Multiferroic behaviour in Sm$_{1-x}$Y$_x$MnO$_3$

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Abstract. We have successfully induced multiferroic behaviour in SmMnO$_3$ by the substitution of Y at the Sm site. Detailed investigations on polycrystalline Sm$_{1-x}$Y$_x$MnO$_3$ ($0 \leq x \leq 0.6$) compounds show that as $x$ is increased, an additional magnetic transition is seen at $\sim 21$ K, for substitution levels around $x = 0.4$. The dielectric properties investigated in the compounds in this temperature range reveal an anomaly coincident with the magnetic transition, indicative of a transition similar to that seen in multiferroics such as TbMnO$_3$. Magnetic and dielectric properties of this new multiferroic system are presented.

1. Introduction

Of a range of materials which exhibit coupling between magnetic and ferroelectric properties, the manganite compounds $R$MnO$_3$ ($R =$ rare earth) have attracted the most interest. The dielectric properties of these materials are highly sensitive to applied magnetic fields, as the ferroelectricity is induced by the complex magnetic ordering, typical of frustrated magnets. For example, in TbMnO$_3$ and DyMnO$_3$, a spontaneous electric polarisation was found to develop due to magnetic ordering, with the application of a magnetic field allowing the direction of this polarisation to be changed [1–3].

TbMnO$_3$ exhibits an incommensurate collinear magnetic order at $T_N \sim 41$ K, with ferroelectric order emerging only at the incommensurate to nearly-commensurate ‘lock-in’ transition at $T_{lock} \sim 27$ K, where the Mn$^{3+}$ magnetic moments become cycloidal ordered. The nature of the coupling between the magnetic and ferroelectric properties in TbMnO$_3$ has been investigated in great depth [4, 5].

Varying the stoichiometry of the $R$MnO$_3$ compounds by substitution at either the $R$ or Mn site allows us to investigate a very wide range of materials and provides us with a handle to tune different physical and magnetic properties in a subtle manner. For example, the compound Eu$_{0.75}$Y$_{0.25}$MnO$_3$ has been shown to exhibit magnetic and dielectric properties which resemble those of TbMnO$_3$ and DyMnO$_3$ [6, 7]. Similar substitution studies can be extended to other non-ferroelectric $R$MnO$_3$ compounds, with a view to inducing multiferroic behaviour.

The $R$MnO$_3$ compounds for $R =$ La–Ho have an orthorhombically distorted perovskite structure (space group $Pbmm$), with a central Mn atom surrounded by an octahedron of oxygen atoms. It is known that the Mn-O-Mn bond angle, $\phi$, is the key structural parameter that can be used for tuning the $R$MnO$_3$ structure, such that it exhibits the additional magnetic order essential in causing multiferroic properties [2, 8]. This angle determines the local distortions in the structure, by measuring the degree of tilting of the Mn-O octahedra. The interaction between the magnetic rare earth moments and Mn$^{3+}$ moments is also thought to be vital to the
Mn\textsuperscript{3+} cycloidal magnetic ordering. The manganites with larger rare earth ionic radius (R = La, Sm, Eu) exhibit non-ferroelectric A-type antiferromagnetic order. As the Mn-O-Mn bond angle \( \phi \) decreases with decreasing rare earth ionic radius [9], the magnetic frustration increases, resulting in the emergence of the cycloidal magnetic ground state, as in the case of TbMnO\textsubscript{3} and DyMnO\textsubscript{3}.

In order to understand the emergence of multiferroic behaviour in the R\text{MnO}_3 compounds, it is highly desirable to study the effects of lattice modulation without the interference from contributions due to large rare earth moments. We have chosen to study the effects in Sm\text{MnO}_3 by substitution at the Sm site with a smaller, non-magnetic dopant, Y, which also reduces the effective moment at the Sm site. We present the results of the study of the coupling between the magnetic and dielectric properties of Sm\(_{1-x}\)Y\(_x\)MnO\(_3\) for 0 \( \leq x \leq 0.6\).

2. Experimental Detail
Polycrystalline samples of Sm\(_{1-x}\)Y\(_x\)MnO\(_3\) (0 \( \leq x \leq 0.6\)) were prepared by a solid state reaction method. Stoichiometric ratios of high purity (99.9\%) Sm\(_2\)O\(_3\), Y\(_2\)O\(_3\) and MnO\(_2\) were mixed well, ground and heated at 1100\(^\circ\)C for 12 hours. The reacted mixture was ground and heated again at 1400\(^\circ\)C for a further 24 hours. The resulting powders were then pressed into pellets and sintered at 1400\(^\circ\)C. X-ray powder diffraction with a Philips PW1720 generator was used to determine phase formation of the compounds. Magnetic properties were measured using a Quantum Design MPMS SQUID magnetometer, in an applied field of 100 Oe. For dielectric measurements, silver contacts were painted onto the pellets, which were then mounted on a multipurpose sample insert for a Quantum Design Physical Properties Measurement System (PPMS). The capacitance of the pellets was measured as a function of temperature at 10 kHz using an Agilent 4294A impedance analyser, and the dielectric constant values were directly inferred.

3. Results and Discussion
3.1. X-ray Powder Diffraction
Powder X-ray diffraction of Sm\(_{1-x}\)Y\(_x\)MnO\(_3\) showed that the compounds were single phase for 0 \( \leq x \leq 0.5\) (Figure 1). Traces of impurity phases could be seen in samples with \( x \geq 0.6\), indicating that this was the solubility limit. It was not possible to refine oxygen positions to a good accuracy from the powder X-ray data, and so the definite values of the Mn-O-Mn bond angles could not be determined by this method. It is clear from examining the phase diagram

![Figure 1. X-ray diffraction patterns for Sm\(_{1-x}\)Y\(_x\)MnO\(_3\)](image)

![Figure 2. Magnetic susceptibility versus temperature for Sm\(_{1-x}\)Y\(_x\)MnO\(_3\) (H=100 Oe)](image)
proposed by Goto et al. [2] that the cycloidal magnetic ordering, and therefore the multiferroic properties, are seen in compounds which have a Mn-O-Mn bond angle close to 145°, as in the case of TbMnO$_3$. Detailed neutron powder diffraction studies are needed to confirm that the Mn-O-Mn bond angle is of a similar value in our samples.

3.2. Magnetic Properties

Pure SmMnO$_3$ is known to exhibit a magnetic transition due to the ordering of the Mn$^{3+}$ spins at $T_N \sim 60$ K [10]. The Néel temperature measured in our samples shows a drop from this value to $\sim 48$ K for $x = 0.4$ and $\sim 46$ K for $x = 0.5$. The size of the observed magnetic susceptibility in the Y-doped samples is seen to decrease by two orders of magnitude from the parent compound. In SmMnO$_3$, there is a small canting of the Mn$^{3+}$ moments, causing a weak ferromagnetic component of the magnetisation. By doping at the Sm site with non-magnetic Y, this ferromagnetic component is rapidly suppressed. Magnetic susceptibility versus temperature plots on the Y substituted compounds show a new, additional magnetic transition developing at $T \sim 21$ K as the doping is increased to $x = 0.4$, and at $T \sim 19$ K for $x = 0.5$ (Figure 2). These temperatures are similar to those of the transitions seen in TbMnO$_3$ and DyMnO$_3$ where the Mn$^{3+}$ moments show a cycloidal ordering. The transition in Sm$_{1-x}$Y$_x$MnO$_3$ is subtle, and appears smeared out due to the polycrystalline nature of the samples. More recent measurements made by us on oriented single crystals indicate a more pronounced cusp in the magnetic susceptibility at this transition [11].

3.3. Dielectric Properties

Measurements of the dielectric properties of the Sm$_{1-x}$Y$_x$MnO$_3$ compounds show that for pure SmMnO$_3$, the dielectric constant decreases smoothly with decreasing temperature, and is featureless. The overall trend seems to be that the magnitude of the dielectric constant decreases with increasing $x$. A well defined peak in the dielectric constant begins to develop as $x$ is increased, being most pronounced for $x = 0.4$ and 0.5 (Figure 3). The peak is observed at the same temperature (19–21 K) at which the cusp in the magnetic susceptibility is seen for both these compositions. This is a clear indication of the coupling between magnetic and dielectric properties in these compounds, similar to that seen in other $R$MnO$_3$ compounds which

![Figure 3. Dielectric constant versus temperature for Sm$_{1-x}$Y$_x$MnO$_3$, measured at 10 kHz](image-url)
exhibit multiferroic behaviour. The exact nature of the magnetic ordering that is responsible for the anomaly in the dielectric properties has to be established. Detailed measurements of the spontaneous electric polarisation are currently being carried out on oriented single crystal specimens.

4. Conclusion
By substituting Sm with Y in SmMnO$_3$, multiferroic properties have been induced. The occurrence of local structural distortions in the Mn-O octahedra brought about by this doping has led to the observation of clearly coupled magnetic and dielectric transitions at $\sim$20 K for substitution levels around $x = 0.4$–$0.5$. Our results indicate that this lattice distortion possibly causes a change in the Mn-O-Mn bond angle sufficient to induce cycloidal magnetic order in Sm$_{1-x}$Y$_x$MnO$_3$, thereby giving rise to multiferroic properties. Detailed measurements of the multiferroic properties of this system are currently being carried out on single crystal specimens. Investigations of the exact nature of the magnetic order in these compounds are essential in order to understand the coupling mechanism.

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