MS41 P18

Crystal structure and OD character of the mineral kettnerite CaBiOFCO₃ Jiří Hybler[a], Michal Dušek[a], Slavomil Ďurovič[b], [a]Institute of Physics, Academy of Sciences of the Czech Republic,Prague, Czech Republic. [b]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia. E-mail: hybler@fzu.cz

Keywords: Kettnerite, OD structure, polytypism

Kettnerite is orthorhombic, space group *Pbaa*, a=5.3641(1), b=5.3641(1), c= 13.5771(2) Å, Z = 4. The structure consists of layers parallel to (001): the Bi-O layers at z=0, Ca-F layers at z =1/2, with atoms arranged in square arrays. Both these layers are pseudotetragonal showing a subcell parameter $a \approx 3.8$ Å. The layers of CO_3 groups are located between the Bi-O and Ca-F layers. The CO_3 groups are approximately parallel to (110) or (1-10) planes with one O atom oriented towards the Bi-O layer while the remaining two O atoms are oriented towards the Ca-F layer. The orientations of CO_3 groups are interlaced, so that each group approximately parallel to (110) is surrounded by four nearest neighbors parallel to (1-10) and vice versa. This arrangement requires description of the whole structure in the proposed supercell. As a consequence, weak and diffuse additional superlattice reflections appear in the diffraction pattern.

The CO_3 layers may connect to the other layers in two different yet geometrically equivalent ways, thus the structure can be considered as an OD structure formed by more than one kind of layers: non-polar Bi-O and Ca-F layers, and polar layers of CO_3 groups with alternating sense of polarity [1]. The strong main reflections can be interpreted as family reflections while the superlattice ones can be attributed to polytype reflections. Their diffuse streaking along **c*** indicates partial stacking disorder. It should be noted, that the quality of polytype reflections varied from sample to sample: relatively well developed reflections as well as diffuse streaks instead, have been observed.

The described structure represents the simplest possible polytype 1*O*. The studied crystals were merohedrally twinned *via* 4[001] operation (the "lost" fourfold axis).

The geometry and symmetry of layers, stacking rule, twinning, derivation of possible polytypes, and displacements of atoms with respect of positions required by the ideal OD model are discussed.

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MS41 P19

Hydronium Ion in Al-bearing Fluorapophyllite Naoya Ishida[a], Mitsuyoshi Kimata[a], [a]*Earth Evolution Sciences, University of Tsukuba, Japan.*
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Keywords: fluorapophyllite, hydronium ion, zeolite

The chemical compositions and hydrous species of seven different fluorapophyllites have been investigated using EMPA, TG-DTA, Micro-Raman spectroscopy and ¹H MAS NMR spectroscopy. Four fluorapophyllites contain aluminum of 0.20, 0.46, 0.54, 0.77 wt%, respectively, with substitution of Si^{4+} for Al^{3+}. Aluminum contents in their fluorapophlyllites correlate with the H_2O ones. They have more water contents than the other Al-free fluorapophlyllites: the former contents of 16.2-16.6 wt% and the latter of 16.1 wt%. The Micro-Raman spectroscopic analysis indicates that Al-bearing fluorapophyllites have significantly stronger bands at 3100 and 3360 cm⁻¹ than Al-free ones. Thus, Al-bearing fluorapophyllites should contain a different hydrous species, where there is a suggestion of the following coupled substitution: Si^{4+} + H_2O for Al^{3+} + H_3O^+. This substitution is the same as that in H-ZSM5 zeolite reported by [1]. In addition, Al-bearing fluorapophyllites contain a significant amount of H_2O, which should be substituted for a monovalent cation (Na^+, K^+), existing as hydronium ion, H_3O^+ [2]. These substitutions make a hydrous fluid more alkaline, where fluorapophyllite crystallizes. Al-bearing fluorapophyllite plays an important role in crystallizing the zeolite minerals in alkaline fluids.

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MS41 P20

On recognition of FA/NMFA-dickite intercalates – total energy vs intensity data Eva Scholtzová, Ľubomír Smrčok, *Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic.* E-mail: uacheva@savba.sk

Keywords: DFT, intercalates, diffraction patterns

Crystal structures of layer silicates intercalated by small organic molecules are frequently disordered. There are two important factors controlling the degree of disorder in such structures – long range interlayer and short range intralayer intermolecular interactions. It has been however realized that even if the original crystal is 3D ordered, there is no guarantee that the structure of intercalated one will be ordered, too. The reason is such that low interaction energies of organic molecules permit several mutual orientations of neighbouring molecules influencing the stacking of the silicate layers. This kind of orientational disorder need not influence the diffraction pattern in a recognizable manner, making thus structure analysis a rather difficult task and its results ambiguous. To study the influence of short range intermolecular interactions on diffraction patterns formamide (FA) and *N*-methylformamide (NMFA) intercalates of dickite (D) were chosen [1,2]. Several model configurations with different orientation of intercalated molecules were proposed and their single crystal diffraction patterns calculated. As a measure of similarity/dissimilarity of diffraction patterns with the reference one standard *R*2 and *R*1 factors were used. Initial orientations of intercalated molecules of FA and NMFA generated using the atomic coordinates taken from [1,2] were optimized by means of DFT calculations in solid state [3,4] and the intercalated structures were sorted by their total energies. Optimized atomic coordinates were used to calculate single crystal diffraction patterns. For FA intercalates it was found that the conformation corresponding to the reported structure was the most stable among all modelled structures. The differences in the total energy for FA intercalates were rather large as they lie within the interval of ~92kJ/mol. On the contrary, for NMFA intercalates the differences not exceeding ~18kJ/mol were observed indicating, that the

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 *Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-845 36 Bratislava, Slovak Republic.* E-mail: lubomir.smrcok@savba.sk

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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MS41 P22

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], *[a]Department of Geological Sciences, University of Manitoba, Canada. [b]Fersman Mineralogical Museum, Moscow, Russia.* E-mail: elena_sokolova@umanitoba.ca

Keywords: faizievite; baratovite; berezanskite

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)Å^3, sp. gr. $P\bar{1}$, Z 1, $D_{calc.}$ 2.846 g/cm^3, 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 Mo$K\alpha$ 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, polylithionite, 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 (Si_6O_{18}) ring, as in baratovite, and a double $(Si_{12}O_{30})$ 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 (LiO_4) tetrahedra and (TiO_6) octahedra with K atoms in large voids, and a sheet of edge-sharing M octahedra (M = Ca >> Na). Each sheet is characterized by a planar cell based on translation vectors, t_1 and t_2, with $t_1 \sim t_2 \sim 9.8$ Å and $t_1 \wedge t_2$ close to 120°. We may write the composition of the four individual sheets within the planar cell t_1,t_2: (1) (Si_6O_{18}); (2) $(Si_{12}O_{30})Na$; (3) KLi_3Ti_2; (4) $(Ca_6Na)F_2$. The crystal structure of faizievite is a hybrid of the structures of baratovite, ideally $KLi_3Ca_7Ti_2(Si_6O_{18})_2(OH)_2$ [1], and berezanskite, ideally $KLi_3 Ti_2 (Si_{12}O_{30})$ (milarite group) [2]. The baratovite block of composition $[K_2(Ca_6Na)Li_6Ti_4(Si_6O_{18})_2F_2]$ involves the sequence of sheets: (3)(1)(4)(1)(3). The berezanskite block of composition $[KNaLi_3Ti_2(Si_{12}O_{30})]$ involves the sequence of sheets: (3)(2)(3). In the faizievite structure, baratovite and berezanskite blocks alternate along [001] sharing a common sheet (3) of composition KLi_3Ti_2. We write the ideal formula of faizievite as an intercalation of baratovite and berezanskite blocks, and count only once any sheet common to two blocks: $(3)(1)(4)(1)(3) + (3)(2)(3) - (3) = [K_2(Ca_6Na)Li_6Ti_4(Si_6O_{18})_2F_2] + [KNaLi_3Ti_2(Si_{12}O_{30})] - [KLi_3Ti_2] = K_2Na(Ca_6Na)Li_6Ti_4(Si_6O_{18})_2(Si_{12}O_{30})F_2.$