

rotational barrier is much smaller than in case of the FA molecule. Interestingly, it was found that the configuration corresponding to the reported structure is not the most stable. The changes in total energy do not correlate with the values of $R2$ and/or $R1$ factors. The values of $R2$ vary within the interval of $<3.57; 14.6>\%$ for D_FA models and $<2.79; 14.54>\%$ for D_NMFA models. If we suppose that two configurations are distinguishable if $R2 > 10\%$, only two models of D_FA and three of D_NMFA pass this test. Considering the values of total energies we can conclude that there is high probability that intercalates with NMFA will be disordered. Second, small differences in diffraction patterns would seriously hamper structure analysis of these types of dickite intercalates.

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MS41 P21

On hydrogen bonding in DMSO and DMSeO – kaolinite intercalates. Ľubomír Smrčok, Eva Scholtzová
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Keywords: kaolinite intercalate, hydrogen bonds, DFT

Kaolinites belong to those minerals, which are known for not yielding single crystals suitable for structure analysis. Two main reasons are structural disorder and sizes of the crystals, which are, as a rule, too small for manipulation in a common laboratory. It is therefore not surprising that diffraction studies of organic intercalates of the minerals from the kaolinite group are done mostly using X-ray powder techniques. Unfortunately, due to disorder and low symmetry of the structures resulting atomic parameters frequently lack desired accuracy. For instance, Si-O bond distances in structures of DMSO/DMSeO – kaolinite intercalates [1] vary from 1.48Å to 1.78Å (DMSO) and 1.59-1.83 Å (DMSeO), the expected value being 1.61Å. Moreover, the lists of atoms typically do not include hydrogen atoms, or their positions are only estimated assuming idealized geometries. However, when trying, for example, calculate vibrational spectra using reported atomic coordinates, much higher accuracy is required. Inasmuch as it not for well-known reasons [2] possible by using only powder data, a computational approach provides useful alternative. In this study the atomic coordinates published in [1] were used as starting values in structure refinement done by energy minimization in solid state using DFT method as implemented in VASP code [3] with the aim to obtain accurate geometry of hydrogen bonds. Starting positions of hydrogen atoms were estimated from idealized geometries of Al-O-H or methyl groups, respectively. The cell parameters retained their values obtained from powder data, the refinement was done in the $P1$ space group. Analysis of refined structural parameters showed, that accuracy of calculated bond distances approaches that of standard single crystal refinements. Analysis of hydrogen bonds geometry revealed, that in both structures molecules of intercalates are fixed to octahedral layer by moderate O-H...O-S(Se) hydrogen bonds with O...O contact distance of 2.78-2.93Å and O-H...O bond angle 175-179°. Keying of intercalates to adjacent net of basal oxygen atoms is accomplished through weak C-H...O bonds with C...O

distances ~ 3.3 Å. Refined O-H and C-H distances are within the intervals 0.97-0.99 Å and 1.08-1.10 Å, respectively. It is demonstrated that structure refinement by energy minimization provides i) more accurate geometrical parameters than powder refinement, ii) complete information on hydrogen bonds. However, such basic information like cell geometry is still to be better obtained by diffraction methods.

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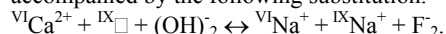
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The crystal chemistry of faizievite, a hybrid of baratovite and berazanskite Elena Sokolova^a, Yulia Uvarova^a, Frank C. Hawthorne^a, Atali A. Agakhanov^b, Leonid A. Pautov^b, ^aDepartment of Geological Sciences, University of Manitoba, Canada. ^bFersman Mineralogical Museum, Moscow, Russia.
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Keywords: faizievite; baratovite; berazanskite

The crystal structure of faizievite, ideally $K_2Na(Ca_6Na)Ti_4Li_6(Si_6O_{18})_2(Si_{12}O_{30})F_2$, a 9.8156(9), b 9.8249(9), c 17.309(2)Å, α 99.209(2), β 94.670(2), γ 119.839(1)°, V 1403.7(4)Å³, sp. gr. $P\bar{1}$, Z 1, D_{calc} 2.846 g/cm³, has been refined to $R_1 = 7.5\%$ for 5044 unique ($F_0 > 4\sigma F$) reflections collected on a Bruker single-crystal P4 diffractometer with a CCD detector and MoK α X-radiation. Faizievite occurs in the moraine of the Dara-i-Pioz glacier, the Alai mountain ridge, Tien-Shan Mountains, northern Tajikistan. It forms rims around grains of baratovite and is associated with aegirine, fluorite, polyolithionite, neptunite, hyalotekite, sokolovaite, pectolite, senkevichite, etc. The crystal structure of faizievite consists of four types of (001) sheets. Si tetrahedra form two types of six-membered rings: a single (Si₆O₁₈) ring, as in baratovite, and a double (Si₁₂O₃₀) ring, as in milarite-group minerals, in the ratio 2:1. Each type of ring forms a distinct sheet (Na atoms occur in a sheet of milarite rings). Two other sheets are: a sheet of corner-sharing (LiO₄) tetrahedra and (TiO₆) octahedra with K atoms in large voids, and a sheet of edge-sharing M octahedra ($M = Ca \gg Na$). Each sheet is characterized by a planar cell based on translation vectors, \mathbf{t}_1 and \mathbf{t}_2 , with $t_1 \sim t_2 \sim 9.8 \text{ \AA}$ and $\mathbf{t}_1 \wedge \mathbf{t}_2$ close to 120°. We may write the composition of the four individual sheets within the planar cell $\mathbf{t}_1, \mathbf{t}_2$: (1) (Si₆O₁₈); (2) (Si₁₂O₃₀)Na; (3) KLi₃Ti₂; (4) (Ca₆Na)F₂. The crystal structure of faizievite is a hybrid of the structures of baratovite, ideally KLi₃Ca₇Ti₂(Si₆O₁₈)₂(OH)₂ [1], and berazanskite, ideally KLi₃Ti₂(Si₁₂O₃₀) (milarite group) [2]. The baratovite block of composition [K₂(Ca₆Na)Li₆Ti₄(Si₆O₁₈)₂F₂] involves the sequence of sheets: (3)(1)(4)(1)(3). The berazanskite block of composition [KNaLi₃Ti₂(Si₁₂O₃₀)] involves the sequence of sheets: (3)(2)(3). In the faizievite structure, baratovite and berazanskite blocks alternate along [001] sharing a common sheet (3) of composition KLi₃Ti₂. We write the ideal formula of faizievite as an intercalation of baratovite and berazanskite blocks, and count only once any sheet common to two blocks: (3)(1)(4)(1)(3) + (3)(2)(3) - (3) = [K₂(Ca₆Na)Li₆Ti₄(Si₆O₁₈)₂F₂] + [KNaLi₃Ti₂(Si₁₂O₃₀)] - [KLi₃Ti₂] = K₂Na(Ca₆Na)Li₆Ti₄(Si₆O₁₈)₂(Si₁₂O₃₀)F₂.

There are minor differences between the chemical compositions of baratovite and berezanskite and their blocks in the crystal structure of faizievite. Baratovite, $\text{KLi}_3\text{Ca}_7\text{Ti}_2(\text{Si}_6\text{O}_{18})_2(\text{OH})_2$, and the baratovite block in faizievite, $\text{K}_2(\text{Ca}_6\text{Na})\text{Li}_6\text{Ti}_4(\text{Si}_6\text{O}_{18})_2\text{F}_2$, are related by the substitution: ${}^{\text{VI}}\text{Ca}^{2+} + (\text{OH})_2 \leftrightarrow {}^{\text{VI}}\text{Na}^+ + \text{F}_2^-$. Berezanskite, $\text{K}^{\text{IX}}\text{L}_3\text{Ti}_2(\text{Si}_{12}\text{O}_{30})$, and the berezanskite block in faizievite, $\text{KNaLi}_3\text{Ti}_2(\text{Si}_{12}\text{O}_{30})$, are related by the substitution: ${}^{\text{IX}}\square \leftrightarrow {}^{\text{IX}}\text{Na}^+$. Therefore assembly of faizievite from baratovite and berezanskite components is accompanied by the following substitution:



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MS41 P23

Crystal structures of new pyrovanadates $\text{A}_2\text{MnV}_2\text{O}_7$ (A = K, Rb) Hamdi Ben Yahia, Etienne Gaudin, Jacques Darriet, *Institut de Chimie de la Matière Condensée de Bordeaux, Université Bordeaux I, 87 Avenue du Docteur Schweitzer, 33608 Pessac Cedex, France.*
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Keywords: Melilite layered structure, Crystal structure determination, Single crystal diffraction

The compounds $\text{A}_2\text{MnV}_2\text{O}_7$ (A = K, Rb) with structures related to the melilite-type [1] have been synthesised. The crystal structures of $\text{K}_2\text{MnV}_2\text{O}_7$, $\text{KRbMnV}_2\text{O}_7$ and $\text{Rb}_2\text{MnV}_2\text{O}_7$ were determined using single crystal samples. The compound $\text{K}_2\text{MnV}_2\text{O}_7$ has tetragonal unit cell parameters $a = 8.6091 \text{ \AA}$, $c = 5.5375 \text{ \AA}$ and crystallize with $P-42_1m$ space group, $Z = 2$ whereas $\text{Rb}_2\text{MnV}_2\text{O}_7$ and $\text{KRbMnV}_2\text{O}_7$ crystallise in $P4_2/mnm$ space group, $Z = 4$ with unit cell parameters $a = 8.5304 \text{ \AA}$, $c = 11.4659 \text{ \AA}$ and $a = 8.5766 \text{ \AA}$, $c = 11.8094 \text{ \AA}$ respectively. The structures contain layers build up by MnO_4 tetrahedra and V_2O_7 pyrovanadate units. The linkage of tetrahedra forms five-membered rings which form sheets parallel to (001). The eight coordinated A alkali cations are positioned between the sheets and form distorted square antiprisms in $\text{K}_2\text{MnV}_2\text{O}_7$ and distorted square prisms in $\text{Rb}_2\text{MnV}_2\text{O}_7$ and $\text{RbKMnV}_2\text{O}_7$.

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MS41 P24

Analysis of structural ordering of mineral solids from microscopic images Yevgeny A. Golubev *Institute of Geology, Russian Academy of Sciences, Syktyvkar, Russia.*
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Keywords: AFM-STM studies of minerals and glasses, supramolecular structures, statistical distribution

We solved a problem of studying of supermolecular structures ordering of natural X-ray amorphous substances. We was shown earlier that the most part of these substances have nanodispersed structure [1]. The most effective method of studying of nanostructured substances is direct observation of their structure by microscopy. In case of a nonregular arrangement of structural units there is a question on a degree of their ordering. The statistical methods are necessary for

studying ordering, allowing to determine local structural characteristics of system. In this work the modernized method of *n-symmetric points* [1, 2] was used. This method based on statistical approximation of dependences of spatial distribution of points (particles), enabled to determine a randomness of points arrangement. At their regularity distribution this method enables to receive the appropriate statistical appraisal, for example, to measure of scale of particles aggregation (on two, on three etc).

We carry out research of supermolecular structures ordering of natural X-ray amorphous substances by SEM and AFM. Among the investigated substances only two have revealed the disorder supermolecular constitution. In the others tendencies to aggregation from two to seven particles in aggregate were found [2].

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MS41 P25

Electron diffraction analysis of amorphous geological materials V.K.Kis^a, M. Pósfai^b, J.L. Lábár^a, I Dódy^c
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Keywords: disordered structures; electron diffraction; mineralogy

Poorly crystalline and amorphous materials occur in a wide range of geological environments. They include aluminosilicate glasses and opals in rocks, highly disordered Fe hydroxides and oxy-hydroxides in soils, and carbons such as soot in the atmosphere or shungite in the lithosphere.

A knowledge of the structure of poorly crystalline materials is useful for deducing formation/precipitation conditions and helps in understanding their physico-chemical behaviour such as adsorption properties, stability and reactivity.

Amorphous structures lack long-range order but can be described by the nearest neighbour interatomic distances. Since a Fourier transformation of diffraction data gives the frequency distribution of interatomic distances, information on the local structure can be inferred from diffraction data. Electron diffraction (ED) has some advantages over X-ray and neutron beam methods in structural studies. The high spatial selectivity of ED allows one to discriminate between the scattering contributions of the individual components of a heterogeneous material. The strong scattering power of electrons makes a short exposure time possible and results in good statistics in the signal. Light elements (such as carbon or oxygen) are also well measurable.

We used electron diffraction measurements to investigate the local structure of volcanic glasses (obsidian and pumice) and atmospheric soot. In the case of volcanic glasses amorphous, partly ordered, and nanocrystalline regions were distinguished and analysed separately. The deconvoluted atomic distances obtained from experimental diffraction patterns through total pair-distribution functions are consistent with distances for ideal SiO_4 tetrahedra. Partly ordered structures in pumices