

## FA2-MS14A-T01

**Double perovskites with broken corner-sharing connectivity of the octahedral framework.** Artem

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The perovskite-based materials demonstrate large variety of functional properties thanks to the unique flexibility of the perovskite structure. There are many degrees of freedom allowing to adopt the perovskite structure for different applications, including adjustment of the tilting distortion of the perovskite octahedral framework, playing with the amount and ordering patterns of cation and/or anion vacancies, formation of intergrowth structures etc. It is always tempting to find novel pathways to modify the perovskite structure and create new families of perovskite compounds thus extending the search field for promising materials. Examples of the inherent ability of the perovskite structure to adopt different distortions will be given by double  $A_2BB'X_6$  perovskites where the B and B' cations demonstrate flexible and rigid coordination environment, respectively. Large size mismatch between the B and B' cations causes non-cooperative rotations of the B'X<sub>6</sub> octahedra increasing the coordination number of the B cations. It leads to losing the corner-sharing connectivity of the octahedral units in the perovskite framework that in turn results in various complicated ordering patterns of rotated B'X<sub>6</sub> octahedra. The structures of such double perovskites with broken corner-sharing connectivity are beyond the commonly known octahedral tilting systems in perovskites. The solution of the K<sub>3</sub>AlF<sub>6</sub> [1, 2] and Sr<sub>3</sub>WO<sub>6</sub> structures will be presented; possible octahedral rotation modes and the stability criteria for such structures will be discussed.

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**Keywords:** perovskite, elpasolite, octahedral tilting

## FA2-MS14A-T02

**From Cathode-Materials to Catalysts: Structures and Redox Behavior of Transition Metal Phosphates as a Basis for Technical Applications.** Robert Glaum

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Anhydrous phosphates of transition metals are showing a large structural diversity, which is much larger than that observed for silicates or sulfates. Isolated phosphate tetrahedra in an oxide matrix, as they occur in oxide-phosphates like Fe<sub>9</sub>O<sub>8</sub>(PO<sub>4</sub>) [1] are found at one end. Two-dimensional phosphate nets, as in ultraphosphates like CuP<sub>4</sub>O<sub>11</sub> [2] are forming the other end of a list of highly-variable structural features. With respect to the transition metal various degrees of condensation of co-ordination polyhedra [M O<sub>n</sub>] and oxidation states can be found in phosphates [3]. Clearly, oxides of transition metals in rather low oxidation states are particularly well stabilized in phosphates (e.g.: Ti<sup>III</sup>PO<sub>4</sub> [4], Cr<sup>II</sup><sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> [5], Cr<sup>II</sup><sub>2</sub>P<sub>2</sub>O<sub>7</sub> [6])

Cathode materials for lithium ion batteries like phosphates **LiMPO<sub>4</sub>** of the olivine structure family are characterized by a kinetically very stable "covalent" metal-phosphate network and high Li<sup>+</sup> ion mobility [7]. Thus, rather high oxidation states like Co<sup>3+</sup>, which are thermodynamically unstable in phosphates, can be accessed by topotactic delithiation at rather low temperatures.

**Gold(III) phosphate AuPO<sub>4</sub>** (PdSO<sub>4</sub> structure type [8]) represents the first example of an insoluble compound with a crystal structure built by square-planar [M<sup>III</sup>O<sub>4</sub>] and tetrahedral [X<sup>V</sup>O<sub>4</sub>] units [9]. The crystal structure of Hg[Pd(PO<sub>4</sub>)<sub>2</sub>] [10] might be regarded as filled AuPO<sub>4</sub> structure type and nourishes the hope that metastable polymorphs of AuPO<sub>4</sub> with open framework structures might be accessible.

Anhydrous oxide-phosphates of the **Lipscombite/Lazulite structure family** are ranging in composition from  $\alpha/\beta$ -Fe<sub>2</sub>O(PO<sub>4</sub>) [11] to  $\epsilon$ -VOPO<sub>4</sub> [12]. In the former, all octahedral voids are occupied by Fe<sup>2+</sup> and Fe<sup>3+</sup>, while in the later one half of the voids is empty. Oxide-phosphates like  $\square_3$ Ti<sup>IV</sup><sub>5</sub>O<sub>4</sub>(PO<sub>4</sub>)<sub>4</sub> [13],  $\square_2$ Ti<sup>III,IV</sup><sub>4</sub>O<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub> [14],  $\square_2$ V<sup>III,IV</sup><sub>4</sub>O<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub> [15], and  $\square$ M<sup>II</sup>V<sup>IV</sup><sub>2</sub>O<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub> (M = Co, Ni, Cu) [16] belong to this structure family with the later series showing significant activity for the selective oxidation of *n*-butane [17]. In an attempt to synthesize a phosphate containing the transition metal in a rather high oxidation state we recently obtained **rhodium(VII)-oxidephosphate RePO<sub>6</sub>** [18]. Its crystal structure is closely related to the ReO<sub>3</sub> structure type, despite the presence of perhenyl cations ReO<sub>2</sub><sup>3+</sup>,  $\angle(O,Re,O) \approx 100^\circ$ , and phosphate tetrahedra as building units.

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**Keywords:** phosphates, catalysts, solid-state batteries

## FA2-MS14A-T03

**Linear and nonlinear optical properties of**

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Crystals of the family of tetragonal, non-centrosymmetric melilites with general composition  $M_2AT_2O_7$  (M = 8-fold coordinated metal cation; A, T = two different types of fourfold coordinated metal cations), have attracted interest as laser host crystals doped with trivalent lanthanide ion lasants already in the late 1960's. Research activities of the following 25 years resulted in a series of melilite crystals as laser

materials. Surprisingly, however, during the last decade nearly no interest in the melilites as optical materials is documented in literature. In a recent study of nonlinear-laser properties of  $\text{Ba}_2\text{MgGe}_2\text{O}_7$  [1] we found that germanate crystals with non-centrosymmetric melilite-type structure can manifest numerous attractive  $\chi^{(2)}$ - and  $\chi^{(3)}$ -interactions with good prospects of their use in experiments of modern laser physics and nonlinear optics. In the present contribution we summarize the results of our investigations of linear optical properties and of stimulated Raman scattering (SRS) of further germanates  $\text{Ba}_2\text{ZnGe}_2\text{O}_7$ ,  $\text{Sr}_2\text{MgGe}_2\text{O}_7$  and  $\text{Sr}_2\text{ZnGe}_2\text{O}_7$ , which all possess an unmodulated melilite-type structure. All four melilite crystals allow the generation of a lasing comb of approximately one octave bandwidth on pumping at  $\lambda_{p1} = 1.06415 \mu\text{m}$ , arising from a SRS-promoting vibration mode at  $\sim 770 - 780 \text{ cm}^{-1}$ , which corresponds to the symmetrical stretching mode  $\nu_3(\text{GeO}_3)$  of the  $[\text{Ge}_2\text{O}_7]$  unit. In addition, for  $\text{Ba}_2\text{ZnGe}_2\text{O}_7$  a second mode,  $\delta_3(\text{GeO}_3)$ , acts as a further SRS-promoting mode. For all four investigated germanate melilites numerous rather efficient  $\chi^{(2)}$ -,  $\chi^{(3)}$ -, and cascaded  $\chi^{(3)} \leftrightarrow \chi^{(2)}$ - photon-photon and photon-phonon parametric interactions are observed. While these phenomena are quite similar for the four germanate melilites their  $\chi^{(1)}$ -based properties (i.e. refractive indices and their dispersion) depend markedly on the chemical composition of the crystals. Going hand in hand with this, the phase matching possibilities for SHG (second harmonic generation) and SFG (sum frequency generation) processes vary within a range from SHG phase matching (SHG-pm) in the visible range ( $\text{Ba}_2\text{MgGe}_2\text{O}_7$ ) to SHG-pm in near IR ( $\text{Sr}_2\text{MgGe}_2\text{O}_7$  and  $\text{Ba}_2\text{ZnGe}_2\text{O}_7$ ) to no possibility for SHG-pm for  $\text{Sr}_2\text{ZnGe}_2\text{O}_7$ . The latter crystal, however, is characterized by an iso-index point [2-4]. The diversity of optical properties of the germanate melilites, together with their nonlinear optical manifestations classifies this crystal family as an attractive group of optical materials.

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**Keywords:** melilites, linear optical properties, nonlinear optics

#### FA2-MS14A-T04

**$\text{Li}_x\text{FeO}_2$  as battery cathode material:  $\text{Li}^+$ /vacancy patterns and reaction energies.** Michele Catti, Mercedes Montero-Campillo. *Dept. of Materials Science, University of Milano Bicocca, Italy.*  
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More environment-friendly and less expensive cathode materials have been extensively sought to replace  $\text{LiCoO}_2$  in lithium batteries. An attractive candidate is  $\text{LiFeO}_2$ , showing a complex polymorphism; some of its phases were considered in the past as active electrochemical materials [1,2]. We have undertaken a combined crystallographic (neutron diffraction) and theoretical (ab initio simulations) study of this system, to elucidate some aspects left open by electrochemical measurements. Preliminary results obtained on the  $\beta'$

(monoclinic) and  $\gamma$  (tetragonal) phases, by neutron diffraction [3] and computational [4] methods, showed that the order-disorder of Li/Fe distribution plays an essential role in determining the mobility of  $\text{Li}^+$  ion in the host framework. Now the hollandite-type (tetragonal) and orthorhombic (o- $\text{LiMnO}_2$ -type) polymorphs of  $\text{LiFeO}_2$  were examined. In particular, the latter phase was shown by electrochemical measurements to actually transform into  $\text{LiFe}_5\text{O}_8$  spinel after few cycles of charge/discharge [2], yet preserving the electrode activity, but with no clear indications of the actual chemical and physical processes therein occurring. First-principles quantum-mechanical simulations (CRYSTAL code, all-electron basis set, hybrid DFT-HF functional) were performed to address two points: (i) the structural changes and energy barriers characterizing the  $\text{Li}^+$  ion transfer, and (ii) the actual charge/discharge reactions taking place in the electrode. Several kinds of superstructures and  $\text{Li}^+$ /vacancy patterns were devised for  $\text{Li}_{1-x}\text{FeO}_2$  ( $0 \leq x \leq 0.5$ ) and  $\text{Li}_{1+x}\text{Fe}_5\text{O}_8$  ( $0 \leq x \leq 2$ ), in order to properly account for vacancy formation and ion mobility during the lithium intercalation-deintercalation processes. The corresponding structures were fully relaxed and their energies were calculated, allowing us to determine the electrochemical potentials for a number of possible cathode reactions. As a result, the processes  $\text{LiFeO}_2 \rightarrow \text{Li}_{1-x}\text{FeO}_2 + x\text{Li}$ ,  $5\text{Li}_{1-x}\text{FeO}_2 + 5x\text{Li} \rightarrow \text{LiFe}_5\text{O}_8 + 2\text{Li}_2\text{O}$ , and  $\text{LiFe}_5\text{O}_8 + x\text{Li} \leftrightarrow \text{Li}_{1+x}\text{Fe}_5\text{O}_8$  are proposed as good candidates to explain the experimental charge/discharge voltage-capacity curves [2]. In the last reaction, both Li and Fe atoms prove to move to octahedral sites on intercalation, changing spinel into a rocksalt superstructure. Thus, the evolution of X-ray powder pattern on cycling is accounted for satisfactorily by simulations based on the least-energy theoretical structures involved in the above series of reactions. Further, pathways of  $\text{Li}^+$  ion mobility within the host frameworks are determined, also providing the corresponding activation barriers.

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#### FA2-MS14A-T05

**Titanium Phosphate Hybrid Materials.** S. García-Granda. *Physical and Analytical Chemistry Department, University Oviedo, 33006 Oviedo, Spain.*  
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Metal salts of phosphoric acid have been known for over a century. In 1964, was obtained the first crystalline such compound,  $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ , which allowed a better understanding of their layered structure and chemical reactivity. Although only two crystalline forms of layered titanium phosphates are known,  $\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\gamma\text{-Ti}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ , many derivatives have been reported, including partially and completely substituted ion-exchanged forms and intercalation compounds. Surprisingly, the  $\gamma$ -layered titanium phosphate is less studied than the  $\alpha$ -phase, even though the  $\gamma$ -layers are more rigid, thicker, acidic and amenable to intercalation processes. Now, we revise the structural and thermal data of the  $\gamma$ -titanium phosphate, using