Magnetic and electric response in multiferroic manganites
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Summary

Multiferroics are materials that display spontaneous ferroelectric and magnetic ordering at the same time. Magnetoelectrics are materials in which an electric polarization can be induced by an applied magnetic field. The cross-coupling between the magnetism and ferroelectricity can potentially be exploited in the construction of novel, multifunctional spintronic devices. However, there are still rather few multiferroics known and the magneto(di)electric coupling in many of them is too weak to be useful for applications. Therefore, a better understanding of the mechanisms of magneto(di)electric coupling is required, as well as finding parameters by which the coupling may be controlled.

There are several typical mechanisms by which multiferroic behaviour can be generated, including ferroelectricity that is induced by spiral magnetic ordering. In this thesis, we mainly focus on investigating the magnetoelectric coupling in spin-spiral systems because the polarization is often highly tuneable using applied magnetic fields, a useful property for future applications. We choose two systems in this class of materials; the orthorhombic rare-earth manganites $R\text{MnO}_3$ and the chromate spinels $M\text{Cr}_2\text{O}_4$. In the $R\text{MnO}_3$ system, we have investigated both the effect of substituting the $R^{3+}$ cation by divalent $\text{Ca}^{2+}$, and the effect of mixing a non-magnetic rare-earth ($\text{Eu}^{3+}$) with a strongly magnetic rare-earth ($\text{Ho}^{3+}$). The aim of these investigations was to find parameters that enable systematic control of the electric and magnetic properties and the coupling between them. In the spinel $M\text{Cr}_2\text{O}_4$, the investigation was focused on understanding the mechanism of the magnetodielectric coupling present in this system.

Another of our investigations focused on better understanding the magnetodielectric coupling in linear magnetoelectric materials. Based on crystallographic and magnetic symmetry arguments we identified $\text{MnTiO}_3$ as a magnetoelectric material. We have used Landau theory to model the experimentally measured magnetodielectric phenomena in this compound.

In Chapter 1, we introduce and explain the terms “multiferroic”, “magnetoelectric” and “magnetodielectric” and the relations between them. We briefly give an overview of known multiferroic materials including the early history of multiferroics, recent discoveries that have led to a revival of
interest in this field, and a general classification of multiferroics with examples and basic theory. We also describe the general issues and goals that have motivated our study.

Chapter 2 focuses on the experimental techniques used in our studies, which involve the preparation of single-crystal samples, structural characterization and physical measurements. Details of standard magnetization, dielectric, and pyroelectric measurements and special techniques such as single crystal neutron diffraction are discussed.

Chapter 3 discusses the effect of Ca-doping in single-crystal Tb$_{1-x}$Ca$_x$MnO$_3$ ($x \leq 0.1$) on the crystal and magnetic structures, magnetocapacitance, and electric polarization. We demonstrate that the presence of Mn$^{4+}$ ions on the perovskite $B$-site plays a significant role in causing the ferroelectricity to disappear with doping. We explain this behavior in terms of the perovskite tolerance factor, a general concept that can be used to predict the ferroelectricity in this system. We also demonstrate the existence of an intermediate state at $x = 0.05$ that resembles a relaxor ferroelectric. Neutron diffraction indicates that the coherence length of the Mn spin-spiral decreases in this composition, without a change in the Mn-spin modulation wavevector. We claim that this forms a new class of relaxor ferroelectrics.

In Chapter 4 we present the phenomenon of a magnetic-field induced ferroelectric to relaxor crossover in Tb$_{0.98}$Ca$_{0.02}$MnO$_3$. This effect can be explained based on a decreasing coherence length of the Mn spin-spiral structure with increasing magnetic field. We propose that the electron hopping rate increases with magnetic field and is responsible for the decreased spiral coherence length. We also show that the wavevector of the Mn spin-spiral structure in Tb$_{0.98}$Ca$_{0.02}$MnO$_3$ does not change at the critical field of 6 T required to induce a polarization flop, which is in contrast to undoped TbMnO$_3$. These results imply that a rotation of the spin-spiral plane with magnetic field plays a more important role in the mechanism of the polarization flop than a transition from an incommensurate to commensurate spin structure.

In Chapter 5 we investigate the effect of doping EuMnO$_3$ with Ho$^{3+}$ in order to compare the magnetic-electric phase diagrams of RMnO$_3$ systems with and without magnetic ordering on the rare-earth site. In the absence of an applied magnetic field, the decrease in the average ionic radius of the rare-earth site with increasing Ho$^{3+}$ content gives rise to behavior resembling that of undoped RMnO$_3$; the ordered Mn spin sublattice evolves from a canted A-type configuration for $x = 0.2$ to a spiral structure at higher doping. We demonstrate that the magnetic moment of the A-site spins might stabilize the Mn-spiral in the $bc$ plane, giving rise to spontaneous polarization along the $c$-axis. However, the polarization decreases as the Ho$^{3+}$ content increases beyond $x = 0.75$, contrary to expectations based on the perovskite tolerance factor. We suggest that this phenomenon is due to a decreasing coherence length or spin component of the spin-spiral structure. When a magnetic field is applied along the $b$-direction, the critical field required to induce a flop of the polarization
to the \( a \)-axis for the \( x = 0.4 \) and \( x = 0.5 \) samples is lower than that in \( \mathrm{TbMnO}_3 \), indicating that the anisotropy of the rare-earth site plays an important role. Moreover, the temperature and field region over which the “flopped” \( ab \)-plane spiral structure is stable is also affected by the \( \mathrm{Ho}^{3+} \) concentration. Based on magnetic and dielectric measurements we construct a magnetic-electric phase diagram for \( \text{Eu}_{1-x}\mathrm{Ho}_x\mathrm{MnO}_3 \).

In Chapter 6, we study the nature of the magnetodielectric coupling in polycrystalline samples of the spinel \( M\mathrm{Cr}_2\mathrm{O}_4 \) (\( M = \text{Mn}, \text{Co}, \text{and Ni} \)). We demonstrate that the residual dielectric constant, that is, the deviation from the high-temperature extrapolated value, increases in the order \( \mathrm{MnCr}_2\mathrm{O}_4 \), \( \mathrm{CoCr}_2\mathrm{O}_4 \) and \( \mathrm{NiCr}_2\mathrm{O}_4 \). This indicates that the spin-orbit coupling and orbital degree of freedom on the tetrahedral site makes a significant contribution to the magnetodielectric coupling. We show that the magnetodielectric response scales approximately with the square of the magnetization \( M^2 \), indicating that the origin of the magnetodielectric coupling in this system is due to the term \( P^2M^2 \) in the Landau free energy expansion.

Finally, in Chapter 7 we use polarization measurements to present experimental evidence for the presence of the linear magnetoelectric effect in \( \mathrm{MnTiO}_3 \), where the electrical polarization is induced by an applied magnetic field. We demonstrate that there is no dielectric anomaly at the onset of magnetic ordering in the absence of magnetic field. This observation is in contrast to previous suggestions that magnetoelectric materials always display strong magnetodielectric coupling. A dielectric anomaly at the magnetic ordering temperature is only observed when a magnetic field is applied. We explain this phenomenon using Landau theory. We find that the dielectric anomalies are linearly correlated with the square of the magnetic field.