

**s11.m1.p5** **Pt-Pd-(Ni) monosulphides: structure refinement and modelling.** T. Evstigneeva<sup>1,2</sup>, S. van Smaalen<sup>2</sup>, R.E. Dinnebier<sup>2</sup>, V. von Seckendorff<sup>3</sup>. <sup>1</sup>*IGEM RAS, Moscow, Russia;* <sup>2</sup>*Lab. of Crystallography, University of Bayreuth, Germany;* <sup>3</sup>*Mineralogical Institute, University of Wurzburg, Germany.*  
Keywords: minerals, phase diagram, powder diffraction.

Cooperite [PtS], braggite [(Pd,Pt,Ni)S], and vysotskite [(Pd,Ni,Pt)S] are common PGE- minerals, that show large limits of isomorphous substitution of the metallic atoms, with the Ni contents ranging from 0 up to ~25 at%. The position of the phase boundaries in the pseudoternary system PtS-PdS-NiS varies significantly with temperature [1-3].

In this contribution we report on the synthesis and characterisation of a series of compounds PtS-PdS-NiS. The goal of this investigation was to better characterise the phase diagram, and to determine the possible site-order of the constituent elements Ni, Pt, and Pd.

More than 60 samples have been synthesised at temperatures of 850 and 725°C. A refined two-phase area occurred in Ni-free samples for a Pd contents between ~25 and 75 mol.%. Our data showed that the two-phase field decreases in size with increasing of Ni content.

High-resolution X-ray powder diffraction showed that the tetragonal lattice parameters of cooperite hardly vary with composition, whereas large variations were observed for braggites. Both cell parameters increased with increasing Pd content, and decreased with increasing Ni content. The ratio  $c_0/a_0$  remains nearly constant.

Rietveld refinements were performed for several of the compounds. The variations in composition and site occupancies as resulted from these refinements will be discussed.

**s11.m1.p6** **Structure of K-rich Birnessite synthesized by Thermal Decomposition of KMnO<sub>4</sub>.** A.C. Gaillot, V.A. Drits, B. Lanson, *Environmental Geochemistry Group - LGIT, University of Grenoble - CNRS, BP53, 38041 Grenoble cedex 9, France.*  
Keywords: mineralogical crystallography.

An K-rich sample of birnessite has been synthesized according to the protocol of Kim et al.<sup>1</sup> by pyrolysis of KMnO<sub>4</sub> at 1000°C. Its crystal structure refined from X-ray powder diffraction (XRD) data is based on a two-layer unit-cell with parameters  $a=5.155\text{\AA}$ ,  $b=2.846\text{\AA}$ ,  $c=14.10\text{\AA}$ ,  $\alpha=\beta=\gamma=90^\circ$ , and a C2/m space-group. Super-reflections, observed on the powder XRD pattern, are related to a super-cell with parameters  $A=7.862\text{\AA}$ ,  $B=3b=8.538\text{\AA}$ ,  $C=c$ ,  $\alpha=\beta=90^\circ$ ,  $\gamma=100.5^\circ$ .

In other members of the phyllo-manganate family, the orientation of the Mn octahedra building up elementary layers is identical in all layers. On the contrary, the peculiarity of this structure is the regular alternation of Mn octahedra orientation from one layer to the other, as described by Kim et al.<sup>1</sup>. As a consequence, adjacent layers are rotated with respect to each other by 180° around the c axis. This unusual stacking mode provides a very stable prismatic cavity for interlayer K<sup>+</sup> cations compensating for the layer charge deficit.

According to chemical analysis layer charge originates mostly from the presence of octahedral Mn<sup>3+</sup> cations, octahedral layers being almost vacancy-free. The presence of these cations, and their unique azimuthal orientation are responsible for the departure from the hexagonal symmetry of the layer ( $a/b=\sqrt{3}.28$ ), as evidenced previously for Na-rich synthetic birnessite<sup>2,3</sup>. Furthermore, as in these Na-rich birnessites, the ordered distribution of heterovalent octahedral Mn cations is responsible for the observed superstructure.

Additionally, one may note that depending on the synthesis conditions samples with various degrees of heterogeneity may be obtained. Heterogeneity results from the coexistence of crystals having different Mn<sup>4+</sup>/Mn<sup>3+</sup> ratios. As a result, contrasting a/b ratios are observed for these crystals because of the unique azimuthal orientation of elongated Mn<sup>3+</sup> octahedra, inducing a strong anisotropic broadening, with 20 $\ell$  reflections being much broader than 11 $\ell$  ones for the same  $\ell$  value.

During the synthesis, the very stable prismatic coordination of the interlayer K<sup>+</sup> cations acts as pillar favoring the formation of a lamellar structure at such high temperature and is responsible for the higher thermal stability of this compound, as compared to other birnessite varieties.

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