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STRUCTURE OF INORGANIC COMPOUNDS

New Data on Vlasovite: Refinement of the Crystal Structure and the Radiation Damage of the Crystal during the X-ray Diffraction Experiment

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Abstract—The crystal structure of vlasovite obtained from the Kipawa alkaline complex in Quebec is refined to $R_F = 0.053$ for 1515 unique reflections with $|F| > 4\sigma(F)$. The parameters of the monoclinic unit are as follows: $a = 11.063(8)$ Å, $b = 10.15(1)$ Å, $c = 8.60(1)$ Å, $\beta = 100.3(1)°$, space group $C2/c$, and $Z = 4$. The X-ray diffraction, electron microprobe, and IR spectroscopic data indicate that, under X-ray radiation, the specimen suffers radiation damage, which is accompanied by a partial removal of Na atoms, incorporation of H_2O molecules into the structure, and, possibly, a change in the configuration of the (Si,O) framework. © *2003 MAIK "Nauka/Interperiodica".*

INTRODUCTION

Vlasovite $Na_2ZrSi_4O_{11}$ is a typical zirconium concentrator in a number of alkaline complexes. In 1961, vlasovite was described as a new mineral from albitized eudialyte-microcline fenites and pegmatoid nepheline syenites of the exocontact zone of the Lovozero massif on the Kola Peninsula, where this compound occurs in the form of colorless transparent grains, replacing eudialyte and associated with microcline, albite, apatite, and fluorite [1].

The crystal structure of vlasovite (space group $C2/c$) was first determined by the photographic method in 1961 for a single crystal from the Lovozero massif [2] and later refined for the same specimen in the same space group [3]. It was found that vlasovite crystals from Ascensian Island in Atlantic are triclinic (space group $P\bar{1}$), but they become monoclinic after heating to 29°C [4]. However, the R factors reported in these studies are relatively large (0.149 and 0.116 for the $0kl$ and $hk0$ reflections, respectively [4]; and $R_{hkl} = 0.101$ for all reflections in [3]). For this reason, we refined the vlasovite structure for a specimen from the Kipawa alkaline complex in Quebec. In the course of our study, we observed the damage of the vlasovite crystal under X-ray irradiation. This phenomenon is of methodological interest and was studied specially. The results of both experimental studies are reported in this paper.

In the largest amounts, vlasovite occurs in the Kipawa alkaline complex in West Quebec (Canada) in the form of single-crystal insulations up to 15 cm long in pegmatites enriched with eudialyte and rinkite [5]. The specimen used in this study originates from Kipawa. In this specimen, transparent light-yellow isomorphic vlasovite grains up to 2 cm across, which are surrounded by a white gittensite border, grow into the assembly consisting of large grains of crimson eudialyte and black alkaline amphibole.

EXPERIMENTAL

The chemical composition of the mineral was determined using electron-microprobe analysis. When studying vlasovite on a Camebax SX 50 wave-dispersion electron microprobe analyzer, we came up against a serious problem of instability of the mineral under the effect of the electron beam: the sodium content measured varied widely with changing operating conditions. For example, at an accelerating voltage of 15 kV, current strength of 30 nA, and beam diameter of 2–3 μm, the Na_2O content was 4–6 wt % (instead of the calculated value of 14.6 wt %). Defocusing of the electron beam over areas 5×5 and 10×10 μm in size increased the Na_2O content to 7–8 and 9–10 wt %,

respectively. A similar dependence of the sodium content on the operating conditions was observed in the energy-dispersion studies of vlasovite on a JXA 50 microanalyzer equipped with an LINK spectrometer: a decrease in the beam current and an increase in the irradiated area resulted in an increase in the sodium content measured. For a current of 2 nA and a beam defocused over an area of 15×15 μm, the following content was obtained reproducibly (average of four determinations, wt %): Na_2O, 14.78; ZrO_2, 29.51; SiO_2, 56.27; total, 100.56. The contents of K, Ca, Sr, Ba, Mg, Mn, Fe, Zn, *REE*, Al, Ti, Hf, F, and Cl were beyond the determination limit. The empirical formula $Na_{2.02}Zr_{1.015}Si_{3.98}O_{11}$ is close to the ideal composition.

The X-ray diffraction intensities were measured from a fragment of the crystal that was subjected to the electron microprobe analysis. The crystal data, data-collection, and structure-refinement parameters are summarized in Table 1.

The unit cell parameters were obtained by the least-squares refinement of the angular parameters for 31 reflections in the range $6.89° \le 2\theta \le 47.83°$.

Absorption correction was introduced using the ψ-scan technique. The structure was solved by direct methods (independent of the earlier data) in space group *C*2/*c* with the SHELX97 program package [6] and refined with the JANA98 program [7]. At this stage, the partial occupancy of Na positions became obvious. Moreover, the difference Fourier synthesis contained peaks of the residual electron density around the Na(1), Na(2), and Zr positions. Correction for anharmonicity of thermal vibrations of these atoms improved R_F to 0.053 and lowered the heights of the residual maxima (Table 1). The final atomic coordinates and thermal displacement parameters are listed in Table 2. The valence-strength balance calculated according to [8] is presented in Table 3. The projection of the structure (drawn with the ATOMS program [9]) is shown in Fig. 1. The interatomic distances in the coordination polyhedra have normal values in the following ranges: Zr–O, 2.062(1)–2.116(1) Å; Na(1)–O, 2.386–2.870(1) Å; Na(2)–O, 2.368(1)–3.014(2) Å; Si(1)–O, 1.599(1)–1.624(1) Å; and Si(2)–O, 1.599–1.6282(7) Å.

The IR spectra of vlasovite (Fig. 2) were recorded with a Specord 75IR spectrophotometer (KBr pellets). The frequencies were measured to an accuracy of ± 1 cm^{-1}. Polystyrene and ammonia were used as standards. To improve the accuracy in measurements of the intensities of the absorption bands, pure KBr was exposed to a reference ray.

Table 1. Crystal data and experimental parameters

Idealized formula	$Na_2Zr[Si_4O_{11}]$
Unit cell parameters, Å	a = 11.063(1), b = 10.15(1), c = 8.60(1), β = 100.3(1)°
Space group; Z	$C2/c$; 4
Cell volume V, Å^3	950.13(3)
Calculated density ρ, g/cm^3	2.975
Absorption coefficient μ, mm^{-1}	1.81
Molecular weight	425.56
F_{000}	824.0
Diffractometer	Ital Structures
Wavelength, Å	0.71073
Maximum 2θ angle, deg	67.98
Total number of reflections	4287
Number of unique reflections	1533
Number of unique reflections with $\|F\| > 4\sigma(F)$	1515
R_{av}, %	11.19
Number of parameters refined	131
R_F	0.053
$wR(\|F\|)$	0.054
$\Delta\rho_{max}$, e/Å^3	1.26
$\Delta\rho_{min}$, e/Å^3	–1.72

STRUCTURAL FEATURES AND THE RADIATION DAMAGE OF VLASOVITE

The structural elements of vlasovite are infinite chains of Si tetrahedra oriented along the [101] direction. The tetrahedra form four-membered centrosymmetric rings, which are linked through isolated Zr octahedra. Each Zr octahedron is connected with four chains. The Si tetrahedra share corners with one another and with Zr octahedral; that is, each oxygen atom is shared by two polyhedra. The cavities of the mixed zeolite-like framework accommodate the Na atoms in two inequivalent positions: the Na(1) and Na(2) atoms are located inside a seven-vertex polyhedron and a distorted octahedron, respectively.

In the specimen studied, the Na(1) and Na(2) positions are sodium-deficient. According to the refinement, the specimen contains only 1.72 Na atoms per formula unit instead of two atoms expected from the idealized vlasovite formula. The charge balance is attained by the formation of less (by half) vacancies, which are randomly distributed over the unit cell. These data are inconsistent with the results of the electron microprobe analysis, according to which the composition of the mineral agrees well with the ideal formula. The inconsistency of these data suggests that, in the course of the X-ray diffraction experiment, the mineral underwent some changes in composition and structure.

Table 2. Atomic coordinates, thermal displacement parameters, multiplicities (Q), and site occupancies (q)

Atom	x/a	y/b	z/c	Q	q	U^*_{eq}, Å$^2 \times 100$
Zr	0.25	0.25	0	0.5	0.5	1.61(2)
Na(1)	0	0.0746(1)	0.75	0.5	0.470(2)	3.21(3)
Na(2)	0	0.3996(2)	0.75	0.5	0.390(3)	5.31(6)
Si(1)	0.26433(3)	0.07226(4)	0.63854(5)	1	1	1.768(9)
Si(2)	0.04980(3)	0.21662(4)	0.42722(5)	1	1	1.846(9)
O(1)	0	0.1604(2)	0.25	0.5	0.5	2.44(4)
O(2)	0.1439(1)	0.1022(1)	0.5053(2)	1	1	3.33(3)
O(3)	0.1160(1)	0.3581(1)	0.4162(2)	1	1	3.22(3)
O(4)	0.0568(1)	0.2305(1)	0.9704(1)	1	1	2.40(3)
O(5)	0.2389(1)	0.1356(1)	0.7998(1)	1	1	2.93(3)
O(6)	0.2880(1)	0.0830(1)	0.1431(1)	1	1	2.18(2)

* The U_{eq} values are calculated from the parameters of anisotropic thermal displacements.

Table 3. Valence balance calculation*

Anion / Cation	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	Σ
Zr				$0.617^{[\times 2]}$	$0.713^{[\times 2]}$	$0.656^{[\times 2]}$	3.972
Na(1)	0.205	$0.055^{[\times 2]}$		$0.167^{[\times 2]}$	$0.094^{[\times 2]}$		0.837
Na(2)			$0.038^{[\times 2]}$	$0.132^{[\times 2]}$		$0.215^{[\times 2]}$	0.770
Si(1)		1.003	0.953		1.070	1.079	4.105
Si(2)	$0.989^{[\times 2]}$	1.005	1.003	1.070			4.067
Σ	2.183	2.063	1.994	1.986	1.877	1.950	

* The left and right superscripts indicate the valence strengths doubled in the calculations of valence balances at the anions and cations, respectively.

The weak fixation of Na atoms, especially Na(2), in the vlasovite structure was already noted in [3, 4] and is confirmed by our data on the partial occupancy of both Na positions (Table 2). The data of electron microprobe analysis clearly indicate that sodium can easily migrate in the bulk of the vlasovite crystal under high-energy radiation. These facts impelled us to perform an additional experiment in order to elucidate the effect of X rays on vlasovite. Rather large pieces (0.3–0.6 mm) of the mineral were cut from the single-crystalline specimen, whose fragments were used for the electron microprobe and X-ray diffraction studies, and exposed to X-ray radiation from a tube with an Mo anticathode operating at a voltage of 30 kV and a current of 5 mA for 19 h. The IR spectra of the mineral were recorded before and after the experiment under the same conditions.

Analysis of the IR spectra demonstrates that substantial changes take place in the vlasovite structure under irradiation. The changes observed in the spectrum of the specimen exposed to radiation, as compared to the spectrum of the starting mineral, are as follows: (1) intense absorption bands corresponding to molecular H_2O appeared at 3500 cm^{-1} (stretching vibrations) and 1645 cm^{-1} (bending vibrations); (2) the bands of stretching vibrations of the Si–O–Si bridge are shifted to lower frequencies (1126 $\longrightarrow$ 1117 and 1093 $\longrightarrow$ 1085 cm^{-1}), and the band of bending vibrations of the

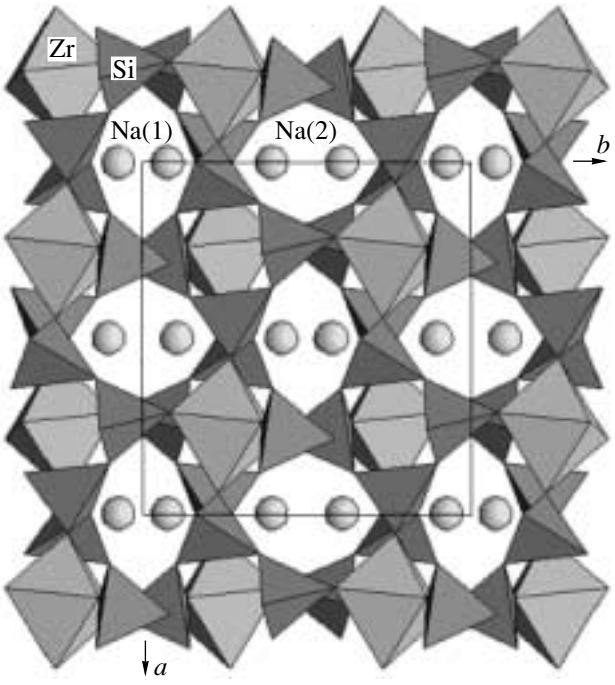

Fig. 1. Vlasovite structure in the projection onto the (001) plane.

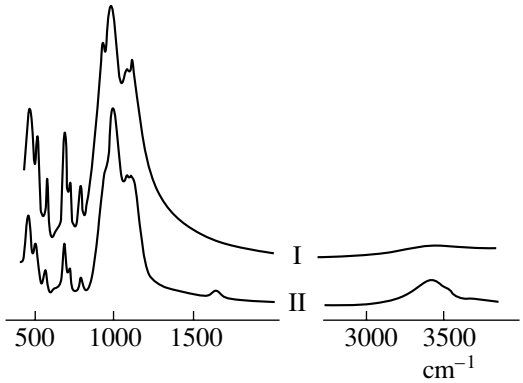

Fig. 2. IR spectra of the vlasovite samples: (I) the starting crystal and (II) the same crystal after 19-h exposure to X rays.

Si–O–Si bridge is shifted from 451 to 455 cm^{-1}; and (3) the band of Si–O stretching vibrations (involving the apical O atoms) at 942 cm^{-1}, which was clearly pronounced in the spectrum of the starting crystal, noticeably weakened and appeared as a shoulder at 945 cm^{-1}. All these changes in the IR spectra indicate the appearance of numerous defects in the framework and the hydration of structurally distorted vlasovite by absorption of atmospheric water. Note that the bands corresponding to the H_2O vibrations cannot be attributed to water molecules adsorbed by KBr. Since the structure analysis revealed a significant Na deficit, we assume that, in the irradiated specimen, water molecules are located in zeolite-like channels that accommodate Na. Most probably, water appeared in the distorted vlasovite structure after the radiation was switched off rather than in the course of irradiation. This provides an explanation of the absence of peaks corresponding to water oxygens in the difference synthesis. The position that could be occupied by a water molecule was calculated under the assumption that the shortest H_2O–O distance is 2.5 Å [10]. The coordinates of the resulting point (x = 0, y = 0.082, z = 0.75) are close to the Na(1) position (Table 2). The H_2O–O distances vary in the range 2.432(2)–3.097(3) Å. Thus, water molecules are presumably located in structural channels, provided these channels have Na vacancies. The Na deficit in the Na(1) and Na(2) positions can be explained within alternative models. First, Na atoms migrate inside the channels, which results in a decrease in the Na(1) and Na(2) site occupancies. In this case, the total Na content in the mineral and the charge balance in the $Na_2Zr[Si_4O_{11}]$ formula remain unchanged. Second, a portion of Na atoms leaves the crystal. The deficit of positive charge can be compensated either by a minor substitution of OH groups for O atoms of the bridging Si–O–Zr vertices or due to the appearance of anionic vacancies in the framework, which would make the framework defective. In the latter case, the general formula of the mineral is $Na_{2-n}Zr[Si_4O_{11-n/2}] \cdot nH_2O$, where $n < 1$. All the structural changes in vlasovite that were described above are irregular; otherwise, we should observe deviations from monoclinic symmetry similar to those described in [4]. We consider no more than possible displacements of Na atoms in the channels or even partial removal of sodium from the crystal, as is the case, for example, in the minerals of the lovozerite group, which undergo decationization and hydration in air [11].

In conclusion, we note that the radiation damage of the crystal in the course of the X-ray diffraction experiment observed in this study can be characteristic of other minerals. Taking this effect into account allows a more critical treatment of the results of structural determinations (particularly, site occupancies of weakly bound cations and water molecules) of unstable compounds, for example, high-alkaline zeolite-like silicates.

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