

## MS16 Structure-property relationships in high pressure crystallography

Chairs: Andrzej Grzechnik, Paul Attfield

### MS16-P1 High-pressure studies of [4]helicene-TCNQ complex

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[4]helicene is a chemical compound composed of four conjugated aromatic rings [see fig. 1]. The molecule is deviated from planarity. This feature is a result of steric interactions between C-H atoms six-membered aromatic rings. The interplanar angle between pairs of adjacent rings of [4]helicene molecule is 26.8°. This compound forms a charge-transfer complex with 7,7,8,8-tetracyanoquinodimethane (TCNQ), where [4]helicene is an electron pair donor and TCNQ is an acceptor. The molecules are arranged in stacks resulting in a sandwich-like columns. Forming a complex causes that the aforementioned angle is reduced to a value of 25.4°. In this report we present the synthesis and structural analyses of [4]helicene-TCNQ complex under different pressures. The complex was studied at atmospheric pressure, 0.44 GPa, 1.68 GPa and 2.1 GPa. Geometrical changes and intermolecular interactions of [4]helicene -TCNQ complex are analyzed under high-pressure.

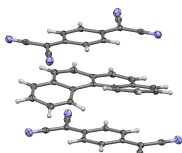


Figure 1. [4]helicene-TCNQ complex.

**Keywords:** [4]helicene, tetracyanoquinodimethane, high-pressure, X-ray diffraction, Raman spectroscopy

### MS16-P2 Stability of $(\text{NH}_4)_2\text{V}_3\text{O}_8$ and $\text{Cs}_2\text{V}_3\text{O}_8$ fersnoites at high pressures

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Vanadates  $\text{A}_2\text{V}_3\text{O}_8$  (A: K, Rb,  $\text{NH}_4$ , Cs) have the fersnoite structure ( $P4bm$ ,  $Z=2$ ) at atmospheric conditions [1-3]. They are built-up of layers of corner-sharing  $\text{V}^{5+}\text{O}_4$  tetrahedra and  $\text{V}^{4+}\text{O}_5$  tetragonal pyramids, separated by the  $\text{A}^+$  cations.  $\text{K}_2\text{V}_3\text{O}_8$  and  $\text{Rb}_2\text{V}_3\text{O}_8$  transform to incommensurate phases at low temperatures [4,5] due to rotations and displacements of rigid  $\text{V}^{5+}\text{O}_4$  and  $\text{V}^{4+}\text{O}_5$  polyhedra.

We have studied pressure-induced structural instabilities of  $(\text{NH}_4)_2\text{V}_3\text{O}_8$  and  $\text{Cs}_2\text{V}_3\text{O}_8$  using single-crystal x-ray diffraction in diamond anvil cells.  $(\text{NH}_4)_2\text{V}_3\text{O}_8$  undergoes a reversible phase transition at 3 GPa to a three-dimensional structure ( $P4/mbm$ ,  $Z=2$ ), formed by corner-sharing  $\text{V}^{5+}\text{O}_4$  trigonal bipyramids and  $\text{V}^{4+}\text{O}_6$  octahedra [1]. The chains of these corner-connected polyhedra form a framework with tunnels along the  $c$  direction. Vanadate framework structures formed of more than one type of coordination polyhedra are frequent at ambient conditions, their common structural feature being the presence of both corner- and edge-shared polyhedra. The framework of the high-pressure polymorph of  $(\text{NH}_4)_2\text{V}_3\text{O}_8$  is unique since all the polyhedra are exclusively connected via common corners.

$\text{Cs}_2\text{V}_3\text{O}_8$  undergoes a reversible phase transition at 4 GPa [3]. Up to the phase transition, the compression has little effect on the polarity of the structure. Above 4 GPa, the structure is still polar but the pseudo-symmetry with respect to the corresponding space group  $P4/mbm$  abruptly increases. Both structures consist of layers of corner-sharing  $\text{V}^{5+}\text{O}_4$  tetrahedra and  $\text{V}^{4+}\text{O}_5$  tetragonal pyramids, separated by the  $\text{Cs}^+$  cations. The unit-cell volumes, at which the phase transitions in  $(\text{NH}_4)_2\text{V}_3\text{O}_8$  and  $\text{Cs}_2\text{V}_3\text{O}_8$  occur, coincide with the unit-cell volume of  $\text{K}_2\text{V}_3\text{O}_8$  at atmospheric pressure.

The unit-cell volumes are reduced by 22% and 20% in  $(\text{NH}_4)_2\text{V}_3\text{O}_8$  and  $\text{Cs}_2\text{V}_3\text{O}_8$  upon compression to approximately 7.0 GPa and 8.6 GPa, respectively. The fact why modulated structures, like those in  $\text{K}_2\text{V}_3\text{O}_8$  and  $\text{Rb}_2\text{V}_3\text{O}_8$  at low temperatures [4,5], are not observed in the fersnoites with larger  $\text{NH}_4^+$  and  $\text{Cs}^+$  cations upon compression is explained by the suppression of rotations and displacements of the polyhedra around the  $\text{V}^{4+}$  and  $\text{V}^{5+}$  cations.

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**Keywords:** mixed-valence vanadates, fersnoite structure, phase transition, high pressure

**MS16-P3** High pressure synthesis of iron complex oxides in high oxidation state ( $\text{Fe}^{4+}$ ,  $\text{Fe}^{5+}$ ): mapping between localized and itinerant behavior

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In 1993 colossal magnetoresistance (CMR) was found in  $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$  at the Curie point where electrical resistance changes by orders of magnitude when a magnetic field is applied. Up to now, most of the known CMR materials are manganese based perovskites – mostly  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  or  $\text{SmBaMn}_2\text{O}_6$  [1]. Analysis of the potential map that was proposed by Kamata et al. [2] suggests that CMR could also be obtained in  $\text{A}_2\text{B}_{1-x}\text{FeO}_3$  (where  $\text{A}=\text{Na, K, Rb}$  and  $\text{B}=\text{Ca, Sr, Ba}$ ) perovskites. These proposed iron based compounds should display similar electrical transport properties to the manganese perovskites being in vicinity to metal-insulator border line in the potential map. Additionally, both families should be isoelectronic:  $\text{Fe}^{3+}$  and  $\text{Fe}^{3.5+}$  have the same electron configuration as  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ . To stabilize these unusually high oxidation states, and to achieve oxygen stoichiometry,  $\text{Sr}_{1-x}\text{A}_x\text{FeO}_3$  ( $\text{A}=\text{Na, K}$ ) have been synthesized by using a unique oxygen high pressure (HP) system recently relocated and already successfully used in our lab [3]. This HP system allows precise control of temperatures (up to 1200 °C), gas pressures (up to 2000 bars) and large production of materials ( $\text{cm}^3$ ). The synthesized materials are phase pure and have structure similar to the parent compound (space group  $Pm-3m$ ). Measurements of the magnetic susceptibilities and electric properties for these materials are currently underway. Determination of the magnetic structure of the materials by neutron powder diffraction has also been scheduled.

### References

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**Keywords:** High pressure synthesis, CMR