

**s6.m1.p3** Structural high-pressure evolution of the tetragonal low-pressure polymorph of  $\text{Mn}_3\text{O}_4$ . R. Miletich<sup>1</sup> and R.J. Angel<sup>2</sup>, <sup>1</sup>Laboratory for Crystallography, ETHZ, Zürich (Switzerland). <sup>2</sup>Bayerisches Geoinstitut, Universität Bayreuth, (Germany).  
Keywords:  $\text{Mn}_3\text{O}_4$ , high pressure, Jahn-Teller effect.

$\text{Mn}_3\text{O}_4$  occurs in nature as hausmannite, a tetragonally distorted spinel, in which  $\text{Mn}^{2+}$  occupies the tetrahedral sites and the  $\text{Mn}^{3+}$  cations are found in the octahedral interstices of the cubic close-packed oxygen lattice. Due to the Jahn-Teller effect of the  $\text{Mn}^{3+}$  cations, the octahedra are uniaxially elongated which results, as a consequence of the cooperative effect between edge-sharing octahedra, in a cubic-to-tetragonal symmetry breaking. Previous high-pressure X-ray powder-diffraction experiments [1] confirmed a transition to a marokite-type high-pressure polymorph of orthorhombic symmetry that occurs between 10 and 12 GPa. Moreover the EDX data yield a bulk modulus of  $137 \pm 3.8$  GPa for a second-order Birch-Murnaghan (BM) equation of state (EoS).

Here we report the results of an experimental high-pressure study on the tetragonal low-pressure polymorph of  $\text{Mn}_3\text{O}_4$  by means of single-crystal diffraction in a diamond-anvil cell. In addition to in total 12 unit-cell parameter data points ( $a$ ,  $c$ ,  $V$ ) in the pressure range 0.0001 to 10.2 GPa, crystal structure refinements at each of the pressures achieved have been performed yielding full structure informations.

Measurements of the unit-cell parameters reveal a considerable compressional anisotropy with the  $c$ -axis being more compressible than the  $a$ -axis. The decreasing  $c/a$  ratio indicates a reduction of the tetragonality with increasing pressure. The structure refinements show that the uniaxial elongation of the  $\text{Mn}^{3+}\text{O}_6$  octahedra gets reduced which is in full agreement with the previously reported regularization as reported from structure modelling [1]. The  $\text{Mn}^{3+}\text{O}_6$  polyhedral compressibility is also compatible with the macroscopic compression behavior thus explaining the compressional anisotropy.

**s6.m1.p4** Mercury halides under pressure, phase diagrams full of surprises. M. Hostettler, D. Schwarzenbach, M. Bonin, H.-P. Weber *Institute of Crystallography, Physics Department, University of Lausanne, CH-1015 Lausanne Switzerland.*  
Keywords: high-pressure, phase transitions, mercury halides.

The mercury halides,  $\text{HgX}_2$  ( $X = \text{I}, \text{Br}, \text{Cl}$ ), form solid phases the structures of which can be interpreted as close packed spheres  $X$  and  $\text{Hg}$  atoms filling interstitial sites. Of all compounds,  $\text{HgI}_2$  has been the most studied. This is due to actual use of the red modification as detector material for x-rays and  $\gamma$ -rays at room temperature<sup>1</sup>. At ambient conditions, two unstable polymorphs exist in addition to the thermodynamically stable red form: an orange phase with a layered structure exhibiting stacking disorder<sup>2</sup>, and a yellow modification<sup>3</sup> related to the structure of the high temperature yellow phase. The structural motifs of these three polymorphs are: corner-shared  $\text{Hg}(\text{I}_{1/2})_4$  tetrahedra, corner-shared  $\text{Hg}_4\text{I}_6(\text{I}_{1/2})_4$  tetrahedra, and  $\text{HgI}_2$  molecules, respectively. At ambient pressure,  $\text{HgBr}_2$  adopts the structure of the yellow room-temperature unstable polymorph of  $\text{HgI}_2$ . This phase is stable at all temperatures up to the fusion. Spectroscopic studies of the  $\text{HgX}_2$  systems<sup>4</sup> have revealed the existence of a variety of high-pressure phases of which the structures have not yet been determined. We undertook high-pressure powder diffraction studies in order to understand the variability of the mercury coordination. No less than nine different phases of  $\text{HgI}_2$  exist in the pressure-temperature range ( $0 < P < 200$  kbar,  $300 < T < 800$  K), showing the phase diagram to be extremely complicated. For  $\text{HgBr}_2$ , five different phases have been observed as a function of pressure. The new phases of  $\text{HgI}_2$  and  $\text{HgBr}_2$  have monoclinic, orthorhombic and trigonal symmetries. Several of the phase transformations studied are clearly reconstructive, producing dramatic changes in the coordination of the mercury atoms. Even more surprising is the observation of an isostructural transition in the iodide. This type of transition is uncommon. Their observation is greatly facilitated by the use of synchrotron radiation.

An overview of all diverse structures, symmetries and types of transitions observed in our high-pressure studies of  $\text{HgI}_2$  and  $\text{HgBr}_2$  will be presented.

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