

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.

- [1] Adams J.M., Jefferson D.A. *Acta Cryst.*, B32, 1976 1180  
 [2] Adams J. M.(1979) *Acta Cryst.* B35, 1979 1084  
 [3] Kresse, G.; Hafner, J. *Phys. Rev.* B48, 1993, 13115.  
 [4] Kresse, G.; Hafner, J. *Phys. Condens. Matter* 6, 1994, 8245

#### MS41 P21

**On hydrogen bonding in DMSO and DMSeO – kaolinite intercalates.** Lubomír Smrčok, Eva Scholtzová  
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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  $\sim 3.3$  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.

- [1] Raupach, M., Barron, P.F., Thompson, J.G., *Clays and Clay Minerals* 1987, 35, 208  
 [2] Smrčok, L., *Z. Kristallogr.* 1995, 210, 188  
 [3] Kresse, G., Hafner, J. (1993). *Phys. Rev.* B48, 1993, 13115, Kresse, G., Furthmüller, *J. Comp. Mat. Sci.* 6, 1996, 15.

#### MS41 P22

**The crystal chemistry of faizievite, a hybrid of baratovite and berazanskite** Elena Sokolova<sup>a</sup>, Yulia Uvarova<sup>a</sup>, Frank C. Hawthorne<sup>a</sup>, Atali A. Agakhanov<sup>b</sup>, Leonid A. Pautov<sup>b</sup>, <sup>a</sup>*Department of Geological Sciences, University of Manitoba, Canada.* <sup>b</sup>*Fersman 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,  $\alpha$  99.209(2),  $\beta$  94.670(2),  $\gamma$  119.839(1)°,  $V$  1403.7(4)Å<sup>3</sup>, sp. gr.  $P \bar{1}$ ,  $Z$  1,  $D_{calc}$  2.846 g/cm<sup>3</sup>, 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 $\alpha$  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, 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 (Si<sub>6</sub>O<sub>18</sub>) ring, as in baratovite, and a double (Si<sub>12</sub>O<sub>30</sub>) 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<sub>4</sub>) tetrahedra and (TiO<sub>6</sub>) 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  $t_1 \sim t_2 \sim 9.8 \Delta$  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) (Si<sub>6</sub>O<sub>18</sub>); (2) (Si<sub>12</sub>O<sub>30</sub>)Na; (3) KLi<sub>3</sub>Ti<sub>2</sub>; (4) (Ca<sub>6</sub>Na)F<sub>2</sub>. The crystal structure of faizievite is a hybrid of the structures of baratovite, ideally KLi<sub>3</sub>Ca<sub>7</sub>Ti<sub>2</sub>(Si<sub>6</sub>O<sub>18</sub>)<sub>2</sub>(OH)<sub>2</sub> [1], and berazanskite, ideally KLi<sub>3</sub> Ti<sub>2</sub> (Si<sub>12</sub>O<sub>30</sub>) (milarite group) [2]. The baratovite block of composition [K<sub>2</sub>(Ca<sub>6</sub>Na)Li<sub>6</sub>Ti<sub>4</sub>(Si<sub>6</sub>O<sub>18</sub>)<sub>2</sub>F<sub>2</sub>] involves the sequence of sheets: (3)(1)(4)(1)(3). The berazanskite block of composition [KNaLi<sub>3</sub>Ti<sub>2</sub>(Si<sub>12</sub>O<sub>30</sub>)] 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 KLi<sub>3</sub>Ti<sub>2</sub>. 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) = [K<sub>2</sub>(Ca<sub>6</sub>Na)Li<sub>6</sub>Ti<sub>4</sub>(Si<sub>6</sub>O<sub>18</sub>)<sub>2</sub>F<sub>2</sub>] + [KNaLi<sub>3</sub>Ti<sub>2</sub>(Si<sub>12</sub>O<sub>30</sub>)] - [KLi<sub>3</sub>Ti<sub>2</sub>] = K<sub>2</sub>Na(Ca<sub>6</sub>Na)Li<sub>6</sub>Ti<sub>4</sub>(Si<sub>6</sub>O<sub>18</sub>)<sub>2</sub>(Si<sub>12</sub>O<sub>30</sub>)F<sub>2</sub>.