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 CrO(H₂O)₆, all ligands are in a cis-conformation while the alkali metal is surrounded by seven O atoms from oxalate groups, completed with two H₂O 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 H₂O molecules, as medium or strong H-bonds, in order to build an extended three-dimensional network. Moreover, from the connection of all the 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 more perform an interesting and unusual conformation mode, since it displays simultaneously the conventional chelating mode i.e the µ₁,η¹ coordination and the rather scarce µ₂,η¹ 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.


Keywords: chelating mode; porous 3D framework; channels

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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 Ca₃SiO₅ (50 to 70 wt % of clinker; 7 polymorphs) and Ca₄SiO₄ (15 to 30 wt %; 5 polymorphs), and two calcium aluminate (5 to 20 wt %). The crystallographic structure of six of the seven polymorphs of Ca₃SiO₅ are known nowadays, among them three were determined in the last eight years [1-3]. The structure of the five polymorphs of Ca₄SiO₄ 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 remain 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 Ca₃SiO₅ and Ca₄SiO₄.

(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 M$^{3+}$BO$_3$-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→ warwickite-type→ vaterite-type→ calcite-type transformations took place in the temperature range 1036-1054 K. Total exothermal effect for the amorphous→ warwickite-type→ vaterite-type transformations correspond to $\Delta H=142.4$ J/g and that of vaterite-type→ calcite-type transition is $\Delta H=85$ J/g. The lattice parameters of the ScBO$_3$-type structure are $a=9.4248$ Å, $b=9.4451$ Å and $c=3.3969$ Å, $\beta=90.309$, and $a=9.3852$ Å, $c=7.8772$ Å, $S.G. = P6_3/mmc$, respectively. The details of the crystal structures will be discussed in the presentation. The work had been financially supported by RFBR grant No.09-02-00363.

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, Malgorzata Tyszka-Czochara, Katarzyna Stadnicka. Jagiellonian University, Faculty of Chemistry, Krakow, Poland. Jagiellonian University, Faculty of Pharmacy, Krakow, Poland.

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A mineral apatite, Ca$_5$(PO$_4$)$_3$(F,OH,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-hydroxyapatite suitable as a mineral part of vertebrates bones, occurs in shape of nano-sized crystals [1,2]. The hydroxyapatite, 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 extend 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 Ca$_{60}$(PO$_4$)$_{60}$(OH)$_{100}$(F,OH,Cl)$_{48}$ (I) and Ca$_{60}$(PO$_4$)$_{60}$(OH)$_{100}$(F,OH,Cl)$_{48}$ (II), were studied. The mineral 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 P63/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.


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

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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, Roman Skála, Jakub Čížek, Jan Drahokoupil, Jan Valenta, Jana Ederová, Viktor Goliáš.

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