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Crystal screening by second order nonlinear optical imaging of chiral crystals (SONICC)

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The recent emergence of stable, handheld ultrafast (~100 fs) laser sources has opened practical access to fundamentally new classes of nonlinear light-matter interactions for characterization crystallization phenomena. In this work, second order non-linear optical imaging of chiral crystals (SONICC) is investigated as a rapid (up to video rate), selective, and ultra-sensitive all-optical method for high-throughputs studies of active pharmaceutical ingredient (API) crystallization phenomena. SONICC relies on second harmonic generation (SHG), or the frequency doubling of light, which is forbidden in unordered media and most achiral salts, but allowed for the overwhelming majority of chiral crystals. This high specificity to chiral crystals combined with an insensitivity to optical scattering and an enormous (~8 decade) dynamic range of linear quantification open new opportunities for high-throughput screenings.

Three proof-of-concept applications of SONICC will be demonstrated for characterization of API formulations; i) polymorph screening from the polarization-dependence of the SHG response, which provides up to 18 unique observables specific to a particular crystal compared to 3 for linear optics, ii) crystallization screening with reliable quantification of trace API crystallinity with sub-parts per million to parts per billion detection limits in powdered APIs and in amorphous polymer formulations (i.e.,4-7 orders of magnitude improvement over most current routine methods for powder analysis), and iii) direct determination of nucleation kinetics within powders and turbid matrices without significant loss of image quality from optical scattering (since only the unscattered incident light contributes to the detected signal). Quantitation and polarization analysis can be performed rapidly with high signal to noise on single crystals less than ~1 μm^3 in size, opening opportunities for performing screenings of hundreds or thousands of conditions with just a few milligrams of purified API when coupled to emerging ultrahigh-throughput microfluidic screening platforms. Furthermore, SONICC is directly compatible with most existing high-throughput screening plates that allow conventional optical imaging without modification. The absence of a background response from disordered media allows the development of simple image analysis algorithms for automated quantification of nucleation rates, crystal growth rates, and activation energies for nucleation.

An overview of the methods and analysis will be presented, along with and a critical discussion of the strengths and limitations of SONICC for practical high-throughput screening and a summary of some of the challenges associated with the measurements. In addition, a description will be provided of the basic instrumentation required for SONICC, which is anticipated to be commercially available in the near future through partnership with Formulatrix.

Keywords: polymorphism, screening, high-throughput

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Prospects and challenges in the synthesis of zeotype materials

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This presentation will cover the challenges in the preparation of discrete zeo-type molecular sieves with emphasis on their complex crystallization mechanism under hydrothermal synthesis conditions. As zeo-type materials, nanosized aluminophosphates (AlPO-5, -11, -18, -41), silicoaluminophosphate (SAPO-5, -11, -18, -41) and titanosilicates (TS-1 and ETS-4) will be presented. The control of precursor suspensions on the nanometric scale allows the preparation of zeo-type nanosized crystals with desired crystalline structures, porosity and particle size.

The focus of this presentation will be on the preparation of nanosized materials from transparent precursor suspensions containing single or mixed templates under controlled microwave or conventional heating. Optimization of the synthesis parameters and detail characterization of the crystallization process provide information on the important design rules for such materials.

Emphasis on green synthesis approaches involving multi-step microwave or conventional heating *via* reusing of non-reacted compounds from precursor suspensions with essential chemical compensation will be presented. The microwave syntheses for nanocrystalline AlPO-*n* and SAPO-*n* have shown almost complete consumption of the organic templates and no disposal of detrimental reagents to the environments. On the other side the preparation of nanocrystals with desired properties and reasonable yield is achieved. The use of microwave instead of conventional heating directs selectively the synthesis of one versus other types of porous materials for extremely short time, thus decreasing the energy consumption and making possible the chemical process to be environmentally benign.

Further the stabilization of the nanoparticles in suspensions using different solvents and surface modifiers together with possible assembling of the zeo-type nanosized materials in thin-to-thick films will be presented.

Keywords: synthesis, nanoparticles, zeo-type materials

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Crystallography, physical properties and applications of sulfosalts

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Sulfosalt minerals are characterized by complex crystal structures with low symmetry [1], [2]. From the total of more than 260 known phases of the sulfosalt family, about 80% crystallize in the orthorhombic and monoclinic system. Therefore, physical properties can be strongly anisotropic and must be described by tensors. Due to important applications in thermoelectric and photovoltaic energy conversion, anisotropic transport properties, like electrical or thermal conductivity, are of basic importance.

The anisotropic electrical conductivity of typical sulfosalts will be investigated and correlated to their crystal structures using in situ methods on a SEM including EDXS, EBSD, and micro-conductivity measurements. Different single crystals of natural grown sulfosalts were oriented, cut, and polished. The electrical conductivities in different directions of the polished and cleaved planes were measured by a 2point and a 4point probe technique. Results were correlated to the crystal orientations and tensors were estimated.

[1] Y. Moëlo, E. Makovicky, N.N. Mozgova, J.L. Jambor, N. Cook, A. Pring, W. Paar, E.H. Nickel, S. Graeser, S. Karup-Møller, T. Balić-Žunić, W.G. Mumme, F. Vurro, D. Topa, L. Bindi, K. Bente, M. Shimizu, *Journal of Mineralogy*,

2008, *20*, 7-46. [2] H. Dittrich, A. Stadler, D. Topa, H.-J. Schimper, A. Basch, *Physica Status Solidi*, **2009**, *A 206 No. 5*, 1034–1041.

Keywords: sulfosalts, crystal structures, transport properties

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Genetic aspects of borophosphate crystal chemistry

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The borophosphate family incorporates a large number of compounds having various structures ranging from densely packed to microporous [1]. They are used as catalysts and phosphors, and have nonlinear optical and sorption properties; they are promising anticorrosive and magnetic materials. This family includes the minerals lüneburgite and seamanite; the second one without shared oxygen vertices between $[B(OH)_4]$ and $[PO_4]$ tetrahedra is formally considered as a borate-phosphate.

New transition metal borophosphates with alkali-metal cations were synthesized under hydrothermal conditions and their crystal structures were determined using single-crystal X-ray diffraction at 100 K. Crystal chemical interpretations of studied phases in correlation with literature data has allowed us to reveal some new features in title group of compounds.

We found a novel structural type of cubic microporous borophosphates that realizes in the framework of two compositions: $KNi_5[P_6B_6O_{23}(OH)_{13}]$ (an ordered phase) and $Na_{0.45}K(Mg_{0.6}Ni_{0.2}Al_{0.2})Ni_2(Ni_{0.5}Al_{0.3}Mg_{0.2})_2[P_6B_6O_{24}(OH)_{12}]$ (a disordered phase having isomorphous and vacancy defects). The structure is built from alternating borate and phosphate terahedra forming 12-membered puckered rings with K^+ ions at the centers. These rings are arranged as in cubic dense sphere packing. A novel feature of these new crystal structures is the presence of linear trimers of face-sharing $[NiO_6]$ octahedral occupying the octahedral interstices of this sphere packing. We have shown that the new compound $KNi_5[P_6B_6O_{23}(OH)_{13}]$ is topologically related to the cyclophosphates $Cs_3V_3(PO_3)_{12}$ [2]) and $NaM(PO_3)_3$ (M=Zn or Mg) [3] as parent structures. It is worth mentioning that another sodium zincophosphate $Na[Zn(PO_4)](H_2O)$, a zeolite-type material "CZP" [4] is considered as archetype for some borophosphates with common formula $A^+_xM(H_2O)_2(BP_2O_8)(H_2O)$, where A = Na, K, Ca, and M = Zn, Co, Ni, Fe, Mn, Cd, Sc, In. The above examples demonstrate a tendency of subsistence of phosphate archetypes for borophosphate compounds. To our knowledge no cases of opposite processes have been cited in the literature up to now.

In connection with two new isoformula compounds, namely $Rb\{(Al,Fe)[BP_2O_8(OH)]\}$ and $K\{(Fe,Al)[BP_2O_8(OH)]\}$ having different configurations and dimensions of borophosphate anions, we showed that the polymorphism of the $[BP_2O_8(OH)]^{4-}$ anion has a morphotropic nature and is related to the substitutions both in the cationic part of the structure and in the octahedral position of the mixed anionic framework. The structure type transformation for borophosphates described by the general formula $A^+\{M^{3+}[BP_2O_8(OH)]\}$ (position A: K, NH_4, Rb Cs; octahedral position M: Al, Ga, Fe, Sc, In) from monoclinic with 1*D* chain borophosphate anion to triclinic with 0*D* borophosphate anion built from 7 tetrahedra, occurs at an R_{A+}/R_{M3+} ratio close to 2.6. The financial support of the Russian Foundation for Basic Research (project 10-05-01068a) is gratefully acknowledged.

[1] B. Ewald, Y.-X. Huang, R. Kniep *Z. Anorg. Allg. Chem.* **2007**, *633*, 1517-1540. [2] A.V. Lavrov, V.P. Nikolaev, G.G. Sadikov, M.J. Vojtekov *Dokl. Akad. Nauk SSSR*. **1981**, *259,* 103-106. [3] I. Abrahams, A. Ahmed, C.G. Groombridge, G.E. Hawkes, T.G. Nunes *J. Chem. Soc. Dalton Trans.* **2000,** 155-160. [4] W.T. A. Harrison, T.E. Gier, G.D. Stucky, R.W. Broach, R.A. Bedard *Chem. Mater.* **1996,** *8*, 145-151.

Keywords: borophosphates, crystal structure, genetic relations

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Debye function analysis and 2D imaging of nanoscale bioapatite in bone tissue

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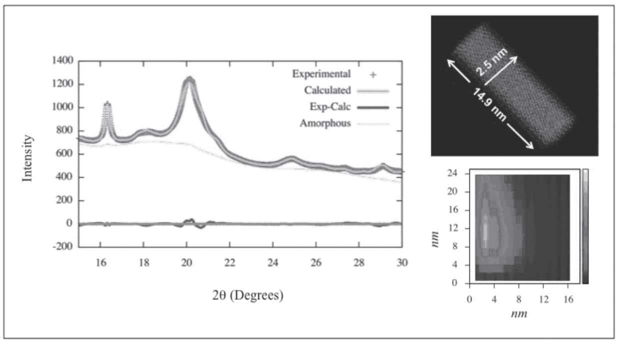
In the field of biomaterials and biomineralization, the investigation of bioapatites, the nanosized mineral component of bone, plays a special role both on the side of fundamental knowledge and as source of inspiration for tissue engineering applications. Many aspects are still under debate. Within such a framework, nanosized bioapatites from engineered bone tissue have been analyzed using, for the first time, a Total Scattering Debye Function Approach (DFA), well suited for modelling both Bragg and diffuse scattering from crystalline materials at the nanoscale [1]. The analysis was carried out by creating a bivariate population of atomistic hydroxyapatite nanocrystal models [2] of increasing size and storing the "sampled" interatomic distances of each nanocrystal in suitable databases to be used in the Debye function analysis.

An average rod-like shape was found to best represent the apatites in all samples, with average sizes and size distributions well matching the gap region of collagen I (see Figure).



The diffraction patterns analyzed by DFA belong to 2D collections of high resolution micro-diffraction signals acquired in scanning mode, at ID13@ESRF, on porous and resorbable bioceramic implants. The same patterns were further used as signal models to extend the DFA results to all the experimental datasets, using a statistical technique known as "Canonical Correlation Analysis" (CCA). CCA 2D maps are then used to image the spatial gradient of bioapatite properties throughout the entire collection. Several similarities with both structural and microstructural features of biogenic apatites and the mineralization process in bone tissue were found [3].

[1] A. Cervellino, C. Giannini, A. Guagliardi, *J. Appl. Cryst* **2010**, *43*, 1534-1547. [2] M.I. Kay, R.A. Young, A.S. Posner *Nature* **1964**, *25*, 1050-1052 [3] A. Guagliardi, A. Cedola, C. Giannini, M. Ladisa, A. Cervellino, A. Sorrentino, S. Lagomarsino, R. Cancedda, M. Mastrogiacomo, *Biomaterials* **2010,** *31*, 8289-8298

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