

FA2-MS16-P32

3-D transition metal phosphate zeotypes: piezochromicity, polymorphism and magnetism. Paul F. Henry^a, Simon A.J. Kimber^{a,b}, Dimitri N. Argyriou^a.
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Materials with both magnetic and electric orders such as the magnetoelectric (ME) multiferroics have received significant attention in recent years. [1-2] The coupling of such behaviours should give rise to technological uses but also lead to rich physics. Often, ferroelectric and magnetic phases have very different ordering temperatures, which suggest that the processes are driven by different microscopic interactions, but for a significant number of materials these coincide and ferroelectricity can be generated by long-range order. Phosphate based materials have been discovered with applications across the whole range of solid state chemistry and physics from battery materials to solid oxide fuel cells and proton conductors. The lithium orthophosphates (LO) LiMPO₄ with M = Mn, Fe, Co and Ni are a prototypical iso-structural group of antiferromagnets (AFs) that show ME below their Néel temperatures. [3-7] Here we present initial work on materials of the type ABPO₄ with A = Rb and Cs and B = Co, Ni and Cu that show novel frameworks based on structures intermediate between that of zeolite ABW and the natural mineral olivine that have the potential to yield interesting properties. In the Cu system, polymorphic piezo-chromic behaviour is observed at RT driven by coordination changes in the Cu polyhedra. The structure can be locked into one of the polymorphs by doping with Ni and the dimensionality of the structure can be tuned by substitution of the A site cation. [8]

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Keywords: powder diffraction, phosphates, phase transitions and structure.

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The crystal structure of magnesianeptunite in the context of neptunite crystal chemistry. Oxana Karimova^a, Olga Yakubovich^b, Alexander Zadorov^c, Victor Gazeev^a, Nikolay Pertsev^a, Anna Ivanova^d.
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The mineral neptunite represents the silicate of titanium and is usually described with an idealized formula LiNa₂K(Fe,Mg,Mn)₂Ti₂O₂[Si₄O₁₀]₂. Its crystal structure has been investigated before by different authors [1-4] and different techniques. For the moment, two structural models of the mineral exist: one is centrosymmetric (space group C2/c) and the second is acentric (space group Cc). A new Mg-rich variety of the mineral was found in changed sandstone

xenolite, dividing larnite skarn from ignimbrite, at Verhnechegemskaya Caldera, Lakargi Mountain locality (North Caucase, Russia). It is formed over ilmenite and accompanied by later less magnesium neptunite. The crystal structure of magnesianeptunite was determined by single crystal X-ray diffraction: $a = 16.3271(7)$, $b = 12.4788(4)$, $c = 9.9666(4)$ Å, $\beta = 115.651(1)^\circ$, $V = 1830.5(1)$ Å³ at 293 K, and refined till $wR_2 = 0.0615$, $R = 0.0251$ in the framework of the space group C2/c. The found formula corresponds to LiK_{0.6}Na_{2.4}(Fe_{0.5}Mg_{0.5})₂Ti₂O₂[Si₄O₁₀]₂, Z=4.

There are two nonequivalent octahedral positions for transition metals (and Mg) in the structure. The first type of octahedra are occupied by iron and magnesium, the second one contain titanium. An ordered distribution of Ti and Fe(Mg) atoms correlate with sizes of polyhedra. Thus, Ti octahedra are more distorted, Ti – O bond lengths change from 1.884(2) to 2.245(2) Å, while M – O distances in (Fe, Mg) polyhedra lie in the interval 1.962(2) – 2.180(2) Å. Alternating pairs of sharing edges Ti and (Fe, Mg) octahedra form columns that are elongated in [1-10] and [110] directions of the unit cell. SiO₄ tetrahedra share the part of oxygen vertices with a formation of an anionic paraframework. Alkaline cations Li⁺, Na⁺ and K⁺ are distributed in different positions and are surrounded by 6 (Li and Na) or 10 (K) oxygen atoms in the first coordination sphere. In addition to the high amount of magnesium, the new variety of mineral is enriched by sodium: 2.4 atoms per formula (apf) distributed among three different structural positions compared to the usual 2 apf. Accordingly, an amount of potassium is reduced: 0.6 apf against 1 apf found for another neptunites.

Crystal structure peculiarities of the neptunite are discussed in correlation with the chemical diversity of mineral varieties.

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Keywords: crystal structure, X-ray diffraction, magnesianeptunite.

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Structural Refinement of M₂Si₅N₈:Eu²⁺ (M=Ca, Sr, Ba) Phosphor for Light Emitting Diode Yong-Il Kim^a, Yun-Hee Lee^a, Kwon-Sang Ryu^a, Kwang Bok Kim^b. ^aKRISS, Yuseong, Daejeon, 305-600, South Korea. ^bKumho Electric, Inc. Gyeonggi, 445-812, South Korea.

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The chip based light emitting diodes (LEDs) as a new light source which have many advantages in energy efficiency, long life time, compactness and environmentally good features over conventional incandescent and fluorescent lamps. Among suitable phosphor materials to produce white light, red color-emitting nitride phosphor M₂Si₅N₈:Eu²⁺ (M=Ca, Sr, Ba) synthesized by a solid state reaction between metallic nitrides showed the emission peak around 650 nm under blue light (480 nm) excitation. The amount of Eu²⁺ ions occupying the crystal lattice in M₂Si₅N₈:Eu²⁺ (M=Ca, Sr, Ba) is closely related to the performance of phosphors such as decay time, color shift and concentration quenching. Hence, this work is focused on determining the site preference and the amount of Eu²⁺ ions in host lattice by means of the combined structural

refinement using X-ray/neutron powder diffraction and energy calculation using quantum mechanics. Among possible cation-disorder models, the model proposed by combined structural refinement in which Eu^{2+} ions occupy two different M sites was corroborated by geometry energy calculation using a first-principle based on the density-functional theory.

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Keywords: phosphor, structure refinement, X-ray neutron diffraction

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Synthesis of model Tantalum(V) complexes for the separation of Niobium and Tantalum. Renier Koen,

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The separation of niobium and tantalum is a complicated process, particularly due to their near identical chemical properties. Niobium(V) and tantalum(V) are both hard metal centres and the halido species are known to readily hydrolyse. Our approach was to synthesize a range of tantalum(V) complexes with a variety of oxygen and nitrogen donor mono-, bi- and tridentate ligands and to compare different aspects of its solid state properties and solution chemistry with similar niobium(V) complexes. Any differences in chemical and/or physical behaviour could potentially be applied to the separation of these two metals. Some of the techniques used to measure these different properties include high temperature sublimation studies, kinetic studies and structural characterization by means of multi nuclear NMR spectroscopy, UV-Vis and IR-spectroscopy [1]. Moreover, single crystal and powder X-ray diffraction were used extensively to evaluate the characteristics of a range of complexes, and the results of four structures containing mono-(halido and pseudo halido) and bidentate hard ligands (O,O and O,N- donor atoms will be presented and discussed [2].

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Keywords: tantalum, separation, sublimation

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Mixed Thio-oxomolybdates $A_2[\text{MoS}_x\text{O}_{4-x}]$ ($A = \text{NH}_4$, K, Rb, Cs; $x = 2, 3$): Synthesis, Structural Chemistry, Properties Anna J. Lehner, Korina Kraut, Caroline Röhr. *Institut für Anorganische und Analytische Chemie, University of Freiburg, Germany.*

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Mixed thio-oxoorthomolybdates(VI) were first synthesized in the 19th century [1]. They have been intensely investigated spectroscopically [2], while there are only basic structural studies of their NH_4^+ and alkali salts [3]. Here we present a detailed systematic examination of the crystal chemistry and

properties of these compounds following a similar approach as previously performed with Na and K thio-oxovanadates by our group [4]. By passing a flow of H_2S gas through basic aqueous solutions of NH_4 /alkali oxomolybdates, brightly colored solutions were obtained and crystalline samples of high purity could be prepared for the series of $A_2\text{Mo}[\text{S}_x\text{O}_{4-x}]$ ($A = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$; $x = 2, 3$). The structures displayed richer polymorphisms than previously assumed. They can be rationalized on the basis of packing and coordination considerations. Four structure types were observed: Whereas all compounds with anions $[\text{MoS}_2\text{O}_2]^{2-}$ form isotypic monoclinic structures $((\text{NH}_4)_2[\text{WS}_2\text{O}_2])$ type, $C2/c$, e.g. $\text{K}_2[\text{MoS}_2\text{O}_2]$: $a = 1122.98(2)$, $b = 707.41(10)$, $c = 970.50(2)$

pm , $\beta = 121.734(1)^\circ$, the K and Cs salts in addition also crystallize with different and novel structure types ($P2_1/c$ and $Pbcn$, respectively). The heavier alkali tri-thiomolybdates crystallize with the orthorhombic $\beta\text{-K}_2[\text{SO}_4]$ type ($Pnma$), which is also formed by the tetra-thiomolybdates. In accordance, a phase width up to the composition $\text{Cs}_2[\text{MoS}_3\text{O}_{0.7}]$ starting from $\text{Cs}_2[\text{MoS}_3\text{O}]$ ($a = 977.7(5)$, $b = 722.7(5)$, $c = 1218.0(8)$ pm) is observed. In all crystal structures the anions $[\text{MoS}_x\text{O}_{4-x}]^{2-}$ are ordered with the oxo ligands occupying sites that are four- to fivefold coordinated by cations and the thio ligands having coordination numbers from 6 to 7. The structural influences of the variation of O/S ratio and the counter ion for the series are discussed. The chemical bonding situation and structure is furthermore completed by the analysis of vibrational data including normal coordinate analysis and FP-LAPW band structure calculations.

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Structural conditionality of changes of physical properties in $\text{K}_3\text{H}(\text{SO}_4)_2$ crystals. I.P. Makarova,

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Structural studies are the central point at the ascertainment of well-formed relationships between chemical composition, atomic structures and physical properties of crystalline materials. To elucidate the nature of anomalies of physical properties with an increase in the temperature in crystals of $\text{K}_3\text{H}(\text{SO}_4)_2$, which belong to superprotonic family of $M_m\text{H}_n(\text{XO}_4)_{(m+n)/2}$ ($M = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$; $X = \text{S}, \text{Se}, \text{P}, \text{As}$), it was carried out the researches of dielectric and optical properties, X-ray structural analysis of single crystals and powder samples, researches of morphology and a chemical composition by means of scanning electronic microscopy and the energy dispersive X-ray spectroscopy.

X-ray diffraction studies of $\text{K}_3\text{H}(\text{SO}_4)_2$ crystals displayed a structural phase transition from the monoclinic phase $C2/c$ to