Upon complex thermolysis in hydrogen the nanoscale
Pd$_2$Rh$_5$ is formed (f/m-3m space group, α = 3.847 Å). The
thermolysis final temperature is 400 °C, the average particle
size is 20 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.

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

FA2-MS16-P53

High resolution X-ray diffraction experiments for
selected minerals. Marcin Stachowiczc, Maura
Malinskaa, Jan Parafiniukb

Faculty of Chemistry, University of Warsaw. bFaculty
of Geology, University of Warsaw.
E-mail: marcin.stachowicz1@gmail.com

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
NaFe$_5$(SO$_4$)$_6$(OH)$_8$ has been mined in Greece and celestine
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
there 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.


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

FA2-MS16-P54

Structural investigations of Li$_3$Ti(MoO$_4$)$_3$. A.
Thomas$^a$, D. Mikhailova$^{a,b}$, H. Ehrenberg$^{b}$

$^a$Institute for Complex Materials, IFW Dresden,
Germany, $^b$Institut für Materialwissenschaft, Technische
Universität Darmstadt, Germany.
Email: a.thomas@ifw-dresden.de

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), Li$_3$V(MoO$_4$)$_3$, was prepared and characterized. It was shown that Li-ions can be reversibly
intercalated and deinserted with formation of Li$_2$V(MoO$_4$)$_3$
and Li$_4$V(MoO$_4$)$_3$ [1]. In the related system Li-Ti-Mo-O, only the
composition Li$_3$Ti$_{0.5m}$(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(IV) and
titanium(III) in one phase. Every stable product which contains
titanium and molybdenum was synthesized from titanium(IV) and
molybdenum(IV) [5]. 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 Li$_3$Ti(MoO$_4$)$_3$ was
synthesized by solid state reaction. It crystallizes in the space

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

FA2-MS16-P55

Synthesis and structural studies of ammonium-
cobalt-nickel phosphates, NH$_4$[Co$_{0.8}$Ni$_{0.2}$P$_2$]H$_2$O.
Laura Torre-Fernández, Camino Trobajo, José R.
García, Santiago García-Granda. Departamentos de
Química Física y Analítica y Química Orgánica e
Inorgánica. Universidad de Oviedo, Spain.

E-mail: torrelaura@uniovi.es
Using powder X-ray diffraction. In 1995, using neutron powder diffraction techniques, Carling et al. determined the crystal structures of \( \text{NH}_4\text{MIIPO}_4\cdot\text{D}_2\text{O} \) (MII = Mn, Fe, Co, Ni) compounds. 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. Apparently, all these layered compounds crystallize in the orthorhombic space group \( \text{Pnnm} \).

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 appears as a function of the composition, showing how the single-crystal diffraction data is capable to manifest structural subleties that had not been described before for this group of materials.


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

E-mail: markus.valkeapaa@tkk.fi

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, \( \text{BaCo}_3\text{O}_5 \), at the moment unidentified phase, \( \text{Co}_3\text{O}_4 \), and \( \text{Y}_0\text{.9Co}_0\text{.1O}_3 \) 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: \( \text{Y}_0\text{.9Co}_0\text{.1O}_3, \text{BaCo}_3\text{O}_5, \text{Co}_3\text{O}_4, \text{YBaCo}_2\text{O}_5, \text{Y}_3\text{O}_7 \) and \( \text{YBa}_2\text{Co}_3\text{O}_6 \). 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.


Keywords: complex oxides, oxide phase diagrams, absorption

FA2-MS16-P57

Lattice dynamics of rutile and anatase: implications for phase stability, Vojtech Vlcek, Gerd Steinle-Neumann, Eva Holbig, Bayerisches Geoinstitut, University of Bayreuth, Germany

E-mail: vojtech.vlcek@uni-bayreuth.de

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 TiO2 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 \( E_g \) 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.