

## Studies of the $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$ ( $x \leq 0.25$ ) Phase Diagram

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**Introduction:** Perovskite manganates are one of the most intensely studied systems, both experimentally and theoretically, in the field of solid-state chemistry. The discovery colossal magnetoresistance<sup>1</sup> and charge-ordering<sup>2</sup> in these manganates added considerable interest to this field of research. With the availability of sophisticated instruments, understanding the physics of these manganates has advanced tremendously. The  $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$  system is very similar to the  $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$  due to the similarity in ionic size and oxidation states of La and Bi. Though, unlike  $\text{La}^{3+}$  ions,  $\text{Bi}^{3+}$  have a tendency to adopt asymmetric coordination environments to accommodate the stereoactive electron lone pair. Previous reports indicate charge-ordering<sup>3</sup> and C-type magnetic ordering in few compositions in the  $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$  series, but the structural details of the charge-ordered states were not presented. Furthermore, the observation of long-range periodic structures with 32 and 36-fold periodicity<sup>4</sup> with respect to the original unit cell indicated a very complex charge-ordering arrangement. This study has been undertaken to explore the details of charge-ordered states: what crystallographic structures correspond to C and CE-type charge-ordered states. Also to understand the phase separation behavior, which seems to be very common in most of the electron doped manganates and whether this behavior is related to inhomogeneities or other factors.

**Methods and Materials:** We have used the high-resolution synchrotron X-ray diffraction (X7A beam line at NSLS, BNL) technique as the main tool in assessing the structural evolution with temperature. Rietveld analysis was done on these data using GSAS. Combining these with the neutron diffraction data as well as the conductivity and SQUID magnetic measurements, a complete phase diagram of the electron-doped region of  $\text{Ca}_{1-x}\text{Bi}_x\text{MnO}_3$  is extracted<sup>5</sup>.

**Results:** A detailed analysis of the synchrotron X-ray diffraction data reveals that all samples were of single phase at room temperature, isostructural with  $\text{GdFeO}_3$  (Space group  $Pnma$ ). At 25K, three distinct phases were observed along the series. The first one observed from  $0.15 \geq x \geq 0.03$ , is characterized by the absence of charge and orbital ordering. This phase was found to be a G-type antiferromagnetically ordered phase from the analysis of neutron diffraction pattern. The second phase, a monoclinic phase (space group  $P2_1/m$ ), observed between  $0.25 \geq x \geq 0.12$ , is characterized by a pronounced orbital ordering, with one of the axes expanding and the other two contracting. This second phase confirmed to be the C-type AFM phase from the neutron diffraction data. The third low temperature phase, observed for  $x \geq 0.20$ , is characterized by orbital and magnetic ordering, is similar to the Wigner crystal structure with a  $4a \times b \times 2c$  unit cell. For the compositions with  $0.10 < x < 0.18$ , the low temperature data confirms the existence of both the orthorhombic as well as the monoclinic phase. The orthorhombic phase being the G-type canted AFM phase as confirmed by the neutron diffraction data. For  $x > 0.18$ , there is a two-phase coexistence with the orthorhombic phase being the Wigner crystal ordered phase and the C-type ordered monoclinic phase. Except for the small region of  $x \sim 0.18$ , all the other compositions exhibited the phase separation phenomenon.

**Conclusions:** We have confirmed that the phase separation behavior observed in this system is not related to compositional variations and other factors must be considered in order to understand the unusual behavior of this system.

**References:** R. von Helmolt, B. Hozapfel, L. Schultz, K. Samwer, *Phys. Rev. Lett.*, **71**,2331 (1993); C.N.R. Rao, A. Arulraj, P.N. Santhosh, A.K. Cheetham, *Chem. Mater.*, **10**, 2714 (1998); W. Bao, J.D. Axe, C.H. Chen and S-W. Cheong, *Phys. Rev. Lett.*, **73**, 543 (1997); Y. Murakami, D. Shindo, H. Chiba, M. Kikuchi and Y. Syono, *Phys. Rev. B* **55**, 15043 (1997); P.N. Santhosh, J. Goldberger, P.M. Woodward, T. Vogt, W. Lee and A. Epstein, *Phys Rev. B*, November 1st issue (2000).