Ammonium-metal(II) phosphates of general formula $NH_4M^{II}PO_4·H_2O$ were first described in 1864 by Debray.[1] 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, $NH_4CoPO_4·H_2O$, was determined in 1968 by Tranqui *et al.* using powder X-ray diffraction.[2] In 1995, using neutron powder diffraction techniques, Carling *et al.* determined the crystal structures of $ND_4M^{II}PO_4·D_2O$ (M^{II} = Mn, Fe, Co, Ni) compounds.[3] In 1999, Yakubovich *et al.* have contributed with the first structure, for $NH_4CoPO_4·H_2O$, obtained by single-crystal (X-ray diffraction) data.[4] 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, $NH_4[Co_{1-x}Ni_xPO_4]·H_2O$ (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 $YBaCo_4O_7$ at temperature range 600–1000 °C <u>Markus Valkeapää</u>, 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 $YBaCo_4O_7$ 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 $YBaCo_4O_7$ phase. Because $YBaCo_4O_7$ 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 $YBaCo_4O_7$ 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 $YBaCo_4O_7$ behaves differently upon temperature increase and decrease. Between 600 and 920 °C, when temperature gradually increases, $BaCoO_{3-\delta}$, at the moment unidentified phase, Co_3O_4, and $Y_{0.98}CoO_3$ are formed. Above 920 °C $YBaCo_4O_7$ forms again. On the other hand, when $YBaCo_4O_7$ 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: $Y_{0.98}CoO_3$, $BaCoO_{3-\delta}$, Co_3O_4, $YBaCo_2O_5$, Y_2O_3 and $YBa_2Co_3O_{9-\delta}$. We shall present these findings in detail and discuss them in relation to other

observed [4], and calculated [5] phase stabilities in the BaO–CoO–Y_2O_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. <u>Vojtěch Vlček</u>, 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 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.

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FA2-MS16-P58

Crystal structures of NaTiO[AsO$_4$], NaTi$_2$[AsO$_4$]$_3$, NaKAl$_2$O[AsO$_4$]$_2$ and Na$_2$KAl$_3$[AsO$_4$]$_4$. <u>Hamdi Ben Yahia,</u> Ute Ch. Rodewald, Rainer Pöttgen. *Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany.*
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The title compounds with structures isotopic to the α-CaTiO[SiO$_4$] [1], Nasicon [2], K$_2$Fe$_2$O[AsO$_4$]$_2$ [3] and K$_3$Fe$_3$[AsO$_4$]$_4$ [4] types have been synthesised by a solid state reaction route using a salt flux. The crystal structures were determined using single crystal data. The compound NaTiO[AsO$_4$] crystallises in space group *P*2$_1$/*c*, Z = 4 with unit cell parameters: *a* = 6.7170(9), *b* = 8.7707(12), *c* = 7.2447(10) Å, *β* = 114.77(1) °, whereas NaTi$_2$[AsO$_4$]$_3$ crystallises in space group *R*$\bar{3}$*c*, Z = 6 with unit cell parameters: *a* = 8.8057(5), *c* = 22.2406(15) Å. The NaKAl$_2$O[AsO$_4$]$_2$ and Na$_2$KAl$_3$[AsO$_4$]$_4$ crystallise with the orthorhombic unit cell parameters *a* = 8.2368(6), *b* = 5.5228(3), *c* = 17.0160(13) Å, S.G. *Pnma*, Z = 4 and *a* = 10.5049(9), *b* = 20.4816(12), *c* = 6.3574(6) Å, S.G. *Cmce*, Z = 4, respectively. NaKAl$_2$O[AsO$_4$]$_2$ and Na$_2$KAl$_3$[AsO$_4$]$_4$ are build up of [Al$_2$As$_2$O$_9$]$^{2-}$ and [Al$_3$As$_4$O$_{16}$]$^{3-}$ layers, respectively. In-between these layers are located the seven or eight coordinated sodium and potassium cations. The structure of NaTiO[AsO$_4$] and NaTi$_2$[AsO$_4$]$_3$ consist of a three dimensional framework of corner-sharing AsO$_4$ tetrahedra and TiO$_6$ octahedra. The negatively charged framworks [TiAsO$_5$] and [Ti$_2$As$_3$O$_{12}$] give rise to different interstices in which are located the seven and six coordinated sodium atoms, respectively.

NaKAl$_2$O[AsO$_4$]$_2$ **NaTiO[AsO$_4$]**

Na$_2$KAl$_3$[AsO$_4$]$_4$ **NaTi$_2$[AsO$_4$]$_3$**
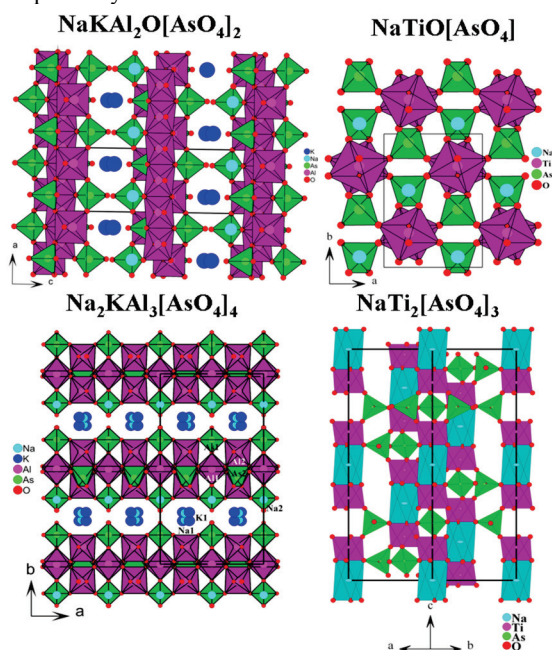
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FA2-MS16-P59

Intermediates in the course of the synthesis of tin(II) bromide, SnBr$_2$. <u>Fei Ye</u>[a], Hans Reuter[a]. *[a]Institute of Chemistry, University of Osnabrück, Germany.*
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Since more than a century, tin(II) bromide, SnBr$_2$, is prepared by heating metallic tin with hydrobromic acid at reflux [1]. It is also known since that time that this reaction proceeds via different solid intermediates which are described to be hydrates of tin(II) bromide or adducts of tin(II) bromide and hydrogen bromide or combinations of hydrates and adducts [2]. In contrast to the importance of this reaction and the long time this reaction is applied there is only little known about the nature and structures of these intermediates. Only *Andersson* published in the early 70th of the last century some preliminary structural results on compounds which he assigned sum formula like 2SnBr$_2$ · H$_2$O [3], 3SnBr$_2$ · H$_2$O [4] and 6SnBr$_2$ · 5H$_2$O [5]. Because no atomic positions were given, we have started to reinvestigate this reaction and its intermediates to close this gap in the chemistry of bivalent tin. Here we present our results on the compound with composition 5SnBr$_2$ · 3H$_2$O · HBr.
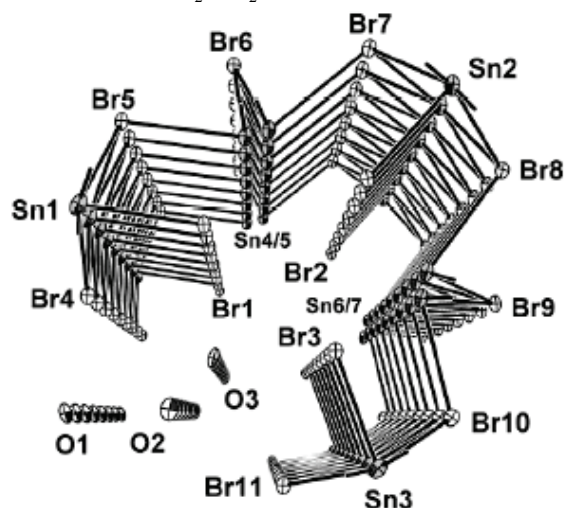
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