Phase Transitions in Magnetoelectric BiMnO$_3$-based Ceramics

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Crystal structure of BiMnO$_{3+\delta}$ ceramics has been studied as a function of nominal oxygen excess using synchrotron and neutron diffraction as well as a magnetometry. Increase in oxygen excess leads to the structural transformations from the monoclinic structure to another monoclinic, and then to the orthorhombic through the two-phase regions. The sequence of the structural transformations is accompanied by a modification of the orbital ordering followed by its destruction.

Analysis of the diffraction data points to the changes of crystal structures from the monoclinic structure (*C2/c*) to another monoclinic (*P2$_1$/c*) and then to the orthorhombic structure (*Pnma*) with nominal increase in the oxygen content which is consistent with available data [1]. The mentioned series of the structural transformations is accompanied by a gradual decrease in the unit cell volume. The deviation from the stoichiometric cation/anion ratio specific to the BiMnO$_{3.08}$ sample leads to a stabilization of the monoclinic structure having lower symmetry, viz. *P2$_1$/c* as compared to the stoichiometric compound - *C2/c*, further decrease in the cations content leads to a stabilization of the non-polar orthorhombic structure *Pnma*. Decrease in the cations content leads to a reduction in magnetization of the compounds as confirmed by our neutron diffraction and magnetization data (Figure 1). The changes in the magnetic
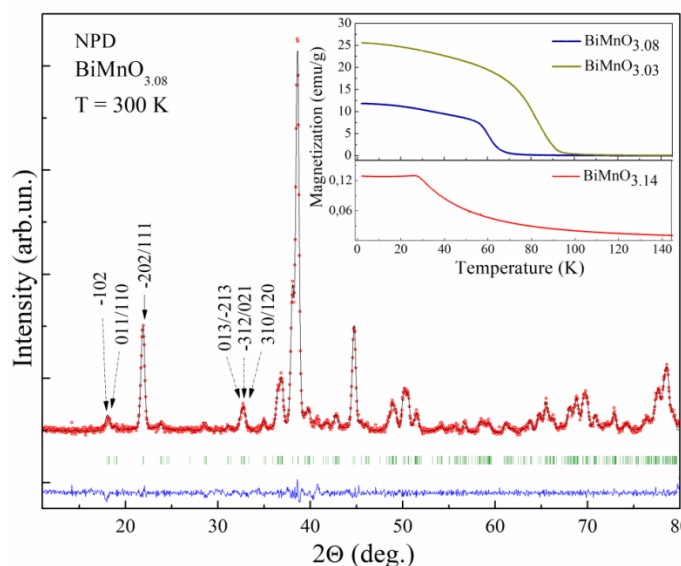

Figure 1. Refined NPD pattern of the compound BiMnO$_{3.08}$ using the space group *P2$_1$/c*. Inset shows M(T) magnetization curves for the compounds BiMnO$_{3+\delta}$ (δ=0.02, 0.08, 0.14) measured in a field-cooled mode (H~100 Oe).

structure are mainly caused by two factors - modification in the orbital ordering of the manganese ions and a dilution of magnetic sublattice by the cations vacancies. The first factor is determined by the geometry of the bond lengths Mn – O and angles Mn – O – Mn, the second factor is associated with a character of vacancies distribution over the A- and B- sublattices of the perovskite structure. The both mentioned factors have different impact on the magnetic structure of the compounds. Thus an increase in the amount of the cations vacancies causes a rearrangement of the orbital order (which is accompanied by a change of the dominant superexchange interactions) followed by a disruption of the orbital ordering and the long range spin order removal.

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[2] Sundaresan, A.; Mangalam, R. V. K.; Iyo, A.; Tanaka, Y.; Rao, C. N. R., Crucial role of oxygen stoichiometry in determining the structure and properties of BiMnO3. J. Mater. Chem. C 2008, 18, (19), 2191-2193.