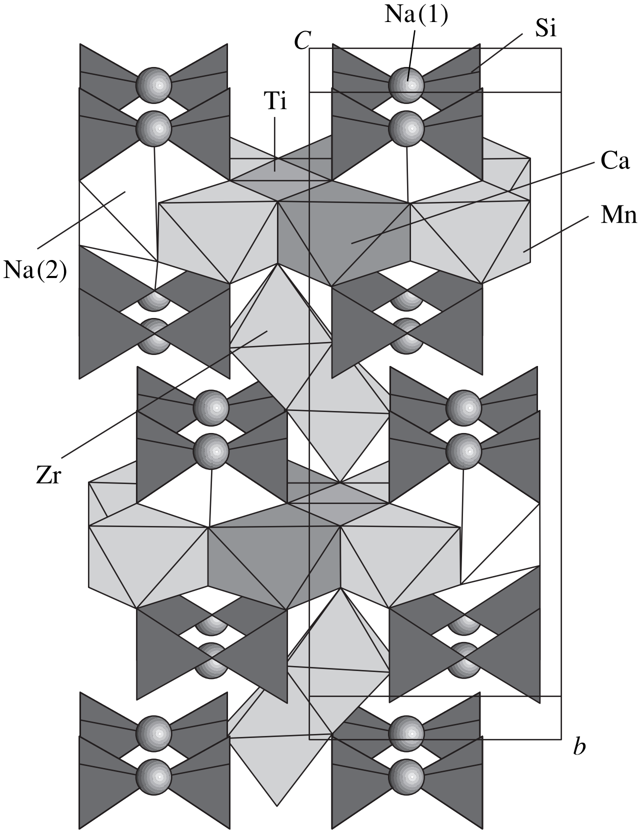
RESULTS AND DISCUSSION

The crystal structure of seidozerite is based on the *HOH* bafertisite-like stacks parallel to the (001) plane [8]. The *O* octahedral layer is composed of (Ti,Zr)O_6-, (Mn,Na,Ti)O_6-, and (Ca,Mn,Na)-octahedra and the eight-vertex Na(2)-polyhedra. All the cationic positions within the octahedra of the *O* layer are only partly occupied.

On the contrary, the (Zr,Ti)O_6-octahedra, which are involved in the heteropolyhedral *H* layers together with the Si_2O_7 diortho groups, are completely occupied. The *HOH* stacks in seidozerite are directly linked to each other via edges shared by the adjacent (Zr,Ti)O_6-octahedra belonging to different stacks. Hence, the seidozerite structure can be described as a mixed framework, whose cavities located between the adjacent *HOH* stacks are occupied by the Na(1) cations occupied in the eight-vertex polyhedra.

The valence balance cannot be calculated with a high degree of accuracy because of the above-mentioned cationic disordering. However, the results presented in Table 5 allow the unambiguous identification of the positions occupied by the F atoms or the OH groups. The O anions in the O(8) position and the F anions belong to the *O* layer, but they are not involved in the Si-tetrahedra.

The modular structures of more than 20 titanosilicates containing the bafertisite-like *HOH* stacks analogous to those found in seidozerite have been considered earlier [8–11]. The crystal structures of some of these minerals are still unknown, and they were assigned to the bafertisite-like group based on the comparison of the unit-cell parameters and the data on their compositions. The correctness of the application of the modular concept to the prediction of unknown structures has already been confirmed in the studies of minerals such as delindeite, perraultite, betalomonsovite, and some varieties of lamprophyllite, whose structures were established more recently. These structures were surveyed in most detail in [11].



Seidozerite structure projected onto the (100) plane.

All titanosilicates of this series have close unit-cell parameters ($a \sim 5.5$ Å, $b \sim 7$ Å) typical of the bafertisite-like *HOH* stacks. The space between these stacks, like that in layered silicates, can involve isolated atoms or atomic groups as well as the fragments of other mineral types. The latter statement is exemplified by the structures of quadruphite and polyphite [12], which contain nacaphite [13] fragments between the layers. The interlayer content (according to Belov's evocative

Table 5. Calculated valence balance

Anion, cation	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	F
Zr		0.675	0.694	0.592	0.436 0.373			0.724	
Ti						0.624	0.682	0.632	
Mn						0.274		0.190	0.220
Na(1)	0.053 0.048	0.156	0.188	0.214 0.125	0.098				0.225
Na(2)	0.094					0.138	0.151		0.262
Ca							0.229	0.152	0.170
Si(1)	1.016	1.030		1.039		0.979			
Si(2)	0.968		1.033		0.965		1.019		
Σ	2.179	1.861	1.915	1.970	1.872	2.015	2.081	1.698	0.877

expression, the "pie filling") determines the *c* parameter, which increases as the filling becomes more complex. The thickness of the *HOH* stacks is ~9–10 Å. In the structures where the interlayer space is occupied only by isolated atoms, the *c*-parameter is ~*n* × 10 Å, where *n* is the number of the *HOH* stacks. The *c* parameter in seidozerite (18.590 Å) indicates that its unit cell contains two symmetrically equivalent *HOH* stacks perpendicular to the [001] axis. In the seidozerite structure, the *HOH* stacks are linked via the shared edges of the Zr-octahedra, and *d* (0 0 1)/*n* has the minimum value (9.068 Å) of all minerals of this series. In the polyphite structure characterized by a large interlayer space, *d* (0 0 1)/*n*, on the contrary, reaches 26.49 Å. Within the framework of the classification of homologous and polysomatic series proposed recently [14], seidozerite, like all bafertisite-like minerals, belongs to the meroplesiotype series. This series is referred to as a merotype series because one fragment, namely, the *HOH* stack, is common to all the members of this series, whereas the second fragment located between the layers is individual for each mineral of this series. At the same time, the bafertisite-like polysomatic series should be considered as a plesiotype series because the *HOH* stacks differ from each other not only in composition but also in topology. Earlier, it has been established that these structural differences can be seen from the fact that the "octahedral" cations within the *H* layers can adopt different coordination numbers (either 6 or 5). Similar to delindeite studied recently, seidozerite exemplifies the plesiotype character of the *HOH* layers associated with the change in the coordination of the cations not only in the *H* layers but also in the *O* layers. Thus, the Na cations involved in the *O* layers in the delindeite and seidozerite structures are located in seven- and eight-vertex polyhedra, respectively, rather than in octahedra.

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