

MS17 P20

Structural aspects of solid state amorphization in $\text{Eu}_2(\text{MoO}_4)_3$ europium molybdate. *Elena Kudrenko¹, Ivan Shmyt'ko, Vitaly Sinizyn, Evgeny Ponyatovsky and Boris Red'kin, Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow district.*
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Keywords: rare-earth compounds, high-pressure amorphization, x-ray diffraction

The samples of $\text{Eu}_2(\text{MoO}_4)_3$ has been investigated by X-ray diffraction method. These samples have been subjected high pressure 9 GPa at room temperature. It was established that powder samples undergo at this pressure solid state amorphization. At consequent annealing with temperature increasing unusual sequence of phase states have been observed. Instead of expected "amorphous" $\rightarrow \alpha \rightarrow \beta$ sequence the "amorphous" $\rightarrow \beta \rightarrow \alpha \rightarrow \beta$ sequence come to pass.

The single crystalline samples in contrast to polycrystalline ones do not undergo solid state amorphization. In this case phase transition from tetragonal β -phase into a new tetragonal high-pressure phase take place. We have shown that in the case of incomplete phase transition " β - phase- high-pressure phase" two phase state has been characterized of existence of wide interphase boundaries. The parameters along the boundaries change continuously from one into other phase. In the case of complete phase transition into high-pressure tetragonal phase at subsequent annealing instead of narrow diffraction reflection halo-like reflections were observed. On the base of these results we have supposed that no amorphization in polycrystalline samples take place. The halo-like reflections in this case characterize the transitional state between high-pressure phase and β -phase, namely the diffraction from the set of transitional boundaries.

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3-D structural determination by powder diffraction on molybdopterin complex *Jey Jau Lee^{*a}, Hwo-Shuenn Sheu^a, Keng S. Liang^a, Baidyanath Ghosh^b and Parag Sinchan Roy^b* ^aNational Synchrotron Radiation Research Center Hsinchu 30076, Taiwan R.O.C. ^b. Department of Chemistry, University of North Bengal, Dist.- Darjeeling – 734013, India. E-mail:jjlee@nsrrc.org.tw

Keywords: molybdenum complexes, structure determination of coordination and pharmaceutical compounds, powder diffraction for unknown samples

The biological function of Molybdenum has been known to be contained in more than 30 distinct enzymes. The molybdenum-cofactor (Mo-co) consists of a mononuclear molybdenum ion coordinated by one or two molybdopterin ligands. Crystallographic results are very rare because of the crystal are very hard to grow up. The few results have demonstrated that the molybdopterin ligands are tricyclic and nonplanar, and that they coordinate the metal through their dithiolene sulfurs.

The molybdopterin ligand may participate in the various electron transfer reactions associated with the catalytic

mechanism of these proteins, as suggested by both oxidation state-dependent changes in the metal coordination environment and the molybdopterin structure, and by the interaction of the molybdopterin with other redox groups within Mo-co-containing enzymes. In here the 2-pivaloylamino-6-acetyl- isoxanthopterin (**1**, H_2L) has been reacted with $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ under suitable conditions in presence of cysteine and Ph_4PBr for synthesizing the new compound $(\text{Ph}_4\text{P})_2[\text{Mo}^{\text{IV}}(\text{L})(\text{cys})_2] \cdot 0.5\text{CH}_3\text{OH}$. Synchrotron powder diffraction studies throw light on its structural aspect. Here we report the 3-D structure determination of bio-mimic molybdenum coordination compounds from synchrotron powder diffraction data. The final refined space group is $\text{P } 2_1$, $a=16.2548(2)$, $b=10.7842(2)$, $c=12.6836(1)$, $\text{Beta}=90.064^\circ$, $z=2$. The asymmetric unit contains more than 400 atoms. The synthesis, reactivity and structure determination from synchrotron radiation powder diffraction will be shown and discussed.

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MS17 P22

Crystal Structures of Synthetic Iron-bearing Tetrahedrites and Tennantites at 25° and 250°C by Rietveld refinement of X-ray and Neutron Diffraction Data *Emil Makovicky^a, Jens W. Andreasen^b, Tonci Balić-Žunić^a, Karen Friese^c, Andrzej Grzecnik^c, Sven Karup-Møller^d, Bente Lebech^b* ^aUniversity of Copenhagen, Denmark, ^bRisoe National Laboratory, Roskilde, Denmark, ^cUniversidad del País Vasco, Bilbao, Spain, ^dTechnical University of Denmark, Lyngby.

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Keywords: Rietveld refinement, tetrahedrite-tennantite, neutron diffraction

Tetrahedrite and tennantite are complex Cu-Sb and Cu-As sulphides with cubic symmetry and extensive substitutions of Fe, Zn, Hg, Ag and other cations for copper. Cu_1S_4 tetrahedra form a tetrahedral framework with large cavities which host clusters of Cu₂ with three-fold coordination and lone electron pairs of Sb (As). These metalloids are positioned as (Sb,As)₃ pyramids in the cavity walls. In spite of extensive research, some fundamental questions, e.g., the structural role of Fe, which starts the substitution process as Fe^{3+} and ends it as Fe^{2+} , and the true nature of 'extremely anisotropic' Cu₂ positions, remained in question.

Rietveld refinement of neutron powder diffraction data on four samples of synthetic, iron-bearing tetrahedrite with 0.40, 1.06, 1.23, and 1.71 atoms Fe in the formula unit $\text{Cu}_{10}(\text{Fe,Cu})_2\text{Sb}_4\text{S}_{13}$ and four samples of synthetic tennantite with 0.12, 0.50, 0.84, and 1.02 atoms Fe in the analogous formula unit with As instead of Sb, indicates unambiguously that iron is incorporated into tetrahedral Cu1 sites and not into triangular Cu2 sites. The refinement results also confirm that Cu₂ is a split, flat-pyramidal site situated statistically on both sides of the S1-S2 triangle. This split is about 0.6 Å in tetrahedrite and about 0.7 Å in tennantite. Unit cell volume and further structural trends have been evaluated by means of linear regression with Fe concentration as the independent variable.

Rietveld refinement of x-ray diffraction data from low-Fe and high-Fe samples of both compounds, obtained at ESRF

(Grenoble) ($\lambda=0.3748$ Å) at 25° and 250°C, respectively, suggests that the coefficient of thermal expansion is highest for samples with low iron substitution. Split of triangular Cu2 positions increases with temperature and the half-occupied Cu2 positions from different coordination triangles approach one another, down to 2.70-2.75 Å in tennantite at 250°C. There is insignificant residual electron density between the split Cu2 half-sites in tetrahedrite at 25°C and its increase with temperature is moderate. The inter-site density is substantially higher in tennantite and it increases considerably with temperature, especially in the low-Fe sample.

MS17 P23

Ion exchange properties for lamellar oxides

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Keywords : partial exchange, soft chemistry, oxide

The investigations about materials dealing with energy have shown that the oxides with a layer structure are potential candidates for solid state electrolytes and for electrodes. In this respect, attention has been focussed on protonic oxides owing to their stability at rather high temperature. Moreover these latter compounds are characterized by their ability to accommodate in the interlayer space ions of different shapes and sizes. They offer the possibility to synthesize some partially exchanged compounds. During this work reactions of some K⁺ and Na⁺ salts (1) with the layered niobic acid HNb3O8 (2) in different ratio (1)/(2) were studied. The partial exchange reaction increases the spacing between the inorganic sheets is discussed in terms of ion size and state of hydration.

MS17 P24

Temperature dependent stability field of nanodomain structures in PZT ceramics using synchrotron powder diffraction Kristin A. Schoenau^a, Michael Knapp^b, Hans Kungl^c, Michael J. Hoffmann^c, Mario Maglione^d, Hartmut Fuess^a ^aMaterials Science, Darmstadt University of Technology, Germany. ^bCELLS, Barcelona, Spain. ^cInstitute of Ceramics in Mechanical Engineering, University of Karlsruhe, Germany ^dICMCB-CNRS, Université Bordeaux I, France.

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Keywords: ferroelectric oxides, in situ synchrotron x-ray powder diffraction, phase stability, nanodomains,

Extraordinarily high piezoelectric properties of ferroelectric lead zirconate titanate, PbZr_{1-x}Ti_xO₃ (PZT), at its so-called morphotropic phase boundary (MPB) between tetragonal and rhombohedral symmetry have raised interest on the structural properties of this compositional area in last years. Discussions involved a coexistence of tetragonal and rhombohedral structures as well as the existence of a monoclinic phase [1]. Recent studies using high-resolution synchrotron x-ray powder diffraction in combination with TEM and EPR at ambient temperature [2, 3] were able to correlate XRD observation with a nanodomain structure. The internal symmetry of the nanodomains is difficult to determine due to strong coherence effects in diffraction experiments, which is in

correspondence with findings for relaxor ceramics using martensitic theory [4]. The fraction of nanodomains within the material besides tetragonal microdomains can be derived using a two-phase Rietveld fit. To investigate the stability field of these nanodomains with changes in temperature dependent on sample composition, in situ diffraction experiments on powders were conducted in transmission mode at the beamline B2, Hasylab, Hamburg Germany. Various parameters derived from Rietveld refinement are found to reflect the changes in domain structure. There are e.g. pronounced changes in volume strain of the tetragonal phase accompanied by the observation of a plateau in the evolution of the c/a-ratio of the tetragonal phase, as seen in Fig.1, which classify the stability range of the nanodomains.

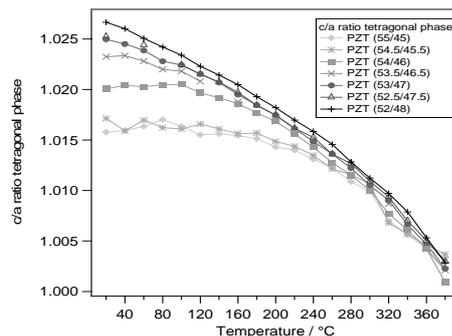


Fig. 1: Temperature-dependent evolution of the tetragonal c/a-ratio for samples out of the compositional range of the MPB.

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MS17 P25

Peculiarity of polymerization of the fullerite C₆₀ in a hexagonal form. N.R. Serebryanaya^a, G.A. Dubitsky^a, V.D. Blank^a, B.N. Mavrin^b, E.A. Skryleva^c, E.V. Skokan^d, V.V. Aksenkov^a, ^aTISNCM, Troitsk, Russia, ^bInstitute of Spectroscopy, Troitsk, Russia, ^cMoscow Institute of Steel and Alloys, Russia, Department of Chemistry, MSU, Russia. E-mail: nadya@ntcstm.troitsk.ru

Keywords: fullerenes, polymerization, high pressure

2D polymerized phases of the hexagonal closed-packed (hcp) modifications of fullerite C₆₀ have been manufactured after the high-pressure-high-temperature treatment at 4 GPa and different temperatures. Polymeric phases of the hcp-form are compared with the polymeric phases of fcc-form obtained at the same conditions. Polymeric phases of both C₆₀ forms have been investigated by X-ray diffraction, X-ray photoelectron (XPS) and Raman spectroscopy methods.

At 450° C the hcp-form is transformed into 2D polymeric rhombohedral phase as the fcc-form. The Raman spectra confirmed that 2D polymeric structures of C_{60_hcp} (orthorhombic and rhombohedral structures) are the same as these of C_{60_fcc}. Unit-cell parameters of 2D polymeric structures of C_{60_hcp} and C_{60_fcc} are calculated.