

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.

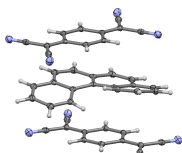


Figure 1. [4]helicene-TCNQ complex.

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, NH_4 , Cs) have the fersnoite structure ($P4bm$, $Z=2$) at atmospheric conditions [1-3]. They are built-up of layers of corner-sharing V^{5+}O_4 tetrahedra and V^{4+}O_5 tetragonal pyramids, separated by the 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 V^{5+}O_4 and V^{4+}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 V^{5+}O_4 trigonal bipyramids and V^{4+}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 V^{5+}O_4 tetrahedra and V^{4+}O_5 tetragonal pyramids, separated by the 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 NH_4^+ and Cs^+ cations upon compression is explained by the suppression of rotations and displacements of the polyhedra around the V^{4+} and V^{5+} cations.

[1] A. Grzechnik et al., *Dalton Trans.*, 2011, **40**, 4572.

[2] J. Yeon et al., *Inorg. Chem.*, 2013, **52**, 6179.

[3] A. Grzechnik et al., *J. Solid State Chem.*, 2016, **238**, 252.

[4] B.C. Chakoumakos et al., *J. Solid State Chem.*, 2007, **180**, 812.

[5] R.L. Withers et al., *J. Solid State Chem.*, 2004, **177**, 3316.