

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

FA2-MS16-P35

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

FA2-MS16-P36

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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Keywords: molybdates, structure-properties relationships, electronic structures

FA2-MS16-P37

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

the trigonal phase R-3m at a temperature ≈ 457 K [1], corresponding to behaviour of dielectric and optical properties. The trigonal phase exists in a very narrow temperature interval in comparison with isostructural $M_3H(XO_4)_2$ crystals [2]. The obtained structural data confirmed the previously proposed mechanism of conduction in crystals of this family: the appearance of a high protonic conductivity is associated with the formation of a qualitatively new system of hydrogen bonds - the dynamically disordered hydrogen bond network, in which both the proton positions in hydrogen bonds and the bond orientations are dynamically disordered. The network of hydrogen bonds thus formed enables protons to move over vacant crystallographically equivalent positions, which leads to anomalously high hydrogen diffusion coefficients and to superionic conductivity. Also it was received the information about solid state reactions (the crystalline state remains), occurring in investigated crystals with an increase in the temperature. The temperature increase above the trigonal phase leads to formation of K_2SO_4 phases in the samples under study. The heating and cooling of the samples lead to formation of $K_2S_2O_7$ phases also. It is necessary to notice, that according to the powder data there are absent diffraction peaks corresponding to $KHSO_4$ compound, which could be formed in $K_3H(SO_4)_2$ samples in the process of solid state reactions, as it is supposed under the literary data. The formation of a multiphase state is confirmed by X-ray diffraction data, scanning electronic microscopy and the energy dispersive X-ray spectroscopy. The study was supported by the Russian Foundation for Basic Research (№09-02-00577).

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Keywords: crystal and powder X-ray diffraction structure analysis, phase transitions and structure, superionic conductivity

FA2-MS16-P38

$Y_4H_8Si_3O_{16}$: A naturally occurring defect silicate of the KDP-structure type. Thomas Malcherek^a, Jochen Schlüter^a, Boriana Mihailova^a, Tomas A. Husdal^b.
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A new type of rare earth (RE) silicate with idealized composition $(Y, Ln)_4H_8Si_3O_{16}$ ($Ln = Gd, Tb, Dy, Ho, Er, Yb$) (YSO) has been identified in a granitic pegmatite of the Stetind quarry, Tysfjord, Northern Norway. The space group symmetry is $I-42d$ and the crystal structure closely corresponds to the KDP-structure type. KH_2PO_4 (KDP) is a well known ferroelectric [1], distinguished by the ordering of hydrogen bonds. Thus in the paraelectric phase of KDP, hydrogen is equally distributed across two equivalent positions along the hydrogen bond, while only one of these positions is occupied in the fully ordered ferroelectric state. In YSO a trivalent rare earth cation substitutes for the monovalent cation of KDP and Si^{4+} substitutes for P^{5+} . Provided the number of hydrogen atoms is constant, one positive charge has to be compensated, which is achieved by Si-vacancies in YSO. X-ray diffraction data has been collected on several single crystals of YSO. The structure refinements on average yield

Si-occupancies of $75 \pm 5\%$. The presence of heavy RE elements on the Y-site has been modelled using the Yb scattering factor curve, resulting in Yb/Y ratios of 1/4. Similar compositions are obtained by electron microprobe analysis, also indicating the presence of other heavy RE cations. Raman microspectroscopy performed on the crystals used for the X-ray structure analysis, confirms the presence of OH-stretching modes. The crystal chemistry of the new compound and possible similarities to KDP in terms of hydrogen bonding are discussed.

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Keywords: hydrogen bonding of minerals, rare-earth compounds, ferroelectrics and related materials

FA2-MS16-P39

Evolution of the Shape of Nanothin Selenium Crystals during their Growth in Amorphous Films. Malkov Andrey^b, Malkov Vyacheslav^a, Strekalovsky Victor^a, Malkov Oleg^b, Puchin Vladimir^c. ^a*Institute of High-Temperature Electrochemistry, Ural Division RAS,* ^b*"ROSNA" Scientific and Production Center,* ^c*Institute of Metal Physics, UD RAS, Ekaterinburg, Russia.*
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The method of transmission electron microscopy was used to study the evolution of a rotational distortion of the lattice and the shape of nanothin ($80 \div 100$ nm) crystals of hexagonal selenium growing in amorphous films at crystallization temperatures of $180 \div 120^\circ\text{C}$.

It was found that the lattice of nanothin selenium crystals growing in amorphous films at crystallization temperatures of $180 \div 150^\circ\text{C}$ undergoes a nonuniform elastic rotational distortion around the [001] direction ($180 \div 160^\circ\text{C}$) or in two mutually perpendicular directions, namely, around [001] and the perpendicular direction of the maximum growth rate (150°C). Nanothin selenium crystals growing in this range of crystallization temperatures have a rectilinear rhombic shape (Fig. 1a,b).

At crystallization temperatures of $140 \div 120^\circ\text{C}$ the lattice of nanothin selenium crystals undergoes a nonuniform elastoplastic rotational distortion around three mutually perpendicular directions [1]. In addition to the aforementioned directions, the lattice of nanothin selenium crystals undergoes a nonuniform rotational distortion around a direction, which is not in the film plane and is perpendicular to the first two directions. It is called an azimuthal distortion. The nanothin selenium crystals, which grow at crystallization temperatures of $140 \div 120^\circ\text{C}$, have a distorted curvilinear rhombic shape (Fig. 1c,d). The sign of distortion of the shape of a nanothin selenium crystal always coincides with the sign of the azimuthal distortion of its lattice (Fig. 1c,d). It can be concluded from this fact that the azimuthal distortion of the lattice of a nanothin selenium crystal determines the azimuthal distortion of its shape.

Fig. 1. Evolution of the shape of nanothin selenium crystals: rhomboid crystals of a rectilinear shape (a, b); nanothin crystals of a curvilinear shape (c, d), $\times 10\ 000$

A model for the evolution of the shape of nanothin selenium crystals has been proposed. This model is based on the assumption that the evolution of the real structure of nanothin