

four Bailey's groups (or OD subfamilies) termed A, B, C, and D, according to shifts and rotations of consecutive layers:  $+a_i/3$  shifts for group A,  $+a_i/3$  shifts and 180 degrees rotation for group B,  $+b/3$  or zero shift for group C,  $+b/3$  or zero shifts and 180 deg. rotation for group D, where  $a_i$  and  $b$  correspond to the edges of hexagonal and orthohexagonal cells, respectively. The ordered polytypes are represented by regular sequences of shifts and/or rotations allowed by the stacking rule of the respective subfamily. More or less disordered crystals are common. Recently, crystal structures of polytypes of cronstedtite 3T, 1T, and 2H2, representing groups A, C, and D, respectively, were refined. No polytype in the group B has been found to date. Subfamilies and polytypes can be identified by following methods: (1) Single-crystal X-ray diffraction (XRD) (2) Selected area electron diffraction (SAED) (3) Electron back scattering diffraction (EBSD) (4) High resolution electron transmission microscopy (HRTEM) Refined structures, X-ray diffraction pattern, HRTEM, and SAED images of several polytypes are presented.

Keywords: layered silicates, HRTEM, single-crystal X-ray diffraction

### P10.05.29

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#### New NaAlSiO<sub>4</sub> polymorphs: Monoclinic and orthorhombic trinepheline

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Recently, a new structural variety of nepheline with composition Na<sub>7.85</sub>Al<sub>7.85</sub>Si<sub>8.15</sub>O<sub>32</sub> was obtained by single crystal growth experiments using a cryolite flux. It crystallizes in space group *P*112<sub>1</sub>,  $a = 9.9897(6)$  Å,  $b = 9.9622(6)$  Å,  $c = 24.979(2)$  Å,  $\gamma = 119.788(4)^\circ$ ,  $Z = 3$ . The crystal structure of monoclinic trinepheline can be explained as a stacking sequence of a conventional nepheline unit cell and one additional layer built exclusively of elliptical rings, as observed in the structure of hexagonal trinepheline. When heated to 373(5) K, monoclinic trinepheline transformed to trinepheline of hexagonal symmetry (space group *P*6<sub>1</sub>). Upon further heating at 473(5) K the crystal structure corresponds to that of conventional nepheline. Furthermore, we have determined the structure of an orthorhombic polymorph of NaAlSiO<sub>4</sub> (*P*na2<sub>1</sub>,  $Z = 36$ ), which was hydrothermally synthesized and described by Klaska in 1974 (Thesis, University of Hamburg). The lattice parameters are related to the *P*6<sub>3</sub> ones through the relationship  $a(\text{ortho}) \approx \sqrt{3}/2 * a(\text{hex}) \approx 8.66$  Å;  $b(\text{ortho}) \approx 1.5 * a(\text{hex}) \approx 14.94$  Å;  $c(\text{ortho}) \approx c(\text{hex}) \approx 25.14$  Å. The crystals were affected by twinning via the sixfold axis. This polymorph is built of the elliptical rings and the resulting layers are comparable to the ones in hexagonal trinepheline. In hexagonal trinepheline, however, the neighbouring layers are rotated with respect to each other. In the orthorhombic modification, the layers are stacked on top of each other in identical orientations. We will also present some results of an *ab-initio* study on Na nepheline (known for showing Na-solid state conductivity) performed within the DFT formalism as implemented in the SIESTA code.

Keywords: single-crystal growth, single-crystal structure analysis, *ab-initio* calculations

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#### Hydrogen positions in beryllate minerals and materials by combined X-ray and neutron diffraction

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For mineral systems information on their structure, including the localisation of light atoms such as hydrogen and beryllium, is of considerable importance as it allows a better understanding of the material behaviour under natural conditions including its paragenesis, phase stability, compressibility/water content and thermal expansion. Many important natural minerals and their analogues are not simple silicates or aluminosilicates, but also incorporate other framework forming species such as the beryllate tetrahedron, BeO<sub>4</sub>. The role of the hydrogen containing species such as H<sub>2</sub>O and OH is also central to determining the structure formed and distribution of non-framework species in the material. We have found that the optimised crystallographic method of determining the full crystal structures of these minerals, including accurate hydrogen positions and framework distributions of Si, Al and Be, is a combined single crystal X-ray - powder neutron diffraction method. Powder neutron diffraction data are collected on the hydrogenous natural material at 120 K and the data analysis simultaneously fits this and the SXD (single-crystal X-ray) data collected at the same temperature. In the presented study the following minerals have been investigated and detailed structures will be presented: 1) Eudidymite and Epididymite. Differences in these compositionally identical minerals, NaHBeSi<sub>3</sub>O<sub>8</sub>, have been determined and results from the orientation of an extra framework hydroxide anion. 2) Leifite Na<sub>2</sub>(Si,Al,Be)<sub>7</sub>(O,OH,F)<sub>14</sub>. 3) Sorensenite Na<sub>4</sub>SnBe<sub>2</sub>Si<sub>6</sub>O<sub>18</sub> 2 H<sub>2</sub>O. 4) Nabesite Na<sub>2</sub>BeSi<sub>4</sub>O<sub>10</sub> 4 H<sub>2</sub>O. 5) Semenovite (Na,Ca)<sub>9</sub>(Ce,La)<sub>2</sub>(Fe<sup>2+</sup>,Mn)(Si,Be)<sub>20</sub>(O,OH,F)<sub>48</sub>.

Keywords: combined X-ray - neutron diffraction, beryllates, hydrogen positions

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#### Structural features of the M-site vacancies and possible hydrogen positions in hydrous forsterite

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The result of the structural refinement [1] of synthetic Fe-bearing hydrous forsterite synthesized at 13.5 GPa and 1400°C [2] revealed that the cation vacancies at the octahedral M sites predominantly occur at the M2 site, in contrast to the case [3][4] of Fe-free hydrous forsterite synthesized at 13.5 GPa and 1300°C [5] revealed that the cation vacancies at the octahedral M sites predominantly occur at the M1 site. In the case of Fe-free hydrous forsterite, the structural strain from the ideal size is larger in M1 site than in M2 site. Two H atoms may replace the Mg atom predominantly at the M1 site to reduce the structural strain, giving the vacancy at the M1 site. In the case of Fe-bearing hydrous forsterite, the Fe atoms occupy both M1 and M2 sites, leading the combinations of Mg-Mg, Fe-Fe, Mg-Fe and Fe-Mg for the occupation of M1-M2 sites. Among these, the combination of Fe-Mg for M1-M2 sites may have maximum structural strain from

the ideal size. For the reduction of the structural strain, two H atoms may replace the Mg atom predominantly at the M2 site, giving the vacancy at the M2 site.

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Keywords: crystallography of minerals, hydrogen bonds, inorganic crystal chemistry

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#### Carnallite and pseudo-carnallite as solid inclusions in blue halite from Klodawa Salt Mine, Poland

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Crystals of carnallite ( $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ) and pseudo-carnallite ( $\text{K}_3\text{Al}_2\text{MgCl}_{11} \cdot 14\text{H}_2\text{O}$ ) were found in blue halite from Klodawa Salt Mine as colourless solid inclusions [1]. Their structures were determined from X-ray diffraction data collected for the single crystals. Both type of crystals are orthorhombic and have similar lattice parameters. Carnallite I:  $a=16.1505(2)$ ,  $b=22.5190(4)$ ,  $c=9.5680(1)$  Å,  $V=3479.8(1)$  Å<sup>3</sup> and II:  $a=16.1440(3)$ ,  $b=22.5128(4)$ ,  $c=9.5672(2)$  Å,  $V=3477.2(1)$  Å<sup>3</sup>. The carnallite structures were refined to  $R1=0.0351$  for I, and  $R1=0.0413$  for II. Pseudo-carnallite I:  $a=16.1446(3)$ ,  $b=22.5206(5)$ ,  $c=9.5535(2)$  Å,  $V=3473.5(1)$  Å<sup>3</sup> and II:  $a=16.1499(3)$ ,  $b=22.5178(5)$ ,  $c=9.5681(2)$  Å,  $V=3479.5(1)$  Å<sup>3</sup>. The pseudo-carnallite structure were refined to  $R1=0.0506$  for I, and  $R1=0.0445$  for II. The crystal structures belong to the same space group Pnna (ITC No. 52) which was also determined for the carnallite from Wathlingen, Hanover, Germany [2]. In the structure of pseudo-carnallite there is only one type of  $\text{Mg}^{2+}$  ion in special position (4 d 2..) coordinating 6 water molecules,  $\text{Mg}^{2+}$  in the general position is substituted by  $\text{Al}^{3+}$  ion surrounded by 4 water molecules and 2 chloride anions in cis-position.  $\text{K}^+$  ions are in the same positions like in carnallite itself. Four chloride anions occupy the general position, one  $\text{Cl}^-$  is in the special position (4 d 2.), and 2 additional  $\text{Cl}^-$  ions are in the general position with site occupancy factor of 0.5. Six water molecules are in the general position and two additional in special positions (4 d 2..).

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Keywords: carnallite, pseudo-carnallite, blue halite

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#### Synthesis and structural studies of the ettringite group of minerals

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The ettringite group of minerals is composed of hydrated calcium sulphate hydroxide minerals that have a common trigonal structure. The group is named after its most common member ettringite, which is itself, a rather uncommon mineral. Ettringite, which has the general formula  $\text{Ca}_6\text{X}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ , where  $\text{X} = \text{Al, Cr, Fe, Mn, Si}$  and the sulphate group can be substituted by carbonate, nitrate or borate groups, occurs naturally but is also an important industrial mineral. Delayed ettringite formation in cement pastes, mortars and concretes is a major cause of softening and disintegration of cements and concretes and this has major implications for the construction industry. A potential application of ettringite that is currently being investigated, is its use in the removal of metal species from waste effluents in industry. This can be achieved by adding calcium oxide and aluminium sulfate to the waste effluent and mixing to form ettringite. When ettringite is formed in the presence of other metal species, they can be incorporated into the ettringite structure either on the  $\text{Al}^{3+}$  site, or on the  $\text{SO}_4^{2-}$  site if they are present as oxyanions. A systematic study of the structural chemistry of Ettringite and its related phases has been undertaken using powder and single-crystal x-ray diffraction and neutron diffraction of both natural and synthetic samples. A detailed analysis of new and existing synthetic analogues of these mineral phases and investigations into potential solid solutions that may exist between different members of the Ettringite group has been carried out. It is my intention to report on the results of this study, with particular emphasis on the synthesis of new analogues and the solid solutions that exist between the different members of the ettringite group.

Keywords: ettringite, solid solutions, structural chemistry

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#### Peculiar site preferences of B and Ga in $\text{MgAl}_2\text{O}_4$ spinel solid solutions

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Single crystals of  $\text{MgAl}_{1.8}\text{B}_{0.2}\text{O}_4$  and  $\text{MgAl}_{2-x}\text{Ga}_x\text{O}_4$  spinel solid solutions were synthesized under the pressure of 5-11 GPa and the flux method, respectively. The crystal structures of spinel solid solution were refined single crystal X-ray diffraction and <sup>27</sup>Al MAS NMR measurements. The site preference of B is peculiar further than that of Al and Mg in  $\text{MgAl}_2\text{O}_4$  spinel. Small B atom occupies the octahedral site, and hardly occupies tetrahedral site to keep the structure with high symmetry. The distribution of Ga are little affected by a change of the temperature. The degree of order-disorder