

**FA2-MS02-P01**

**The Crystal Chemistry of Huntite-like  $RM_3(BO_3)_4$  Polytypes.** Elena Yu. Borovikova<sup>a</sup>, Victoria S. Kurazhkovskaya<sup>a</sup>, Elisaveta V. Koporulina<sup>a</sup>, Nikolay I. Leonyuk<sup>a</sup>, Elena L. Belokoneva<sup>a</sup>. <sup>a</sup>*Department of Crystallography and Crystal Chemistry, Moscow State University, Russia.*  
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The rare earth borates with the common formulae  $RM_3(BO_3)_4$ , where R – Nd, Ga, Y, and M – Al, Ga, Cr, Fe, isostructural to natural mineral huntite are studied by IR spectroscopy method. The interest to the new rare earth borates causes by the combination of their functional characteristics - nonlinear optical, laser, active-nonlinear, etc. – in a combination to high thermal, chemical both mechanical stability and unique heat conductivity [1]. The given phases crystallize in space group R32 or C2/c. Compounds with rhombohedral structure are formed at the lowest temperatures up to ~880 – 900°, phases with symmetry C2/c crystallize at higher temperatures ~1040 – 1050°. The comparison of structures [2] has shown that they have polytypic nature and are described in the best way in order-disorder terms [3]. Only rhombohedral phases with huntite structure (R32) possess the important physical properties. These phases cannot be divided by the powder X-ray diffractometry methods. On the basis of the prepared factor-group analysis the we have assigned the bands, characteristic for compounds with the different space groups. IR spectra of the both rhomboedral and monoclinic phases often contain bands with low intensity, characteristic for another polytype. This fact is the evidence that inclusions of one polytype in another are characteristic for studied borates. Rhombohedral polytype with different octahedral cations and different rare-earth elements can be both homogeneous, and containing inclusions of the opposite ordered layers. In borates with the small cation Al, irrespective of type of a rare-earth element, always there are fragments of monoclinic phases. Almost homogeneous rhombohedral phases can be obtained with larger octahedral cations Ga, Cr and more particularly Fe. Among the rare-earth elements the larger Nd assists the inclusion of monoclinic ordered layers to rhombohedral polytype. Nd – Al and Nd – Cr borates are characterized by monoclinic structures, but at the same time they may contain some fragments with an arrangement of layers, characteristic for rhombohedral phases. Thus, revealed earlier polytypic character of structures of investigated borates, representing uniform family, and described by the law of theory OD - an order-disorder - finds convincing acknowledgement at research IR of spectra of crystals.

[1] Popova E.A, Leonyuk N.I., Popova M.N. et al., *Phys. Review B*, **2007**, 76, 1 [2] Belokoneva E.L., Timchenko T.I. *Crystallography* 1983, 28, 6, 1118 (in Russian). [3] Dornberger – Shiff K., *Deutsche A., Akad. Wiss. Berlin* **1964**, 3, 1.

**Keywords: infrared spectroscopy; polytypism; rare-earth compounds**

**FA2-MS02-P02**

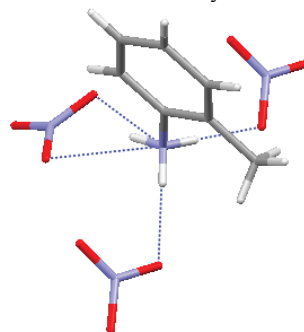
**Structural Study of Amino Acid Salts Consisting of Mineral Anions.** Rim Benali-Cherif<sup>a</sup>, Amani Direm<sup>a</sup>, Nourredine Benali-Cherif<sup>a</sup>. <sup>a</sup>*Institut des Sciences et Technologie. Centre Universitaire de Khenchela 40000, Algeria.*  
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Amino acids are interesting materials for NLO applications. Their importance is due to the fact that all the amino acids have chiral symmetry and several compounds crystallize in noncentro-symmetric space groups [1]. Thus, salts of amino acids with different organic/inorganic acids have been explored.

Several new complexes incorporating natural amino acids and mineral anions have been recently crystallized [2] and their structural, optical [3], thermal properties and structural phase transitions [4] have been investigated.

In this present work, which is part of project of searching for potential new hybrid compounds obtained by the addition of amino acids with mineral acids, we will discuss crystalline structures of new salts based on mineral anions and natural amino acids reported in the CSD Database.

All materials of this type are characterized by the presence of strong N–H...O hydrogen bonds (Figure below) connecting anionic and cationic entities together which participate in the stability and the cohesion of crystal structures.



*N–H...O interactions in 2-Methylanilinium nitrate [5].*

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**Keywords: natural amino acids; hydrogen bonds; hybrid compounds; X-ray diffraction**

**FA2-MS02-P03**

**New Structural Features in  $RbCr^{III}(C_2O_4)_2(H_2O)_2$  (II).** Malika Hamadène<sup>a</sup>, Hamza Kherfi<sup>a</sup>, Achoura Guehria-Laïdoudi<sup>a</sup>, Slimane Dahaoui<sup>b</sup>, Claude Lecomte<sup>b</sup>. <sup>a</sup>*Laboratoire de Cristallographie-Thermodynamique, USTHB, Alger, Algérie.* <sup>b</sup>CRM<sup>2</sup>,

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A bimetallic Rb/Cr oxalate polymer (compound II) has been synthesized under hydrothermal conditions with selected starting salts and then investigated structurally at low temperature. Several discrepancies have been found with the reported room-temperature diaqua ( $\mu$ -oxalato) chromium III rubidium (compound I) [1]. Indeed, the structures of the two compounds I and II are completely different, due probably to the synthetic conditions. According to the authors, the compound I crystallizes in space group C2/m and has a layered structure with the Cr, Rb atoms and one oxygen from water molecule lying on special positions. Moreover, the unique oxalate ligand forms a bridge between metal centers. The Cr atom is coordinated to 2 bidentate-chelating oxalates and 2 aqua ligands in a trans-conformation and any water molecule has been found around the 8-coordinated Rb atom. At 100K, the compound II shows a new atomic arrangement, which represents a novel structure type with interesting structural features. First, in the more distorted octahedra  $\text{CrO}_4(\text{H}_2\text{O})_2$ , all ligands are in a cis-conformation while the alkali metal is surrounded by seven O atoms from oxalate groups, completed with two  $\text{H}_2\text{O}$  molecules which are bridging the Cr and Rb metals in chains of one edge-shared polyhedra, running along [100] direction. The two independent ligands play several roles, as bridging the metal atoms in the two other directions or interacting with the  $\text{H}_2\text{O}$  molecules, as medium or strong H-bonds, in order to build an extended three-dimensional network. Moreover, from the connection of the all different units in the 3D framework, two kinds of channels appear and run respectively along the [100] and [010] directions, with rhombic and rectangular section. It is noteworthy to underline that one of the two organic ligands offers an interesting and unusual conformation mode, since it displays simultaneously the conventional chelating mode i.e the  $\mu_2$ - $\eta^4$  coordination and the rather scarce  $\mu_2$ - $\eta^3$  chelating mode, involving two O atoms of the same carboxylate function. The diaqua dioxalate rubidium chromium(II) investigated at low temperature, exhibits distinct structural differences if compared with the reported previously double alkali and transition metal oxalates which have all layered structures [2][3]. This result can be related to the parameters governing the single crystal synthesis.

[1] Koltish, U.; *Acta Cryst.*, **2004**, C60, n° 3, m129- m133). [2] Gleizs, A.; Maury, F.; Galy, J., *Inorg. Chem.*, **1980**, 19, 2074. [3]. Schwendtner, K.; Koltish, U. *Acta Cryst.*, **2004**, E60, m659-m661

**Keywords:** chelating mode; porous 3D framework; channels

#### FA2-MS02-P04

**Polymorphism of Silicates of Anhydrous Cement as Treasury for the Most Advanced Concretes.** Frederic Dunstetter<sup>a</sup>, Mireille Courtial<sup>a,b</sup>, Marie-

Noelle de Noirfontaine<sup>a</sup>. <sup>a</sup>LSI, Ecole Polytechnique, F-91128 Palaiseau, France. <sup>b</sup>Université d'Artois, F-62408 Bethune, France.

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Anhydrous cement is a mixture of the so-called clinker – an artificial rock made in cement kiln – and various additives. Clinker contains at least four major phases. Two calcium silicates  $\text{Ca}_3\text{SiO}_5$  (50 to 70 wt % of clinker; 7 polymorphs) and  $\text{Ca}_2\text{SiO}_4$  (15 to 30 wt %; 5 polymorphs), and two calcium aluminates (5 to 20 wt %). The crystallographic structure of six of the seven polymorphs of  $\text{Ca}_3\text{SiO}_5$  are known nowadays, among them three were determined in the last eight years [1-3]. The structure of the five polymorphs of  $\text{Ca}_2\text{SiO}_4$  is known since the 80's [4,5] but an important effort is still in progress in order to understand the complex twin and microstructural features [6].

During the subsequent hydration of cement, in order to produce concrete, the phases of clinker dissolve and various hydrated species precipitate and constitute the “glue” of the final material. Since the initial compounds disappear during hydration, only a very low effort was dedicated to the study of physicochemical properties of the anhydrous phases.

The situation is now very different, for the new high performance concretes developed since the 90's contain less and less water in the initial mixture. Then, more and more (0% to 40 vol %) anhydrous clinker now remains in this type of concrete. An important component of the very high strength (200 to 800 MPa, to be compared to 30 MPa for the ordinary concrete) is due to the very high Young modulus of the four phases of clinker (130 GPa) compared to all the other phases (20 to 30 GPa for the hydrates and 70 GPa for silica).

Therefore, the last decade has seen a renewal of the study of all basic physicochemical properties of the phases of clinker.

Within this context, we present here the actual status of the crystallographic knowledge of polymorphism of the two silicates  $\text{Ca}_3\text{SiO}_5$  and  $\text{Ca}_2\text{SiO}_4$ .

[1] F. Dunstetter et al. *Cem. Concr. Res.* 36 **2006** 39-53. [2] V.K. Peterson et al. *J. Am. Ceram. Soc.* 87 1625-1634 **2004**. [3] A.G. De la Torre et al. *Cem. Concr. Res.* 38 **2008** 1261-1269. [4] W.G. Mumme et al. *N. Jb. Miner. Abh* 169 35-68 **1995**. [5] H. Saalfeld et al. *Z. Kristallogr* 155 65-73 **1981**. [6] K. Fukuda et al. *J. Am. Ceram. Soc.* 91 4093-4100 **2008**.

#### FA2-MS02-P05

**Structure of Metastable  $\text{ScBO}_3$  Phases.** Elena Kudrenko<sup>a</sup>, Vladimir Morozov<sup>b</sup>, Ivan Shmyt'ko<sup>a</sup>, Gennadi Strukov<sup>a</sup>, Tatjana Fursova<sup>a</sup>. <sup>a</sup>Institute of Solid State Physics Russian Academy of Sciences, Chernogolovka, Moscow distr. 142432, Russia. <sup>b</sup>Moscow State University, Department of Chemistry, Moscow, 119899, Russia.

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New metastable phases have been found during the annealing of the amorphous  $\text{ScBO}_3$  sample at the different temperatures. The analysis of X-ray powder diffraction