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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 (μ -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 H_2O 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 H_2O 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 μ_2 - η^4 coordination and the rather scarce μ_2 - η^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

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Polymorphism of Silicates of Anhydrous Cement as Treasury for the Most Advanced Concretes. Frederic Dunstetter^a, Mireille Courtial^{a,b}, Marie-

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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 Ca_3SiO_5 (50 to 70 wt % of clinker; 7 polymorphs) and Ca_2SiO_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 Ca_3SiO_5 are known nowadays, among them three were determined in the last eight years [1-3]. The structure of the five polymorphs of Ca_2SiO_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 Ca_3SiO_5 and Ca_2SiO_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**.

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Structure of Metastable ScBO_3 Phases. Elena Kudrenko^a, Vladimir Morozov^b, Ivan Shmyt'ko^a, Gennadi Strukov^a, Tatjana Fursova^a. ^aInstitute of Solid State Physics Russian Academy of Sciences, Chernogolovka, Moscow distr. 142432, Russia. ^bMoscow State University, Department of Chemistry, Moscow, 119899, Russia.

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New metastable phases have been found during the annealing of the amorphous ScBO_3 sample at the different temperatures. The analysis of X-ray powder diffraction

(XRPD) patterns revealed the new compound to have a vaterite-type and warwickite-type structure, respectively. The modification with vaterite-type structure is known for other rare earth borates, for example, YBO_3 and YbBO_3 , as a stable form. The warwickite-type phase is known for $\text{M}_1^{3+}\text{M}_2^{2+}\text{OBO}_3$ -type compounds. ScBO_3 was believed earlier to have calcite-type structure type only. Non-equilibrium processes during heating-quenching cycles lead to form new metastable phases in ScBO_3 . We carried out detailed studies of ScBO_3 structural transformations by differential scanning calorimetry and *in situ* x-ray powder diffraction techniques. The quenched samples were characterized by IR spectroscopy, as well as XRD. We revealed that non-reversible sequence of amorphous \rightarrow warwickite-type \rightarrow vaterite-type \rightarrow calcite-type transformations took place in the temperature range 1036-1054 K. Total exothermal effect for the amorphous \rightarrow warwickite-type \rightarrow vaterite-type transformations correspond to $\Delta H=142.4$ J/g and that of vaterite-type \rightarrow calcite-type transition is $\Delta H=85$ J/g. The lattice parameters of the ScBO_3 warwickite-type structure are $a=9.4248$ Å, $b=9.4451$ Å and $c=3.3969$ Å, $\beta=90.309$, S.G.= $P2_1/n$ and ones of the vaterite-type structure are $a=3.8952$ Å, $c=7.8772$ Å, S.G. = $P6_3/mmc$, respectively. The details of the crystal structures will be discussed in the presentation.

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Keywords: complex oxides; nanomaterials; X-ray powder diffraction

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Mineral Apatite as a Periodic Model of Surface to Living Cell Growth. Marzena Suder^a, Małgorzata Tyszkiewicz-Czochara^b, Katarzyna Stadnicka^a. ^a*Jagiellonian University, Faculty of Chemistry, Krakow, Poland.* ^b*Jagiellonian University, Faculty of Pharmacy, Krakow, Poland.*

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A mineral apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$ as a main source of phosphorus in nature, has a great importance in designing materials useful for medical purposes. Moreover, it is worth to say, that the mineral single-crystal apatites can obtain size up to several centimeters [1]. In comparison to above, a calcium deficient carbonate-hydroxylapatite suitable as a mineral part of vertebrates bones, occurs in shape of nano-sized crystals [1,2]. The hydroxylapatite, with a chemical composition similar to biological apatites and its proved biocompatibility, is broadly applied in medicine and stomatology [3]. It is interesting to what extent the different crystallographic orientation of the single-crystal faces has influence on living cell growth. Two types of geological crystals of different origin, with molecular formulas $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{1.38}(\text{OH})_{0.62}$ (I) and $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{1.09}(\text{OH})_{0.86}\text{Cl}_{0.05}$ (II), were studied. The material was characterized by various methods – polarizing microscopy, single-crystal X-ray diffraction and energy-dispersive X-ray spectroscopy for the evaluation of surface chemistry. In both cases lattice symmetry was found to be hexagonal with the point group

$P6_3/m$ and following unit cell parameters: $a=9.3839(4)$ Å, $c=6.8867(3)$ Å for (I) and $a=9.4058(4)$ Å, $c=6.8807(3)$ Å for (II). A basis to assume right model of the surface of the following faces: (10-10), (0001) and (10-11) was structural analysis. Subsequently, a chosen cell line of human fibroblasts has been grown on the prepared crystal plates with orientations (10-10), (0001) and (10-11). We hope that the studies will shed light on the understanding of living cell – apatite substrate interactions at atomic level.

[1] Phosphates: Geochemical, geobiological, and materials importance, edited by Kohn M.J, Rakovan J., Hughes J.M., Reviews in *Mineralogy and Geochemistry*, vol. 48, Mineral. Soc. Am. **2000**. [2] Glimcher M.J. Bone: Nature of the Calcium Phosphate Crystals and Cellular, Structural, and Physical Chemical Mechanisms in Their Formation, Reviews in *Mineralogy & Geochemistry*, **2006**, 64, 223. [3] Biomaterials Science An Introduction to Materials in Medicine, edited by Ratner B.D., Hoffman A.S., Schoen F.J., Lemons J.E., Elsevier Academic Press **2004**, 2nd edition.

Keywords: biomaterials; apatites; single-crystal X-ray diffraction

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Kinetics of the Dehydroxylation and Mullitization Processes of Nanotubular Halloysite Mineral.

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A mineral clay deposit from the locality “Guelma”, was investigated. The exploitation of the results of chemical, X-rays, IR and differential thermal analyses shows that the raw material is essentially formed with halloysite. Examined with S.E.M., the clay particles have a nanotubular form with 100 to 300nm in length and 20 to 50 nm in external diameter. The activation energy of dehydroxylation was determined as 160 kJ.mol⁻¹, while the value for mullitisation is 844 kJ.mol⁻¹.

Keywords: halloysite; natural nanotube; kinetics of dehydroxylation

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Defects in Fluorite Structure Caused by Natural Irradiation. Vojtěch Vlček^e, Roman Skála^a, Jakub Čížek^d, Jan Drahoukoupil^b, Jan Valenta^c, Jana Ederová^f, Viktor Goliáš^e. ^a*Academy of Sciences of the Czech Republic, v.v.i. Institute of Geology, Prague, Czech Republic.* ^b*Academy of Science of The Czech Republic, v.v.i., Institute of Physics, Prague, Czech Republic.* ^c*Charles University in Prague, Department of Chemical Physics and Optics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic.* ^d*Charles University in Prague, Department*