Magnetodielectric coupling in MnCr$_2$O$_4$ spinel

N. Mufti, G.R. Blake, T.T.M. Palstra

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands

ARTICLE INFO

Available online 11 February 2009

Keyword:
Magnetoelectric
Multiferroic
Spinel

ABSTRACT

We have investigated the magnetic and dielectric properties of polycrystalline samples of the spinel MnCr$_2$O$_4$. Below the ferrimagnetic ordering temperature at $T_f \approx 43$ K, both magnetization and dielectric measurements show signatures of the onset of a conical structure at $T_C \approx 17$ K and a lock-in temperature at $T_S \approx 14$ K. These values are similar to those previously reported for single-crystal samples, where the spiral structure is short-range ordered (SRO) at low temperatures. The application of magnetic field suppresses the dielectric anomaly at $T_f$, indicating that the coherence length of the ordering increases. MnCr$_2$O$_4$ exhibits a symmetrical magnetodielectric response between $T_f$ and $T_S$ that scales with the square of the magnetization. This suggests that the magnetodielectric coupling originates from the $P^2M^2$ term in the free energy expansion. The magnetodielectric response becomes asymmetric with respect to field below $T_f$.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Multiferroics, materials in which ferromagnetism and ferroelectricity coexist, have attracted much attention in recent years. If the coupling between the magnetic and ferroelectric order (magnetodielectric coupling) is strong enough, multiferroics potentially allow the manipulation of electric and magnetic moments by magnetic and electric fields, respectively. However, there are still rather few multiferroics known and the magnetodielectric (MD) coupling in many of them is weak. This is largely due to the fact that in typical ferroelectric oxides the creation of an electric dipole moment involves charge transfer between the occupied 2p-orbitals of oxygen and the empty d-shell of the metal ions. The common mechanism of ferroelectricity thus excludes transition metals with partially filled d-orbitals and hence the coexistence of magnetic moments and ferroelectric order [1]. Nevertheless, in recent years an increasing number of multiferroics have been discovered in which ferroelectricity arises from different mechanisms. For example, ferroelectricity can be directly induced by frustrated magnetic ordering in materials such as TbMnO$_3$, TbMn$_2$O$_5$, and Ni$_2$V$_2$O$_8$ [1–4], which naturally leads to strong magnetodielectric coupling. One feature common to many of the frustrated magnet multiferroics is the existence of a spiral or helical spin structure. Here, the direction of the spontaneous polarization is perpendicular to both the magnetic propagation vector and to the spin plane of the spiral. Although the microscopic mechanisms involved in the magnetodielectric coupling in this class of multiferroics are being widely studied both experimentally and theoretically, in many cases the mechanisms are not fully understood, especially regarding the strength of the coupling. Therefore, it is important to investigate magnetodielectric coupling in a wide range of frustrated magnet multiferroics.

The materials MCr$_2$O$_4$ (M = Mn and Co) are ferromagnetic spinels, in which the M$^{2+}$ cations occupy the tetrahedral (A) sites and the Cr$^{3+}$ cations occupy the octahedral (B) sites. The onset of collinear ferrimagnetic ordering occurs at 51 and 93 K in single-crystal samples, respectively [5]. A further magnetic transition occurs at $T_f \approx 18$ and 26 K, respectively, where a short-range-ordered (SRO) spiral component develops giving a conical magnetic structure. The largest coherence lengths of the spiral at low temperatures are of the order of 10 nm for MnCr$_2$O$_4$ and 3.5 nm for CoCr$_2$O$_4$, respectively. Nevertheless, whatever the correlation length of the spiral, it is thought to be the result of weak geometrical frustration on the spinel B-site; magnetic exchange interactions between the A and B sites limit but do not completely suppress the frustration. Recently, Yamasaki et al. have reported the presence of ferroelectricity in CoCr$_2$O$_4$ single crystals [7], making it one of the few materials to exhibit the coexistence of ferromagnetic and ferroelectric states. The onset of polarization occurs at $T_f \approx 26$ K along the (110) direction and the polarization can be reversed by switching the direction of the applied magnetic field. This strong magnetodielectric coupling is in good agreement with the theoretical prediction of the spin current model for magnetic ferroelectricity proposed by Katsura et al. [8]. These results prompted us to investigate the magnetic and dielectric properties of MnCr$_2$O$_4$, which has a similar magnetic structure to that of CoCr$_2$O$_4$. Moreover, the nature of

* Corresponding author. Tel.: +31 50 363 4440; fax: +31 50 363 4441. E-mail address: t.t.m.palstra@rug.nl (T.T.M. Palstra).

0304-8853/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2009.02.023
the magnetodielectric coupling in these systems has been little explored.

2. Experiment

Polycrystalline MnCr₂O₄ was prepared by solid state reaction using a stoichiometric mixture of MnO₂ and Cr₂O₃. The mixture was pelletized by applying hydraulic pressure at 600 bar and sintered at 1300°C in flowing argon for 24 h. X-ray powder diffraction at room temperature was performed using a Bruker D8 diffractometer with Cu-Kα radiation. Magnetization measurements were performed using a Quantum Design MPMS-7 SQUID magnetometer. The capacitance was measured using an AH-2500A capacitance bridge and a Quantum Design PPMS.

3. Results and discussion

Room-temperature powder X-ray diffraction measurements showed that the MnCr₂O₄ sample was single-phase; MnCr₂O₄ adopts the cubic spinel structure with space group Fd-3m. The lattice parameter of our sample was 8.3970(9) Å, close to the previously reported value of 8.410 Å [9].

The magnetic susceptibility of MnCr₂O₄ at different magnetic fields is shown in Fig. 1 (a). The onset of ferrimagnetic ordering at $T_N$=43 K at 0.1 T is close to the value previously reported for polycrystalline samples at 45 K [9], but lower than that reported for single crystals at 51 K [5]. The value of $T_N$ initially increases with applied magnetic field and then becomes difficult to identify, as the transition becomes broader. We also observe anomalies at $T_s$=18 K and $T_f$=15 K, which correspond to the temperatures where the spiral component appears and to the “lock-in” transition at which the spiral becomes fully developed, as reported by Tomiyasu et al. [5]. The behavior of our polycrystalline sample thus resembles that of single crystals, in contrast to the polycrystalline samples of CoCr₂O₄ studied by Lawes et al. [6], for which it was argued from specific heat data that the correlation length of the spiral state is sample dependent; in the polycrystalline samples a long-range ordered (LRO) spiral develops below $T_s$ [6].

The temperature dependence of the dielectric constant of MnCr₂O₄ is shown in Fig. 1 (b). Three anomalies are apparent at approximately the same temperatures as the magnetic transitions. This result is more similar to the dielectric properties of single-crystal CoCr₂O₄ [7] than those of polycrystalline samples, for which no dielectric anomaly was observed at $T_s$ [6]. The small difference in transition temperatures between the magnetization and dielectric measurements is probably due to differences in temperature between the sensor and sample during heating. When a magnetic field is applied, the dielectric anomalies at $T_N$=43 K and $T_f$=15 K are both suppressed. In the case of $T_f$, this is most likely due to the broadening of the ferrimagnetic transition that occurs with increasing magnetic field (see Fig. 1(a)). We suggest that the suppression of the dielectric anomaly at $T_f$ results from an increase of the correlation length of the magnetic spiral structure. We note that in the absence of a magnetic field MnCr₂O₄ has two sets of SRO spiral domains with propagation vectors parallel to the $[110]$ and $-[110]$ directions for an easy axis parallel to $[110]$; the correlation length is approximately 10 nm below $T_s$ [5]. When an external magnetic field is applied the spins will tend to align with the field, and consequently the propagation vectors in the two types of domains will also become aligned in the same direction. Therefore, we expect the correlation length of the spiral structure to increase with field, resulting in a suppression of the dielectric anomaly at $T_f$. This scenario is based on our dielectric and magnetic measurements, and further measurements such as neutron scattering are needed to confirm it.

Fig. 2 shows the magnetization and magnetodielectric response measured as a function of magnetic field at different temperatures below $T_N$. The most striking feature in the magnetization is a step-like increase at $H$=0.2 T; there is almost no difference in the behavior of the magnetization with field at representative temperatures below $T_f$ (5 K), $T_s$ (17 K), and $T_N$ (25 K). In contrast, magnetocapacitance measurements, shown in Fig. 2 (b), show unusual behavior in which the profile of the magnetocapacitance develops from an asymmetric shape at temperatures below $T_f$ to a symmetric shape in the region between $T_f$ and $T_s$. The magnetocapacitance is plotted in terms of the magnetodielectric response, defined as $MD = \varepsilon(H) - \varepsilon(0)/\varepsilon(0)$, where $\varepsilon(H)$ is the dielectric constant under field and $\varepsilon(0)$ is the dielectric constant in zero-field. Although our data are insufficient to fully explain the asymmetric magnetodielectric behavior, we suggest that the increasing correlation length of the spiral structure with increasing field below $T_f$ might be responsible. In this scenario we assume that the magnetodielectric response on going from the SRO (low magnetic field) to LRO (high magnetic field) state is smaller than that arising in the opposite direction. Further investigation of the magnetodielectric response on single crystals might give a better understanding of this phenomenon. Similarly asymmetric behavior has previously been observed in Mn₃O₄, for which it was argued that the asymmetry is due to the magnetic hysteresis present at low temperatures [10]. We exclude this argument because we do not observe magnetic hysteresis in our magnetization measurements, as shown in the insert of Fig. 2 (a).
Fig. 3 shows superimposed plots of the magnetodielectric response and the square of the magnetization measured at 17 K; the magnetodielectric response is symmetric here. The response scales with the square of the magnetization. This suggests that the magnetodielectric coupling originates from the $P^2 M^2$ term in the free energy expansion, which is always allowed by symmetry in ferroelectromagnetic materials [11]. Nevertheless, the magnetodielectric effect in MnCr$_2$O$_4$ is much smaller compared to other multiferroics such as TbMnO$_3$, which has a magnetocapacitance of ~10%, even though the ferroelectricity in MnCr$_2$O$_4$ is also induced by the magnetic structure. This result indicates that improper ferroelectricity, such as ferroelectricity induced by the magnetic structure, is no guarantee of obtaining a large magnetodielectric effect.

4. Summary

We have investigated the magnetic and dielectric properties of polycrystalline samples of the spinel MnCr$_2$O$_4$. Both the magnetization and dielectric measurements resemble those of single-crystal samples [5], which is in contrast to a previous report of polycrystalline CoCr$_2$O$_4$ [6], for which the properties are sample dependent. The suppression of the dielectric anomaly at $T_f$ indicates that the correlation length of the conical magnetic structure increases with applied magnetic field. In the region between $T_s$ and $T_f$, MnCr$_2$O$_4$ exhibits symmetric magnetocapacitance that scales with the square of the magnetization. Thus, the magnetodielectric coupling in this state appears to originate from the $P^2 M^2$ term in the free energy. The magnetocapacitance becomes asymmetric with respect to field below $T_f$.

References