



Upon complex thermolysis in hydrogen the nanoalloy  $\text{Pd}_{0.5}\text{Rh}_{0.5}$  is formed ( $Fm\text{-}3m$  space group,  $a = 3.847 \text{ \AA}$ ). The thermolysis final temperature is  $400 \text{ }^\circ\text{C}$ , the average particle size is  $20 \text{ nm}$ .

The work has been supported by RFBR Grant 08-03-00603, Presidium SB RAS interdisciplinary project No 112 and State contract № P960 of Federal target program «Scientific, Research And Teaching Specialists In Russia» 2009–2013.

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**Keywords:** crystal structure analysis, X-ray phase determination, thermal decomposition.

#### FA2-MS16-P53

**High resolution X-ray diffraction experiments for selected minerals.** Marcin Stachowicz<sup>a</sup>, Maura Malinska<sup>a</sup>, Jan Parafiniuk<sup>b</sup> Krzysztof Woźniak<sup>a</sup>.

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Jarosite is used as a by-product of the metal-processing industry as well as a common supergene mineral in ore deposits, and is associated with acid-mine waste. Jarosite is thought to exist on Mars, and its presence suggests that water existed on Mars in the past [1]. Celestine is the most abundant strontium mineral and is the principal commercial source of strontium [2].

The high resolution X-ray diffraction experiments have been carried out for series of natural minerals. Natrojarosite  $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$  had been mined in Greece and celestine  $\text{SrSO}_4$  in Poland. These compounds crystallize in the trigonal R-3m and orthorhombic Pnma space groups, respectively.

The multipole model within the Hansen-Coppens formalism [3] is applied for crystals containing disorder and heavy atoms. In American Mineralogist Crystal Structure Database are four structures of Celestine [2,4-6] all ordered, however fitting of the multipole models of electron density leads to identification of small degree of disorder. Several multipole model refinement strategies have been applied and compared to find the most suitable one. Topological analysis of electron densities estimated from multipole models gives opportunity for better understanding intermolecular interactions and bonding properties in these minerals.

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**Keywords:** X-ray crystallography of minerals, charge density inorganic materials

#### FA2-MS16-P54

**Structural investigations of  $\text{Li}_3\text{Ti}(\text{MoO}_4)_3$ .** A. Thomas<sup>a</sup>, D. Mikhailova<sup>a,b</sup>, H. Ehrenberg<sup>a</sup>

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Complex molybdates with 3d transition metals crystallizing in a NASICON-type structure are promising materials for Li-storage during Li-insertion and deinsertion. Recently, a new molybdate with V(III),  $\text{Li}_3\text{V}(\text{MoO}_4)_3$ , was prepared and characterized. It was shown that Li-ions can be reversibly intercalated and deinserted with formation of  $\text{Li}_2\text{V}(\text{MoO}_4)_3$  and  $\text{Li}_4\text{V}(\text{MoO}_4)_3$  [1]. In the related system Li-Ti-Mo-O, only the composition  $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$  with Ti(IV) and the same crystal structure type is known [2]. There are no examples in the literature for the coexistence of molybdenum(VI) and titanium(III) in one phase. Every stable product which contains titanium and molybdenum was synthesized from titanium(IV) and molybdenum(IV/VI) compositions, for example  $(\text{Ti}_x\text{Mo}_{1-x})_5\text{O}_{14}$  [3] and  $\text{TiMo}_2\text{O}_8$  [4]. If titanium (III) and molybdenum(IV) were used as educts, molybdenum(IV) was reduced to metal and titanium(III) was oxidized to titanium(IV) [5].

A new phase with the composition  $\text{Li}_3\text{Ti}(\text{MoO}_4)_3$  was synthesized by solid state reaction. It crystallizes in the space group *Pnma* and is isostructural to  $\text{Li}_3\text{V}(\text{MoO}_4)_3$ . Similar electrochemical properties as for  $\text{Li}_3\text{V}(\text{MoO}_4)_3$  are expected [1]. The material shows the same plateau at ca.  $1.8 \text{ V}$  during galvanostatic cycling against a Li-anode, which indicates the same two-phase mechanism during first Li-insertion. The similarity of  $\text{Li}^+$  and  $\text{Ti}^{3+}$  radii for octahedral oxygen coordination leads to mixed cation occupancy in the structure, which can be varied by different synthesis conditions. A difference in the lattice parameters for two samples, prepared at different temperatures, between  $a = 5.05876(8) \text{ \AA}$ ,  $b = 10.4833(1) \text{ \AA}$  and  $c = 17.5653(2) \text{ \AA}$  to  $a = 5.0715(1) \text{ \AA}$ ,  $b = 10.5096(2) \text{ \AA}$  and  $c = 17.6050(3) \text{ \AA}$  confirms this assumption. In comparison the lattice parameters of  $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$  are:  $a = 5.0467(12)$ ,  $b = 10.454(3)$  and  $c = 17.538(4)$  [2].

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**Keywords:** NASICON-type structure, Li-insertion, cation mixed occupancy

#### FA2-MS16-P55

**Synthesis and structural studies of ammonium-cobalt-nickel phosphates,  $\text{NH}_4[\text{Co}_{1-x}\text{Ni}_x\text{PO}_4]\cdot\text{H}_2\text{O}$ .**

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Ammonium-metal(II) phosphates of general formula  $\text{NH}_4\text{M}^{\text{II}}\text{PO}_4 \cdot \text{H}_2\text{O}$  were first described in 1864 by Debray.<sup>1</sup> These compounds have been used as pigments for protective paint finishes on metal and as fire retardants in paints and plastics, and they can be also applied as catalyst, fertilizers and magnetic devices.

The first crystal structure for a member of this family,  $\text{NH}_4\text{CoPO}_4 \cdot \text{H}_2\text{O}$ , was determined in 1968 by Tranqui *et al.* using powder X-ray diffraction.<sup>2</sup> In 1995, using neutron powder diffraction techniques, Carling *et al.* determined the crystal structures of  $\text{ND}_4\text{M}^{\text{II}}\text{PO}_4 \cdot \text{D}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mn, Fe, Co, Ni}$ ) compounds.<sup>3</sup> In 1999, Yakubovich *et al.* have contributed with the first structure, for  $\text{NH}_4\text{CoPO}_4 \cdot \text{H}_2\text{O}$ , obtained by single-crystal (X-ray diffraction) data.<sup>4</sup> Apparently, all these layered compounds crystallize in the orthorhombic space group  $Pmn2_1$ .

In this communication, we report the single crystal X-ray data obtained for a family of ammonium-cobalt-nickel phosphates,  $\text{NH}_4[\text{Co}_{1-x}\text{Ni}_x\text{PO}_4] \cdot \text{H}_2\text{O}$  ( $x = 0.00, 0.20, 0.35, 0.50, 0.65, 0.80, 1.00$ ). In this series, although all crystals are orthorhombic, the space group is appears as a function of the composition, showing how the single-crystal diffraction data is capable to manifest structural subtleties that had not been described before for this group of materials.

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**Keywords: phosphate, ammonium, nickel, cobalt**

#### FA2-MS16-P56

**Phase stability of  $\text{YBaCo}_4\text{O}_7$  at temperature range 600–1000 °C** Markus Valkeapää, Jenni Jäämaa, Maarit Karppinen *Department of Chemistry, Aalto University School of Science and Technology, Espoo, Finland*  
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In addition to the reversible capture and release of oxygen in  $\text{YBaCo}_4\text{O}_7$  at 200–400 °C, changes in the samples' oxygen content also take place at temperatures above 700 °C [1]. The latter are only partially reversible and are due to the decomposition and re-formation of the  $\text{YBaCo}_4\text{O}_7$  phase. Because  $\text{YBaCo}_4\text{O}_7$  is a candidate for oxygen separation [2] and SOFC cathode [3] materials, it is important to characterize in detail its behaviour at different temperatures. In the present work, heat-treatment experiments in a box furnace for two identical batches of  $\text{YBaCo}_4\text{O}_7$  powders were carried out. Furnace temperature was increased (decreased) stepwise from 600 °C to 1000 °C (1000 °C to 600 °C). After a one day dwell at each temperature a sample was taken out and characterized with XRPD. This procedure gave us thirty-one diffraction patterns from both batches, analysis of which reveals that  $\text{YBaCo}_4\text{O}_7$  behaves differently upon temperature increase and decrease. Between 600 and 920 °C, when temperature gradually increases,  $\text{BaCoO}_{3.5}$ , at the moment unidentified phase,  $\text{Co}_3\text{O}_4$ , and  $\text{Y}_{0.98}\text{CoO}_3$  are formed. Above 920 °C  $\text{YBaCo}_4\text{O}_7$  forms again. On the other hand, when  $\text{YBaCo}_4\text{O}_7$  is placed in a pre-heated furnace at 1000 °C, and temperature is gradually decreased, the phase decomposes at 840 °C with the following decomposition products:  $\text{Y}_{0.98}\text{CoO}_3$ ,  $\text{BaCoO}_{3.5}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{YBaCo}_2\text{O}_5$ ,  $\text{Y}_2\text{O}_3$  and  $\text{YBa}_2\text{Co}_3\text{O}_{9.5}$ . We shall present these findings in detail and discuss them in relation to other

observed [4], and calculated [5] phase stabilities in the  $\text{BaO-CoO-Y}_2\text{O}_3$  system.

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**Keywords: complex oxides, oxide phase diagrams, absorption**

#### FA2-MS16-P57

**Lattice dynamics of rutile and anatase: implications for phase stability.** Vojtěch Vlček, Gerd Steinle-Neumann, Eva Holbig. *Bayerisches Geoinstitut, University of Bayreuth, Germany*  
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Titanium dioxide is technologically important material widely used as pigment for its high refractive index and semiconductor with wide band gap. As an important chemical substance titanium dioxide is a subject of many studies and understanding of its behavior is crucial for improvement of its use in material science and physics.

Rutile, anatase and brookite are the most stable polymorphs of  $\text{TiO}_2$  that can be synthesized at ambient conditions and experimental results [1] show rutile structure as the stable one. Static *ab-initio* all-electron calculations using projector augmented-wave method were applied to reproduce the experimental results; however, they predict anatase to be stable over rutile. As the difference between rutile and anatase is very small, the phonon contribution to the lattice energy plays therefore very important role and is a main subject of this study.

The linear response calculations were done in the harmonic approximation using *abinit* software. The dielectric constant tensor and Born effective charges were evaluated and are in good agreement with previous theoretical studies even though any additional correction of the electronic band gap was not used. In comparison with the other published data our results predict smaller differences between rutile and anatase.

By analyzing the displacement eigenvectors we were able to make an assignment of the phonon modes. Compared to other results only slight shifts are observed for rutile. Moreover the eigenvectors revealed ambiguous character of high energy vibrations; especially the  $E_u$  modes exhibit mixed character and their distinction may not be reasonable. The rutile structure also shows a very small stability field with respect to volume of the unit-cell and *soft modes* appear for very small volume change.

From the phonon dispersion curves the thermodynamic properties were calculated. For temperatures close to 0 K the total energies of rutile and anatase structure are similar; however, for increased temperatures anatase is energetically favored.

The results display very different lattice dynamics of these polymorphs and revealed possible anharmonic behavior of rutile even at very low temperatures that most probably influences its stability significantly.

[1] Ranade M. R., Navrotsky A., Zhang H. Z., Banfield J. F., Elder S.