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 TCNQ, where [4]helicene is an electron pair donor and TCNQ is an acceptor. The molecules are arranged in stacks resulting from rotations and displacements of rigid V³O⁴ and V⁴⁵ polyhedra.

We have studied pressure-induced structural instabilities of (NH₄)V₃O₈ and Cs₅V₅O₁₈ using single-crystal x-ray diffraction in diamond anvil cells. (NH₄)V₃O₈ undergoes a reversible phase transition at 3 GPa to a three-dimensional structure (P4/mbm, Z=2), formed by corner-sharing V⁵O₈ trigonal bipyramids and V⁴⁵ 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 (NH₄)V₃O₈ is unique since all the polyhedra are exclusively connected via common corners.

Cs₅V₅O₁₈ 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 V⁵O₈ tetrahedra and V⁴⁵ tetragonal pyramids, separated by the Cs⁺ cations. The unit-cell volumes, at which the phase transitions in (NH₄)V₃O₈ and Cs₅V₅O₁₈ occur, coincide with the unit-cell volume of K₃V₃O₈ at atmospheric pressure.

The unit-cell volumes are reduced by 22% and 20% in (NH₄)V₃O₈ and Cs₅V₅O₁₈ upon compression to approximately 7.0 GPa and 8.6 GPa, respectively. The fact why modulated structures, like those in K₃V₃O₈ and Rb₂V₂O₇ at low temperatures [4,5], are not observed in the fresnoites with larger NH₄⁺ and Cs⁺ cations upon compression is explained by the suppression of rotations and displacements of the polyhedra around the V⁵⁺ and V⁴⁵ cations.


Keywords: [4]helicene, tetracyanoquinodimethane, high-pressure, X-ray diffraction, Raman spectroscopy
Keywords: mixed-valence vanadates, fresnoite structure, phase transition, high pressure

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

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In 1993 colossal magnetoresistance (CMR) was found in La\(_{1-x}\)Ba\(_x\)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 La\(_{1-x}\)Sr\(_x\)MnO\(_3\) or SmBaMnO\(_6\) [1]. Analysis of the potential map that was proposed by Kamata et al. [2] suggests that CMR could also be obtained in A\(_{1-x}\)B\(_x\)FeO\(_3\) (where A=Na, K, Rb and B= 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 iso-electronic: Fe\(^{4+}\) and Fe\(^{5+}\) have the same electron configuration as Mn\(^{3+}\) and Mn\(^{4+}\) in La\(_{1-x}\)Sr\(_x\)MnO\(_3\). To stabilize these unusually high oxidation states, and to achieve oxygen stoichiometry, Sr\(_{1-x}\)A\(_x\)FeO\(_3\) (A=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 (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


Keywords: High pressure synthesis, CMR