

High-pressure behaviours of HoMn_2O_5 and BiMn_2O_5

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The mixed valence RMn_2O_5 compounds ($\text{R} = \text{Bi}$ and rare earths) are one of the most studied families of multiferroic materials. They order antiferromagnetically at low temperatures ($T_N \approx 40$ K) and on further cooling undergo a sequence of (in)commensurate magnetic phase transitions. Slightly above the Néel temperature T_N , they become ferroelectric. Noda et al. [1] indicated that the effects of the magnetic field and hydrostatic pressure are strongly dependent on the R atom in the RMn_2O_5 systems. Compressing these materials is supposedly analogous to applying magnetic field [2].

In this work, we were interested in examining the effect of hydrostatic pressure on the crystal structures of BiMn_2O_5 and HoMn_2O_5 at room temperature with single-crystal x-ray diffraction in diamond anvil cells. Although structurally similar, these materials slightly differ in their fine structural details and low-temperature features due to the electron lone (E) pair on the Bi^{3+} cation. Thus, our aim was to study their high-pressure behaviours and see whether the presence of the E pair in BiMn_2O_5 leads to significant differences when compared to HoMn_2O_5 .

The experiments were carried out using a HUBER four-circle diffractometer equipped with a marCCD165 detector at the D3 beamline ($\lambda \approx 0.4$ Å). The intensities were integrated and corrected with the program XDS [3]. All the synchrotron diffraction data were analyzed and refined using the program JANA2006 [4].

The two compounds are isomorphous and are built of infinite chains of Mn_1O_6 octahedra linked through Mn_2O_5 tetragonal pyramids and $\text{Bi}(\text{Ho})\text{O}_8$ polyhedra [5]. The slight difference between BiMn_2O_5 and HoMn_2O_5 is apparent when the coordination spheres around the Bi and Ho atoms are considered. Both could be described as distorted bicapped trigonal prisms. However, the degree of distortion in the BiO_8 polyhedron is larger than in the HoO_8 polyhedron as two of the Bi-O distances in the prism are substantially longer than the rest. This effect could be assigned to the presence of the E pairs on the Bi^{3+} cation. An inspection of the electron density around the Ho and Bi positions reveals another difference: while the electron density around Bi has a shape which can easily be approximated taking into account a second-order tensor for its displacement parameters, the shape around Ho suggests the presence of anharmonic effects. The modelling of the Ho position using a tensor of 4th order leads to a decrease of the overall agreement factors. This observation allows two possible interpretations: (1) either the Ho site does not occupy only one single position within the HoO_8 polyhedra but rather it represents an average of several positions or (2) the thermal movement of Ho is truly anharmonic.

The crystal structures of BiMn_2O_5 and HoMn_2O_5 are stable upon compression to at least 7.00 GPa and 5.91 GPa, respectively, at room temperature. The pressure dependence of the normalized lattice parameters and unit-cell volumes is presented in Figure 1. Both materials are very similar: (1) they are the most compressible along the a axis, (2) the lattice contractions along the b and c directions are nearly the same. Their P-V data could be fitted by a second-order Birch-Murnaghan equations of state ($B' = 4.0$) with the zero-pressure bulk modulus $B_0 = 138(2)$ GPa and the unit-cell volume at ambient pressure $V_0 = 370.7(2)$ Å³ for BiMn_2O_5 and $B_0 = 173(3)$ GPa and $V_0 = 350.7(1)$ Å³ for HoMn_2O_5 . The difference in the bulk moduli results from BiMn_2O_5 being relatively more compressible than HoMn_2O_5 along the a axis.

The crystal structures of the two manganites behave different at high pressures as reflected in the bond valence sums (bvs) around the Mn-positions. At ambient pressure, the bvs for the Mn1 position are very close to the ideal value of 4 in both compounds (Bi: 3.920(10) v.u., Ho: 4.066(12) v.u.), while for the Mn2 position they are nearly 3 (Bi: 3.077(10), Ho: 3.170(11) v.u.). At higher

pressures, the bvs for Mn1 in the Bi-compound increase drastically, while the bvs for Mn2 does not change significantly with pressure. In the Ho-compound, on the other hand, the bvs around Mn1 is hardly influenced by pressure and the bvs for Mn2 increases only slightly. This might be an indication of pressure-induced charge transfer between the two Mn sites, which has strongly different character in both compounds. A similar effect was already postulated in [6] to explain the phase transitions at low temperatures.

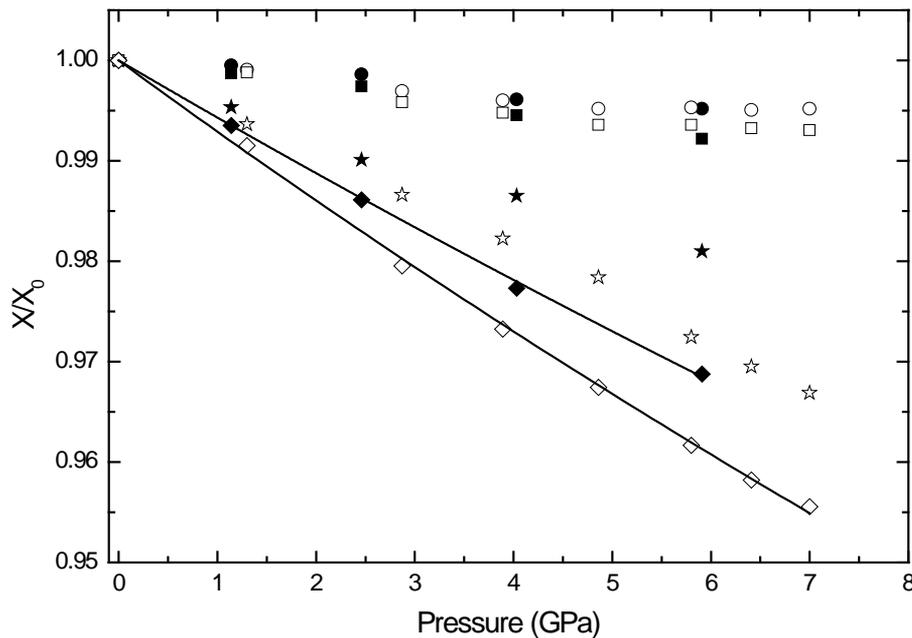


Figure 1: Pressure dependence of normalized lattice parameters and unit-cell volumes in BiMn₂O₅ (open symbols) and HoMn₂O₅ (solid symbols). The a , b , and c lattice parameters are drawn as stars, circles, and squares, respectively. The unit-cell volumes are drawn as diamonds. The lines represent the second-order Birch-Murnaghan equations of state ($B' = 4.0$).

References

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