Structural and Magnetic Properties of the Novel $Sr_{1-x}Ba_xMnO_3$ Multiferroics

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The ABO_3 perovskite structure is a very simple cubic construction of octahedral transition metals that offer tremendous opportunities, when coupled with alkaline or rare earth elements, for the creation of diverse materials physics and chemistry and novel phenomena.

$SrMnO_3$ is no exception. Several years ago [1], we have demonstrated the creation of this metastable phase through an elaborate multistep synthesis process that allows the avoidance of its energetically more favorable hexagonal counterpart. $SrMnO_3$ is a cubic room temperature paramagnet with a magnetic transition to the G-type spin configuration at temperatures below ~230 K. Structurally, the spatial symmetry must be broken in response to the magnetic ordering but no clear evidence has been seen in the diffraction data [1]. Nonetheless, examining the structural trends of Ca and Ba substituted SrMnO3 revealed the development of severe local strains as a function of increasing the A-site ionic size that result from the stretching of the Mn-O bonds to values significantly beyond their equilibrium length all while maintaining 180° Mn-O-Mn bond angles, Fig. 1. As shown in the figure, the magnetic transition temperature, T_N, increases continuously from ~120 K of the distorted $CaMnO_3$ structure until it peaks at ~230 K at the cubic $SrMnO_3$ composition. Upon further substitution with the larger Ba ions, the unit cell volume continues to increase linearly but the T_N becomes partially suppressed. In reference, we successfully proposed an empirical equation that describes this T_N behavior in terms of bond-angles and *A*-site ionic size variance. It was clear from that work that local size variations lead to significant tensions and strains coupled with a locally broken spatial symmetry due to a delicate balance of long range magnetic ordering and short range fluctuations.

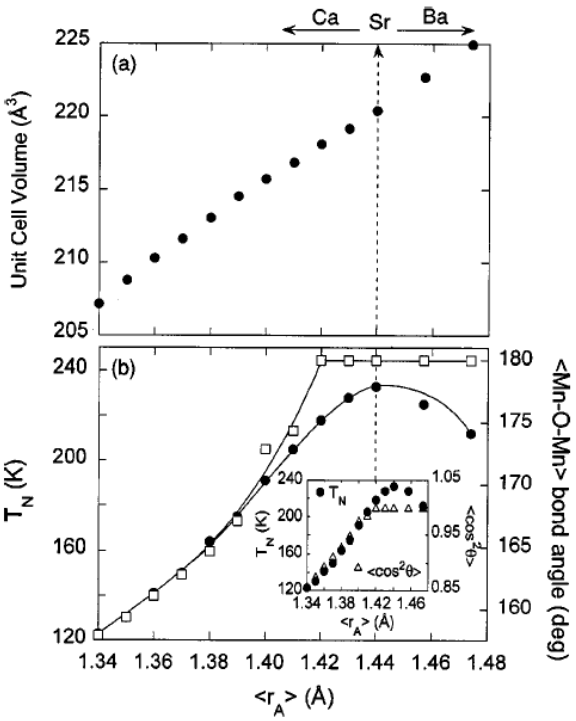

Figure 1 *(a) Room temperature unit-cell volume for $Sr_{1-x}Ca_xMnO_3$ and $Sr_{1-y}Ba_yMnO_3$. (b) T_N (filled circles) and (Mn-O-Mn) bond angle (θ) (open squares) as a function of $\langle r_A \rangle$; The inset shows T_N and $\langle \cos^2\theta \rangle$ (open triangles) plotted as a function of $\langle r_A \rangle$. Figure and caption from ref. [1]*

Recently, Sakai *et al*. [2] demonstrated the successful growth of $Sr_{1-x}Ba_xMnO_3$ single crystals grown under conditions well beyond their thermodynamic equilibrium. Using this method, the Tokura group was able to extend the solubility limit of these materials to x ~ 0.5 but

most importantly they observed high temperature ferroelectric properties (T_E ~350-400 K) and huge polarization values of ~25 $\mu C/m^2$ comparable with the best values achieved in $BaTiO_3$ based ferroelectrics. Additionally, these heavily substituted compositions were found to remain antiferromagnetic as expected but with lower T_N's (~200 K). As such, $Sr_{1-x}Ba_xMnO_3$ materials are considered to be unique true multiferroics in which both the ferroelectric and magnetic order parameters occur at the same Mn sublattice. At the same time, a large number of published theoretical papers highlight the high multiferroic potential of pure and substituted $SrMnO_3$ when subjected to large internal or external pressures [see for example refs 3-8].

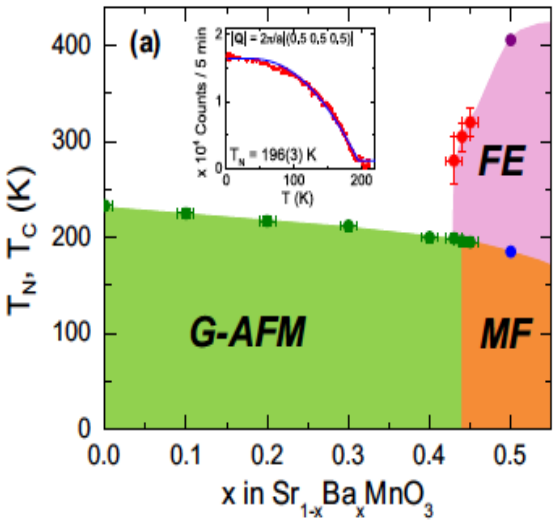

Figure 2 *Phase diagram of $Sr_{1-x}Ba_xMnO_3$ showing extended solubility in which severely strained compositions exhibit multiferroic properties with strongly coupled order parameters. Sakai's data* [2] *also included. Figure from Refs 9-10.*

Recently, we have successfully further developed our synthesis methods and have been able to extend the solubility limit of the $Sr_{1-x}Ba_xMnO_3$ phase diagram in bulk materials [9,10] to approach substitution levels close to those achieved by Sakai's single crystals. Similar ferroelectric and magnetic properties were measured for our compositions with x > 0.43. Preliminary neutron diffraction data collected at POWGEN show a series of structural and magnetic transitions that correlate with T_E and T_N's. Partial or full suppression of the magnetic transition temperature is observed as a function of the Ba content. In this talk, I will present the bulk of our measurements and discuss the materials magnetic and nuclear structures and their correlation to their physical properties.

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