

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

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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