

o.m2.p11 Investigation of the structure and phase transitions in the novel a-site substituted perovskite compound $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. G.O. Jones & P.A. Thomas, *Crystallography Group, Physics Department, University of Warwick, Coventry, CV4 7AL, U.K.*

Keywords: sodium bismuth titanate, perovskite, structure determination.

Sodium Bismuth Titanate, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT), has the perovskite structure, general formula ABO_3 . This is one of a limited number¹ of perovskite compounds where substitution occurs at the A-cation site, the vast majority substituting on the B-site. NBT was first described by Smolenskii and co-workers², and despite numerous investigations there still remains significant controversy in relation to the ferroic nature of the different phases and the temperature range over which they exist.

An extensive study of the crystal structure and phase transitions has been carried out using neutron powder diffraction. The fundamental sequence of phase transitions from the high-temperature prototypic cubic structure to one of tetragonal and then rhombohedral structure occurs, with coexistence phases being observed.

The results of powder profile refinements have revealed the rhombohedral phase, space group $R3c$, exhibits an anti-phase oxygen octahedra tilt system described by a^-a^- (according to Glazer's notation³), resulting in a doubled unit cell, with parallel cation displacements. As the temperature is increased the rhombohedral superstructure reflections of the type odd-odd-odd with $k \neq 1$, disappear and tetragonal superstructure reflections of the type odd-odd-even appear. The tetragonal phase has been solved in the non-centrosymmetric polar space group $P4bm$. The structure possesses an unusual combination of in-phase oxygen octahedra tilts described by $a^0a^0c^+$ and anti-parallel cation displacements along the polar axis⁴. Although tilted tetragonal perovskites have the capability of showing ferroelectric properties through cation displacements, until now no system has been found that exploits this ability. Since A-cation displacements along $[001]$ are not driven by the octahedral tilts, it has been contended that they result from the need to accommodate the stereo-active lone pair on Bi^{3+} . A further increase in temperature diminishes the tetragonal superstructure reflections until the final phase transition into the cubic perovskite ($\text{Pm}\bar{3}m$), structure occurs. Cation displacements and octahedral distortions for the different phases are reported.

o.m2.p12 Photoinduced crystallographic transition in the gmr like perovskite compound $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. E. Fauth¹, E. Suard², V. Caignaert³, ¹Swiss Light Source, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland, ²Institut Laue Langevin, 38042 Grenoble Cedex, France, ³Laboratoire CRISMAT, ISMRA, 14050 Caen, France
Keywords: neutron diffraction, charge ordering, phase transition.

In the GMR-like insulating perovskite compounds $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{Nd}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, we observed by means of synchrotron and neutron powder diffraction an orthorhombic to monoclinic distortion ($Pnma$ to $P2_1/m$, $\beta \sim 90.2^\circ$) transition at $\sim 200\text{K}$. The monoclinic phase accounts well of the charge ordering (CO) of Mn^{3+} and Mn^{4+} ions occurring in these compounds. This CO state consists of an alternating sequence along the c axis of MnO_6 octahedra occupied either by $\text{Mn}^{4+}/\text{Mn}^{3+}$ ions or uniquely by Mn^{3+} ions, the latter octahedra being highly "Jahn-Teller" distorted¹. This CO state shows similarities to the charge ordering observed in the parent compound $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ with the notable exceptions that 1) we do not observe a doubling of the crystallographic unit cell along the a axis, 2) we directly observed the monoclinic distortion through the splitting of characteristic peaks (e.g. 202). From the Mn magnetic point of view, $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{Nd}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ differ completely, the former being ferromagnetic below $T_C \sim 120\text{K}$, the latter exhibiting CE antiferromagnetism (AF) below $T_N \sim 140\text{K}$ with an additional ferromagnetic component (canting) below $\sim 70\text{K}$.

In $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, the CO monoclinic state collapses under the flow of synchrotron radiation (25 keV) below 30K. However, the kinetics of the CO state melting appeared to be strongly temperature dependent. A similar CO collapse was already reported in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ³ and was explained by the coexistence of AF-insulating and ferromagnetic-metallic phases whose relative ratio depends on X-ray illumination². This model can no more be used in our Nd based compounds since 1) $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ does not exhibit long range antiferromagnetism, 2) no photoinduced effect was observed in $\text{Nd}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ which exhibits the same magnetic structure than $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. Synchrotron and neutron (with and without external magnetic field) data will be presented and compared to existing models describing the effect of CO melting under different kinds of perturbation such as magnetic field or X-ray illumination.

[1] Park, J. H., Woodward, P.M., Parise, J. B., Reeder, R. J., Lubomirsky, I. & Stafsudd, O. (1999). *Chem. Mater.* 11, 177-183.

[2] Smolenskii, G. A., Isupov, V. A., Agranovskaya, A. I. & Krainik, N. N. (1960). *Soviet Physics Solid State* 2 (11), 2982-2985.

[3] Glazer, A. M. (1975). *Acta Cryst.* A31, 756-762.

[4] Jones, G. O. & Thomas, P. A., In Press, *Acta Cryst. B*.

[1] Millange F. "Low Temperature Orthorhombic to Monoclinic Transition Due to Size Effect in $\text{Nd}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$: Evidence for a New Type of Charge Ordering", *J. Solid State Chem.* (1996) 127:131

[2] Cox D.E. "Structural changes, clustering, and photoinduced phase segregation in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ", *Phys. Rev. B* (1998) 57:3305

[3] Kiryukhin V. "An X-ray-induced insulator-metal transition in a magnetoresistive manganite", *Nature* (1997) 386:813.