

FA2-MS14A-T01

Double perovskites with broken corner-sharing connectivity of the octahedral framework. Artem Abakumov^{a,c}, Graham King^b, Patrick Woodward^b,Evgeny Antipov^c. ^aEMAT, University of Antwerp, Belgium. ^bDepartment of Chemistry, Ohio State University, USA. ^cDepartment of Chemistry, Moscow State University, Russia.E-mail: artem.abakumov@ua.ac.be

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'X₆ 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'X₆ 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 K₃AlF₆ [1, 2] and Sr₃WO₆ structures will be presented; possible octahedral rotation modes and the stability criteria for such structures will be discussed.

[1] Abakumov A. M. et al., *Inorg. Chem.* 2009, 48, 9336. [2] Abakumov A. M. et al., *J. Solid State Chem.* 2006, 179, 421.

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

Inst. of Inorg. Chemistry, University of Bonn, Germany.

E-mail: rglaum@uni-bonn.de

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 Fe₉O₈(PO₄) [1] are found at one end. Two-dimensional phosphate nets, as in ultraphosphates like CuP₄O₁₁ [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_n] 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^{III}PO₄ [4], Cr^{II}₃(PO₄)₂ [5], Cr^{II}₂P₂O₇ [6])

Cathode materials for lithium ion batteries like phosphates **LiMPO₄** of the olivine structure family are characterized by a kinetically very stable "covalent" metal-phosphate network and high Li⁺ ion mobility [7]. Thus, rather high oxidation states like Co³⁺, which are thermodynamically unstable in phosphates, can be accessed by topotactic delithiation at rather low temperatures.

Gold(III) phosphate AuPO₄ (PdSO₄ structure type [8]) represents the first example of an insoluble compound with a crystal structure built by square-planar [M^{III}O₄] and tetrahedral [X^VO₄] units [9]. The crystal structure of Hg[Pd(PO₄)₂] [10] might be regarded as filled AuPO₄ structure type and nourishes the hope that metastable polymorphs of AuPO₄ with open framework structures might be accessible.

Anhydrous oxide-phosphates of the **Lipscombite/Lazulite structure family** are ranging in composition from α/β -Fe₂O(PO₄) [11] to ϵ -VOPO₄ [12]. In the former, all octahedral voids are occupied by Fe²⁺ and Fe³⁺, while in the later one half of the voids is empty. Oxide-phosphates like \square_3 Ti^{IV}₅O₄(PO₄)₄ [13], \square_2 Ti^{III,IV}₄O₃(PO₄)₃ [14], \square_2 V^{III,IV}₄O₃(PO₄)₃ [15], and \square M^{II}V^{IV}₂O₂(PO₄)₂ (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 RePO₆** [18]. Its crystal structure is closely related to the ReO₃ structure type, despite the presence of perhenyl cations ReO₂³⁺, $\angle(O,Re,O) \approx 100^\circ$, and phosphate tetrahedra as building units.

[1] Venturini, G. et al., *J. Solid State Chem.* 1984, 53, 1. [2] Glaum, R. et al., *Z. Anorg. Allg. Chem.* 1996, 622, 1839. [3] Glaum, R., *Thesis of Habilitation*, Univ. of Gießen, 1999. [4] Glaum, R. et al., *J. Solid State Chem.* 1996, 126, 15. [5] Glaum, R., Schmidt, A., *Z. Anorg. Allg. Chem.* 1997, 623, 1672. [6] Palatinus, L. et al., *Acta Crystallogr.* 2006, B62, 556. [7] Ehrenberg, H. et al., *Solid State Sciences* 2009, 11, 18. [8] Dahmen, T. et al., *J. Alloys Compd.* 1994, 216, 11. [9] Panagiotidis, K., *Ph. D. thesis*, Univ. Bonn, 2009. [10] Panagiotidis, K. et al., *Z. Anorg. Allg. Chem.* 2009, 635, 1969. [11] Elkaim, E. et al., *Acta Crystallogr.* 1996, B52, 428. [12] Girgsdies, F. et al., *Solid State Sciences* 2006, 8, 807. [13] Reinauer, F., Glaum, R., *Acta Crystallogr.* 1998, B54, 722. [14] Schoeneborn, M. et al., *J. Solid State Chem.* 2008, 181, 1367. [15] Benser, E. et al., *Chem. Mater.* 2007, 19, 4341. [16] Benser, E. et al., *Z. Anorg. Allg. Chem.* 2008, 634, 1677. [17] Glaum, R. et al., *Chem. Ing. Tech.* 2007, 79, 843. [18] Islam, S., *planned Ph. D. thesis*, Univ. of Bonn.

Keywords: phosphates, catalysts, solid-state batteries

FA2-MS14A-T03

Linear and nonlinear optical properties of germanate melilites. P. Becker^a, A.A. Kaminski^b, H. Rhee^c, H.J. Eichler^c, J. Liebertz^a, L. Bohaty^a. ^aInstitute of Crystallography, University of Cologne, Germany.^bInstitute of Crystallography, Russian Academy of Sciences, Moscow, Russia. ^cInstitute of Optics and Atomic Physics, Technical University Berlin, Germany.E-mail: petra.becker@uni-koeln.de

Crystals of the family of tetragonal, non-centrosymmetric melilites with general composition M₂AT₂O₇ (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