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**Keywords:** sulfosalts, crystal structures, transport properties

### MS.54.3

*Acta Cryst.* (2011) A67, C127

#### Genetic aspects of borophosphate crystal chemistry

Olga Yakubovich,<sup>a</sup> Werner Massa,<sup>b</sup> Ian Steele,<sup>c</sup> Olga Dimitrova,<sup>a</sup> <sup>a</sup>Department of Crystallography, Moscow State University, (Russia). <sup>b</sup>Department of Chemistry, Philipp-University, Marburg, (Germany). <sup>c</sup>Department of Geophysics, University of Chicago, (USA). E-mail: yakubol@geol.msu.ru

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 tetrahedra 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  $A^+M(H_2O)_2(BP_2O_8)(H_2O)$ , 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 1D chain borophosphate anion to triclinic with 0D borophosphate anion built from 7 tetrahedra, occurs at an  $R_{A^+}/R_{M^{3+}}$  ratio close to 2.6. The financial support of the Russian Foundation for Basic Research (project 10-05-01068a) is gratefully acknowledged.

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**Keywords:** borophosphates, crystal structure, genetic relations

### MS.54.4

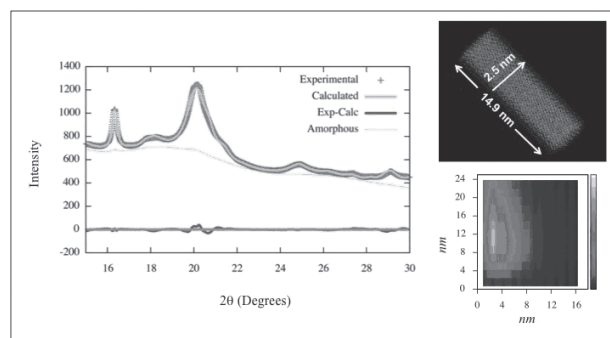
*Acta Cryst.* (2011) A67, C127

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

Antonietta Guagliardi,<sup>a</sup> Alessia Cedola,<sup>b</sup> Cinzia Giannini,<sup>a</sup> Antonio Cervellino,<sup>c</sup> Maddalena Mastrogiacomo,<sup>d</sup> <sup>a</sup>Istituto di Cristallografia, CNR, Bari (Italy). <sup>b</sup>Istituto di Fotonica e Nanotecnologie, CNR, Roma (Italy). <sup>c</sup>Paul Scherrer Institute, PSI-SLS, Villigen (Switzerland). <sup>d</sup>Dipartimento di Oncologia, Biologia e Genetica, Università di Genova, Genova (Italy). E-mail: antonella.guagliardi@ic.cnr.it

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].

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**Keywords:** bone, debye function analysis, microdiffraction