

structure and characterization, polycrystalline X-Ray diffraction

### P11.16.125

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#### Structural and thermal analytical study on *trans*-diammine-bis(nitrito) complex of Pd(II) and Pt(II)

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Aqueous ammonia solutions of Pd(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> and Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> are used, after impregnations and heat treatments between 150 and 350 °C, for a successful sensitization of SnO<sub>2</sub> layers for CO gas [1]. In order to identify the active sensing chemical species of residues from the Pd or Pt solutions, a detailed study on thermal decomposition of solid *trans*-Pd(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> (**1**) and *trans*-Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> (**2**), crystallized from the used solutions, has been carried out. Compounds **1** and **2** have been characterized by their FTIR spectra and XRD profiles. Their composition and *trans* configuration have also been identified by reference IR spectra [2] and XRD reference patterns (PDF 00-45-598 and PDF 00-54-155) [3]. The crystal and molecular structure of *trans*-Pd(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> (**1**) has been determined by single crystal X-ray diffraction (R = 0.0515). The obtained crystallographic data of the triclinic crystals of (space group *P*-1, *a* = 5,003(1) Å, *b* = 5,419(1) Å, *c* = 6,317(1) Å,  $\alpha$  = 91.34(2)°,  $\beta$  = 111.890(10)°,  $\gamma$  = 100.380(10)°) has been found close to that was reported earlier [4]. A better understanding of mechanism and dynamics of the gas evolution from these solid complexes **1** and **2** probably sensitive to shock seems to be essential during a scaling up of sensor fabrication.

#### References

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Keywords: theophylline, co-crystals, salt

### P11.16.126

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#### Crystal structure of synthetic hydrotungstite, WO<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)

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Hydrotungstite, WO<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O) or H<sub>2</sub>WO<sub>4</sub>(H<sub>2</sub>O) (PDF 00-016-0166 and 00-018-1420) occurs as an alteration product in the oxidized zone of a hydrothermal tungsten ore deposit at the Calacalani mine in Bolivia, and thin films of hydrotungstite have been used as humidity sensors. It is reported to crystallize in *P2/m* with *a* = 7.379(5), *b* =

6.901(5), *c* = 3.748(5) Å, and  $\beta$  = 90.36(16)°. The powder pattern of a greenish yellow precipitate from an inductively-coupled plasma (ICP) specimen preparation of a W-containing sample matched that of hydrotungstite well, but the unit cell and powder pattern were more complicated than had been reported. Application of lattice matching techniques to the reported unit cell yielded the chemically-plausible analogue “yellow molybdic acid”, MoO<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>, which has the ICSD formula type AX5. A further search for Mo-containing compounds having this formula type yielded the mineral sidwellite, MoO<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>, which crystallizes in *P2<sub>1</sub>/n* with *a* = 10.487(1), *b* = 13.850(1), *c* = 10.617(1) Å, and  $\beta$  = 91.62(9)°, and has been studied using neutron powder diffraction. The sidwellite cell is an 8 × supercell of the reported hydrotungstite cell, and the sidwellite structure served as a good initial model for a Rietveld refinement of the hydrotungstite structure. The hydrogen positions were determined by a quantum chemical geometry optimization, which permitted analysis of the hydrogen bonding pattern. The structure consists of corner-sharing layers of tilted WO<sub>6</sub> octahedra in the *ac* plane. Pointing into the interlayer region *trans* to each tungsten atom are a coordinated water molecule and a W=O group. The interlayer region is occupied by water molecules, which are hydrogen bonded to the layers. Hydrotungstite is properly formulated [WO<sub>3</sub>(H<sub>2</sub>O)](H<sub>2</sub>O). The structure of the mineral tungstite, WO<sub>3</sub>(H<sub>2</sub>O), has been reported, but the topologies of the layers in sidwellite and tungstite differ. A combination of quantum calculations and Rietveld refinement was used to determine the best model for the topology of the hydrotungstite layer. The quantum calculations help establish the relative energies of hydrotungstite and tungstite.

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#### Periodic properties of atomic matter

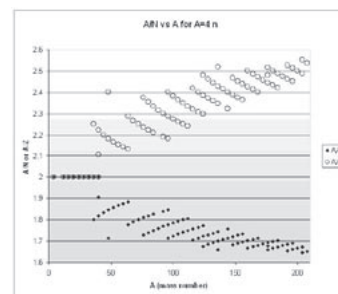
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A relationship between the periodicity of atomic matter with natural-number patterns was unveiled recently<sup>1</sup>. Almost a century ago W.D. Harkins<sup>2</sup> noted that for stable nuclides the proton/neutron ratio converged to a value *Z/N* of 0.62 (the neutron had not been discovered at that time). This value has now been recognized as the number tau, well known in number theory and popularly referred to as the ‘golden ratio’<sup>3</sup>. The periodic nature of the stable nuclides has also been demonstrated in other ways, such as by considering experimentally observed properties of nuclides including the nuclear binding energy (NBE), spin, abundance and thermal cross section. There is an undeniable link to number theory: Fibonacci numbers, the golden ratio and Farey sequences, established without any assumptions about the nuclear properties of the 264 known stable nuclides. Fig. 1. *A/N* or *A/Z* vs. mass number for nuclides with *A*=4*n* converge to limiting values close to tau+2 or tau+1.

[1] J.C.A. Boeyens, *Cryst. Eng.*, 4 (2001) 61.

[2] W.D. Harkins, *J. Am. Chem.*



Soc., 39 (1917) 856.

[3] J.C.A. Boeyens with D.C. Levendis, Number Theory and the Periodicity of Matter, 2008, Springer.

Keywords: periodicity, nuclides, Farey-sequence

**P11.05.128**

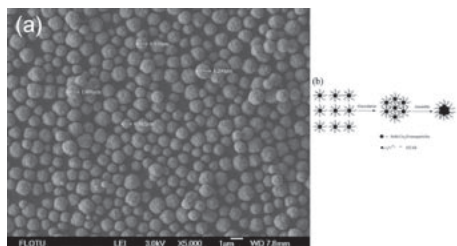
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**Preparation of cuprous oxide microspheres via HTAB-assisted glucose reduction approach**

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Cuprous oxide microspheres are widely used as catalysis, coatings, disinfection and anodic materials due to their unique assemble structures and their perfect dispersion and fluid properties. Cuprous oxide microspheres are usually fabricated by the thermal oxidation and the chemical vapor deposition which need high temperature or by the solution reduction which use the expensive or toxic materials as formaldehyde, sodium hypophosphite or  $\text{KBH}_4$  as the reducing agents. Herein a moderate method was suggested to synthesis cuprous oxide microspheres via the hexadecyltrimethyl ammonium bromide (HTAB)-assisted glucose reduction approach, using  $\text{CuSO}_4$  as the raw material. Dispersive uniform cuprous oxide microspheres (800-900nm) composed of crystalline nano-particles (8.5-13 nm) were synthesized by mixing  $\text{CuSO}_4$  and glucose solutions in the presence of HTAB at room temperature followed by aging of the mixture at 70-80°C for 0.5 h (Fig. 1a). The presence of HTAB promoted the formation of cuprous oxide nano-particles as well as the subsequently assembly of the nano-particles to the cuprous oxide microspheres (Fig. 1b).



Keywords: microspheres, cuprous oxide, glucose

**P11.11.129**

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**Crystal structures and high-temperature phase transition of  $\text{Sr}_2\text{MSbO}_6$  (M=Sc,Cr,Fe) double perovskites**

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The  $\text{Sr}_2\text{MSbO}_6$  (M=Sc,Cr,Fe) materials have been elaborated by the standard solid state reaction method, and their structures studied with X-ray powder diffraction method, at room temperature (RT) and at high temperatures (HT). At RT, the crystal structures of these materials were found to have a monoclinic symmetry:  $\text{Sr}_2\text{ScSbO}_6$ , with  $P2_1/n$  space group, and cell parameters  $a=5.6783(1)$ ,  $b=5.6923(1)$ ,  $c=8.0257(1)$  Å,  $\beta=89.98(1)$ ;  $\text{Sr}_2\text{FeSbO}_6$ , with  $I2/m$

space group, and with  $a=5.6148(1)$ ,  $b=5.5954(4)$ ,  $c=7.9002(1)$  Å,  $\beta=90.02(4)$ ; and, finally,  $\text{Sr}_2\text{CrSbO}_6$ , with  $I2/m$  space group, and cell parameters  $a=5.5574(1)$ ,  $b=5.5782(1)$ ,  $c=7.8506(1)$  Å,  $\beta=90.06(2)$ . Depending on the M cation size, the  $\text{M}^{3+}$  and  $\text{Sb}^{5+}$  cations can be entirely or partially ordered, in the two distinct B-sites of the double perovskite structure. In the Sc compound, the  $\text{Sc}^{3+}$  and  $\text{Sb}^{5+}$  cations are totally ordered; in Cr and Fe, the  $\text{M}^{3+}$  ( $\text{Cr}^{3+}, \text{Fe}^{3+}$ ) and  $\text{Sb}^{5+}$  cations are partially ordered: the degree of the ordering is 99.4% and 92%, respectively. At HT,  $\text{Sr}_2\text{ScSbO}_6$  undergoes three structural phase transitions:  $P2_1/n \rightarrow I2/m \rightarrow I4/m \rightarrow \text{Fm-}3m$ , at about 400 K, 560 K and 650 K, which, to the best of our knowledge, is the first time that such a rich phase-transition sequence has been observed in this kind of materials.  $\text{Sr}_2\text{CrSbO}_6$  and  $\text{Sr}_2\text{FeSbO}_6$  were found to present the  $I2/m \rightarrow 4/m \rightarrow \text{Fm-}3m$  PT sequence: the first PT is discontinuous, and the second, continuous. In  $\text{Sr}_2\text{CrSbO}_6$ , the PT take place at about 500 and 660 K. In  $\text{Sr}_2\text{FeSbO}_6$  the first PT starts to take place at 400 K, and shows a temperature interval, 400 to 420 K, in which both phases, monoclinic and tetragonal, co-exist; the second PT, from the tetragonal structure with  $I4/m$  to the cubic structure with the  $\text{Fm-}3m$ , is observed above 500 K.

Keywords: transition-metal perovskites, powder diffraction method, phase transitions

**P11.01.130**

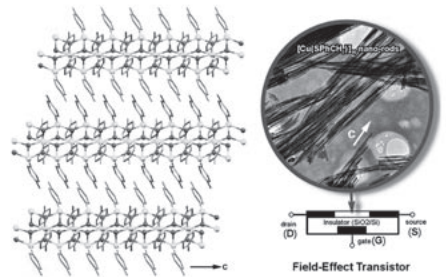
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**Powder structure determination of a series of homoleptic copper(I)-arythiolate conducting polymers**

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Homoleptic copper(I) arylthiolates  $[\text{Cu}(\text{p-SC}_6\text{H}_4\text{X})_n]$  (X =  $\text{CH}_3$ , 1, H 2,  $\text{CH}_3\text{O}$  3, tBu 4,  $\text{CF}_3$  5,  $\text{NO}_2$  6,  $\text{COOH}$  7 and n = infinity) were insoluble crystalline solids.[1] Structure determination using powder diffraction revealed that 1-3 and 6 formed 1-D polymers with Cu atoms bridged by arylthiolate ligands. Weak intra-chain pi-pi stacking interactions are present in 1-3. In 6, the intra-chain pi-pi interactions are insignificant and the chain polymers are associated via non-covalent C-H...O hydrogen bonding interactions. As revealed by TEM, the solid samples of 1-5 and  $[\text{Cu}(\text{SCH}_3)_n]$  contained homogeneously dispersed crystalline nano-rods whereas smaller plate nano-crystals were found for 6 and 7. SAED further confirmed that the chain polymers of 1-3 and  $[\text{Cu}(\text{SCH}_3)_n]$  similarly grow along the long axes of their nano-rods. The nano-rods of 1-5 and  $[\text{Cu}(\text{SCH}_3)_n]$  exhibited p-type field-effect transistor behavior with charge mobility of  $10\text{E-}2$  to  $10\text{E-}5$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ . Their charge mobility is correlated to their unique chain-like copper-sulfur networks, and the para-substituent of arylthiolate ligand alter the ultimate particle morphology and charge transport properties.



**$[\text{Cu}(\text{SPhCH}_3)]_n$  nano-rod FET device**

[1] Chem. Eur. J. 2008, 14, 2965.

Keywords: *ab initio* powder structure determination,