

MS18. Thermoelectric materials - from fundamental science to applications

Chairs: Oliver Oeckler, Sylvie Hébert

MS18-P1 Interplay between structural transitions and thermoelectric properties in a Mn hollandite

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Na_xCoO_2 and misfits are still the best p type thermoelectric oxides, with the combination of a large Seebeck coefficient, together with a metallic behaviour at 300K, and small values of thermal conductivities [1-3]. Their unique thermoelectric properties come from the presence of CoO_2 layers made of edge shared CoO_6 octahedra, with Co^{3+} and Co^{4+} in low spin states. New families of oxides have since then been investigated to find new potential thermoelectric materials. Among them, hollandites present an interesting crystallographic structure with (i) ribbons made of edge shared octahedra, and (ii) the presence of tunnels, in which large cations can be inserted. Several hollandites have been investigated, with both p and n type doping, and large power factors have been observed [4-5]. In this poster, the results obtained in the case of $\text{Ba}_x\text{Mn}_8\text{O}_{16}$ hollandite will be presented, with the evidence of a structural transition at high T. The impact of this structural transition on the transport properties will be discussed.

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MS19. Topology of crystal structures

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MS19-P1 Crystal chemistry of Al-phosphate minerals with complex H-bond networks

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The (PO_4) oxyanion combines with over 30 elements to form natural phosphates, which are among the most complex and variegated compounds in all the mineral world, displaying a large number of recognized phases (about 300), most of them featuring hydrogen as hydroxyl groups and water molecules. Thus, hydrogen bond displays a crucial role in stabilizing the hydroxy-hydrated phosphate frameworks, providing the additional bond-valence contribution to the anions. Hence, the oxygen atoms of (PO_4) groups easily interact with neighbor cationic environments in the structure. For this reason, many phosphates are characterized by the presence of an intricate network of O-H...O interactions, joining the polyhedral units and making up the three dimensional framework (Humnicki & Hawthorne, 2002). In this sense, the study of such complex structures is achieved by means of Single-Crystal X-Ray Diffraction, with the contribute of powder FTIR spectroscopy, being the latter a powerful tool for the study of hydrogen in minerals, especially in presence of high OH/H₂O contents.

In this work, we present the structure investigations of selected aluminum phosphates: vauxite $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, wardite $\text{NaAl}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, wavellite $\text{Al}_3(\text{PO}_4)_2(\text{OH},\text{F})_3 \cdot 5\text{H}_2\text{O}$, augelite $\text{Al}_2(\text{PO}_4)(\text{OH})_3$, whiteite $\text{CaFeMgAl}_2(\text{PO}_4)_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Ventrucci *et al.*, 2015, and references therein). Main crystallographic features (bonds, angles, interactions) were examined and compared with those obtained from phosphate literature, and the networks of hydrogen bonds were further analyzed according to the Libowitzky (1999) relationship, for the range of D-H...A bond systems in the structure, in order to compare results of OH frequencies from FTIR spectra with those observed by X-ray refinement.

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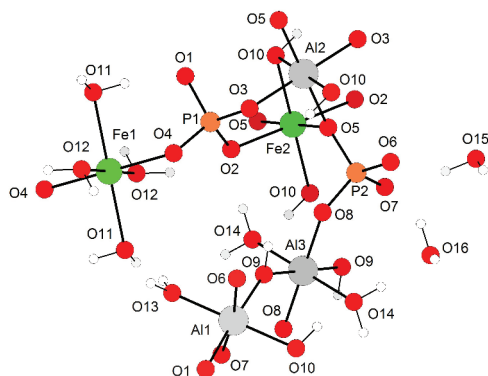


Figure 1. Cationic and anionic environments for vauxite.

Keywords: phosphates; structure refinement; hydrogen bonds; FTIR

MS19-P2 Constructing new porous materials based on polymeric cage metallocloxanes

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We report on structural features and electronic properties of polymeric metallocloxanes obtained by X-ray studies, magnetic measurements and theoretical calculations. Polymer structure of metallocloxanes (MOS) under discussion composed from cage monomeric units containing various number of transition metals (Cu, Ni, Mn, Fe) interconnected by alkali-metal ions and weak interatomic interactions (hydrogen bonds or stacking interactions). The type of supramolecular architecture (1D, 2D or 3D, see Figure 1) can be controlled by variation of ionic radii of alkali metal, the nature of solvent used for crystallization and addition of chelating ligands. These factors also affect the size of MOS monomeric units which can include 2-11 transition metal atoms forming metaloxide core partially coated by cyclic and acyclic siloxanolate ligands. Magnetic measurements have shown the pronounced ferro- and antiferromagnetic properties depending on number and the nature of transition metal in MOS core.

It was demonstrated by powder X-ray diffraction (XRD) and XAFS studies that polymer structure established at low temperature by single crystal XRD in the most of cases retained at room temperature. The role of metallocloxanes as structure building units, the topology of resulting nets and accessibility of the voids were analyzed. In addition, the strength of coordination bonds and weak interatomic interactions responsible for the stabilization of polymer structures were estimated in terms of R. Bader's QTAIM theory.

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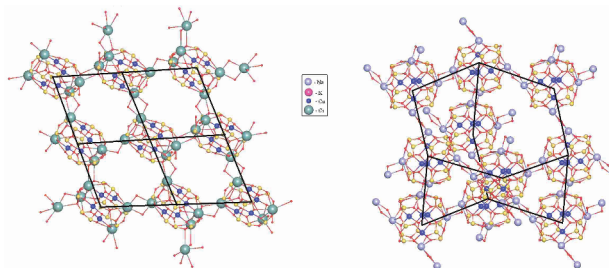


Figure 1. Fragments of the sql and dia nets in the structures of sodium (left) and cesium (right) coppersiloxanes

Keywords: metallocloxanes, coordination polymers, structure building unit, magnetic properties, QTAIM studies.