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Crystal structure and OD character of the mineral kettnerite CaBiOFCO_3 Jiří Hybler^a, Michal Dušek^a, Slavomil Ďurovič^b, ^aInstitute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic. ^bInstitute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia. E-mail: hybler@fzu.cz

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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 10. 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.

[1] Hybler, J., Dušek, M.: Accepted for publication in *Eur. J. Mineral.*

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Hydronium Ion in Al-bearing Fluorapophyllite Naoya Ishida^a, Mitsuyoshi Kimata^a, ^a*Earth Evolution Sciences, University of Tsukuba, Japan.* E-mail: ishida12@arsia.geo.tsukuba.ac.jp

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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 fluorapophyllites correlate with the H_2O ones. They have

more water contents than the other Al-free fluorapophyllites: 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: $\text{Si}^{4+} + \text{H}_2\text{O}$ for $\text{Al}^{3+} + \text{H}_3\text{O}^+$. 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, Lubomír Smrčok, *Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic.* E-mail: uacheva@savba.sk

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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 $R2$ and $R1$ 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 ~ 92 kJ/mol. On the contrary, for NMFA intercalates the differences not exceeding ~ 18 kJ/mol were observed indicating, that the