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FAST TRACK COMMUNICATION

Magnetic field induced ferroelectric to relaxor crossover in $Tb_{1-x}Ca_xMnO_3$

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Abstract

The influence of magnetic field on the electrical properties of $Tb_{1-x}Ca_xMnO_3$ has been investigated by means of dielectric, polarization and neutron diffraction measurements. A field of 6 T applied along the *b*-axis induces a crossover from ferroelectric to relaxor behavior for the $x = 0.02$ compound at temperatures close to the ferroelectric transition. The mechanism of this field induced crossover involves a decrease in the coherence length of the Mn-spin-spiral structure due to increasing electron hopping rates associated with double exchange. Moreover, a large negative magnetocapacitance is observed at the freezing temperature for $x = 0.05$, which originates from suppression of the relaxor state and thus represents a new mechanism of magnetocapacitance.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Much of the interest in multiferroic materials lies in the prospect of controlling charge by applying a magnetic field and controlling spin by applying a voltage. The ferroelectricity in $TbMnO_3$ can be controlled by an applied magnetic field [1]. For example, when a magnetic field is applied parallel to the *a*- or *b*-axis, the polarization vector rotates by 90° from the direction $P \parallel c$ to $P \parallel a$. This so-called polarization flop is accompanied by a large magnetocapacitance effect. In contrast, when a magnetic field is applied along the *c*-axis, the polarization is suppressed. Similar behavior has been observed for $DyMnO_3$ [2, 3]. The polarization in both of these materials is a consequence of a spiral-Mn-spin structure. The direction of the polarization is given by $\boldsymbol{P} \parallel \boldsymbol{e}_3 \times \boldsymbol{Q}$, where $\boldsymbol{e}_3 = \sum_i S_i \times S_{i+1}$ is the spin rotation axis of the spiral and $\boldsymbol{Q}$ is the propagation vector [4]. The direction of the polarization is thus perpendicular to both the spin rotation axis and the propagation vector. For $TbMnO_3$ the polarization flop coincides with a transformation from an incommensurate (IC) to commensurate Mn-spin configuration with propagation vector (0, 0.25, 0), whereas in $DyMnO_3$ no change in the propagation vector occurs with the polarization flop [5, 6]. In $TbMnO_3$, it had earlier been suggested that the change of incommensurability from $q_{Mn} = 0.28$ to 0.25 induces exchange striction, altering the Mn–O–Mn bond angles and leading to ferroelectricity [5, 7, 8]. However, Aliouane *et al* recently used neutron diffraction to demonstrate that the field induced polarization flop occurs due to a discontinuous rotation of the Mn spiral plane from the *bc* plane to the *ab* plane [9]. When a magnetic field is applied along the *a*-axis or *b*-axis, the spin rotation axis changes from the *a*-axis to the *c*-axis in both cases, while the propagation vector remains along the *b*-axis. Therefore, the polarization flops from the *c*-axis to the *a*-axis.

Previously, we reported on the dielectric and ferroelectric properties of low-doped $Tb_{1-x}Ca_xMnO_3$ with $x < 0.1$ [10]. It was demonstrated that on increasing the level of Ca doping, the ferroelectricity is gradually suppressed via an intermediate state at $x = 0.05$ with behavior resembling that of a relaxor–ferroelectric: a broad frequency-dependent peak in the real part of the temperature dependence of the dielectric susceptibility [11]. The intermediate state is associated with a decreased coherence length of the Mn-

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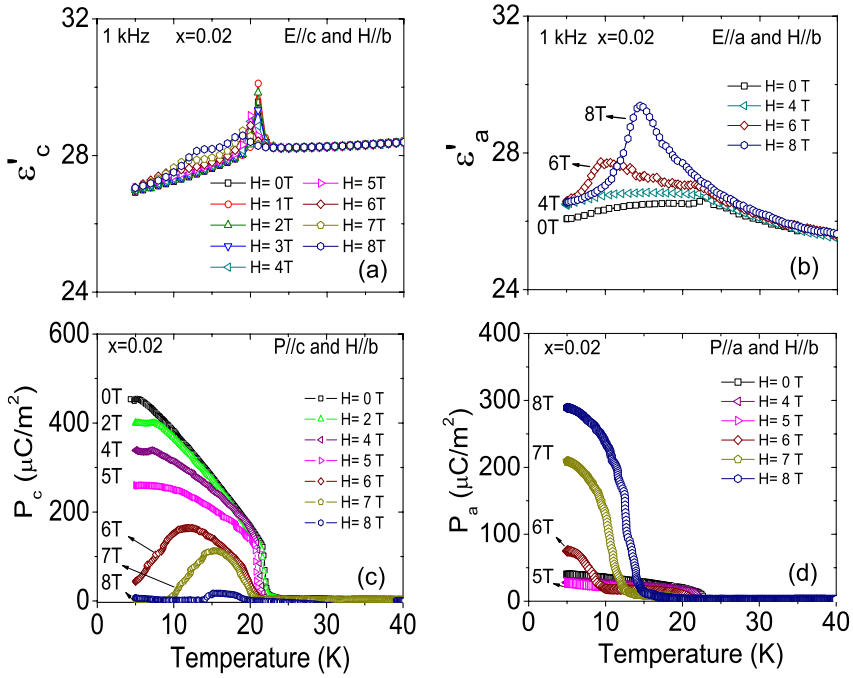

Figure 1. Temperature dependence of the dielectric constant of $Tb_{0.98}Ca_{0.02}MnO_3$ along (a) the c-axis and (b) the a-axis, measured at 1 kHz; temperature dependence of the spontaneous polarization along (c) the c-axis and (d) the a-axis for various magnetic fields applied along the b-axis.

spin-spiral structure caused by the weakening of the next-nearest-neighbor superexchange interactions [10]. The relaxor behavior in this system is induced by the magnetic structure and it thus represents a new class of relaxor–ferroelectric. Therefore, it is interesting to investigate the effect of applied magnetic field on $Tb_{1-x}Ca_xMnO_3$. We have used dielectric and neutron diffraction measurements to show that increasing the magnetic field along the b-axis induces a crossover from a ferroelectric to a relaxor–ferroelectric state for $x = 0.02$ at temperatures close to the ferroelectric transition. We also demonstrate a large negative magnetocapacitance at the freezing temperature for $x = 0.05$, which represents a new mechanism of magnetocapacitance.

2. Experimental details

Single crystals of $Tb_{1-x}Ca_xMnO_3$ were grown using a floating zone furnace [10]. Magnetic properties were measured using a Quantum Design MPMS-7 SQUID magnetometer. The dielectric constant was measured using an Agilent 4284A LCR meter and an Andeen-Hagerling 2500A capacitance bridge in combination with a Quantum Design Physical Properties Measurement System. Polarization measurements were performed using a Keithley 6517 electrometer; the samples were cooled in a poling electric field of ∼150 V mm^{-1}. Single-crystal neutron diffraction experiments were carried out at the Berlin Neutron Scattering Center (BENSC) using the double-axis E4 instrument. Single crystals of approximate size 5 mm × 5 mm were oriented with the bc plane in the scattering plane. Cooling and application of external magnetic fields up to 6 T were achieved using a horizontal cryomagnet HM1. This geometry allowed magnetic fields to be applied along either the b-axis or the c-axis of the crystal.

3. Experimental results

Figure 1 shows the temperature dependence of the dielectric constant (ε) and polarization (P) of $Tb_{0.98}Ca_{0.02}MnO_3$ parallel to the c-and a-axes in various magnetic fields applied along the b-axis. The magnetic field was applied at 50 K, and the sample was then cooled to 5 K in a field before measurements were taken on warming. At zero field we observe a sharp peak in the dielectric constant at $T \sim 21$ K for $E \parallel c$, which corresponds to the ferroelectric transition. For $E \parallel a$ this peak is much less pronounced. When a magnetic field is applied it becomes broader and shifts towards lower temperature at fields above 5 T ($T_C \sim 19$ K at $H = 8$ T). This is in contrast to the case for undoped $TbMnO_3$, for which the dielectric peak at the ferroelectric transition remains essentially unchanged in magnetic fields up to 9 T [1, 3]. At $H \geqslant 6$ T a second peak is apparent at $T \sim 12$ K, which shifts to higher temperature as the magnetic field increases. The spontaneous polarization $P \parallel c$ is strongly suppressed above 6 T at all temperatures and vanishes at 8 T. In contrast, for $P \parallel a$ the spontaneous polarization increases suddenly at 6 T and becomes larger with increasing magnetic field, while the onset of polarization shifts to higher temperature. This behavior is similar to that previously observed for undoped $TbMnO_3$, where the polarization flops from the c-axis to the a-axis with magnetic field applied along the b-axis or a-axis. However, the critical field required to flop the polarization in the $x = 0.02$ sample is slightly higher than that required for undoped $TbMnO_3$ (∼4 T for $H \parallel b$) [1, 3]. The small values of P_a measured in low fields are probably due to slight misalignment of the crystal and electrodes.

In order to investigate the origin of the broadened peak in $\varepsilon(T)$ at high magnetic field, we measured the temperature

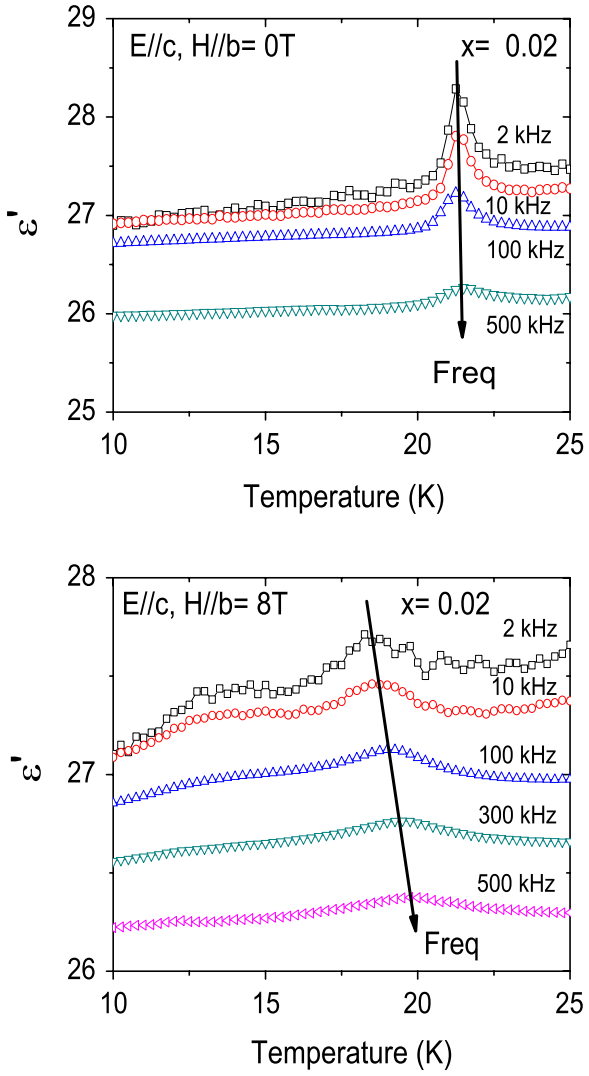

Figure 2. Temperature dependence of the dielectric constant of $Tb_{0.98}Ca_{0.02}MnO_3$ measured at various frequencies in zero field (upper panel) and in a field of $H = 8$ T applied along the b-axis (lower panel).

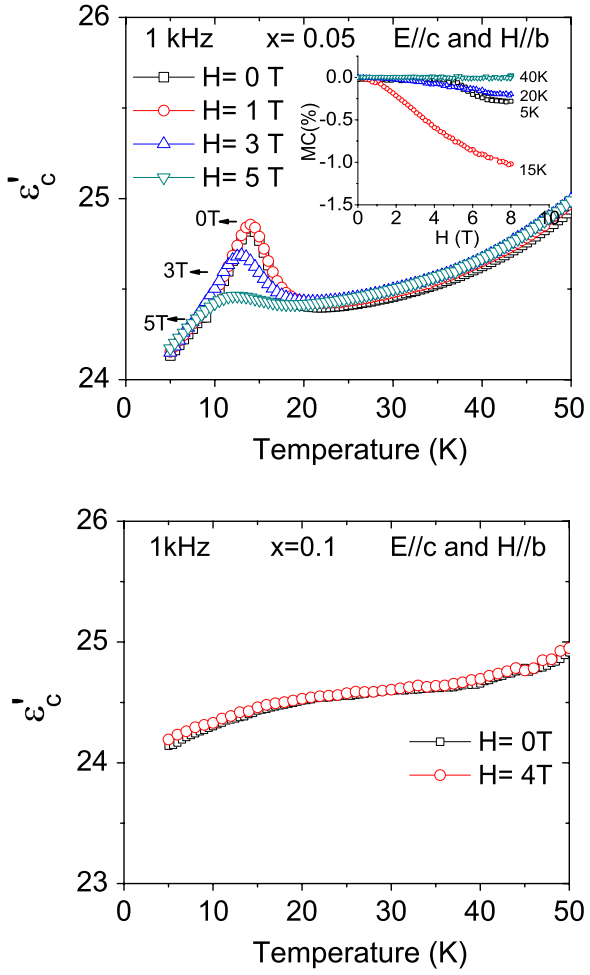

Figure 3. Temperature dependence of the dielectric constants of $Tb_{0.95}Ca_{0.05}MnO_3$ (upper panel) and $Tb_{0.90}Ca_{0.10}MnO_3$ (lower panel) for $E \parallel c$ at different magnetic fields. The magnetic field was applied along the b-axis. The inset shows the magnetic field dependence of the capacitance of $Tb_{0.95}Ca_{0.05}MnO_3$ at different temperatures.

dependence of the dielectric constant at different frequencies, both in the absence of a magnetic field and in a field of $H = 8$ T applied along the b-axis. As shown in figure 2, the position of the sharp peak in $\varepsilon(T)$ is independent of the frequency at zero field. However, in a field of $H = 8$ T the peak becomes broader and shifts to higher temperature as the frequency increases. These features are typical of a relaxor–ferroelectric state. A second peak at $T \sim 13$ K, which corresponds to the temperature at which the a-axis polarization appears, becomes less distinct at high frequency.

The dielectric constant of the $x = 0.05$ sample along the c-axis exhibits behavior typical of a relaxor–ferroelectric. We previously reported that the peak in dielectric constant is suppressed and shifted towards higher temperature with increasing frequency [10]. When a magnetic field is applied along the b-axis ($H \parallel b$), the peak in the dielectric constant is also suppressed, but shifted towards lower temperature (see figure 3). The maximum in this broad peak, at T_m, is associated with the dynamic freezing of the polar domains. The suppression of T_m with field indicates that the relaxor state gradually vanishes. The inset shows the magnetocapacitance of the $x = 0.05$ sample along the c-axis, defined as $[C(H) - C(0)]/C(0)$, where $C(H)$ is the capacitance measured in a field and $C(0)$ is the capacitance in zero field. The magnetocapacitance is negative at all temperatures, with the greatest magnitude at ~15 K, which corresponds to T_m. For the $x = 0.1$ sample, the temperature dependence of the dielectric constant does not show features typical of ferroelectric behavior. Moreover, the capacitance does not change on applying a magnetic field. This provides more evidence that the $x = 0.1$ composition is no longer ferroelectric, as reported previously [10].

In order to understand the ferroelectric properties of the $x = 0.02$ sample in more detail, we investigated the magnetic structure of the Mn sublattice in magnetic fields applied along the b-and c-axes using neutron diffraction. The crystal was mounted with the a-axis perpendicular to the scattering plane and to the magnet, allowing measurements to be performed in the bc plane. In this geometry all of the characteristic Mn-

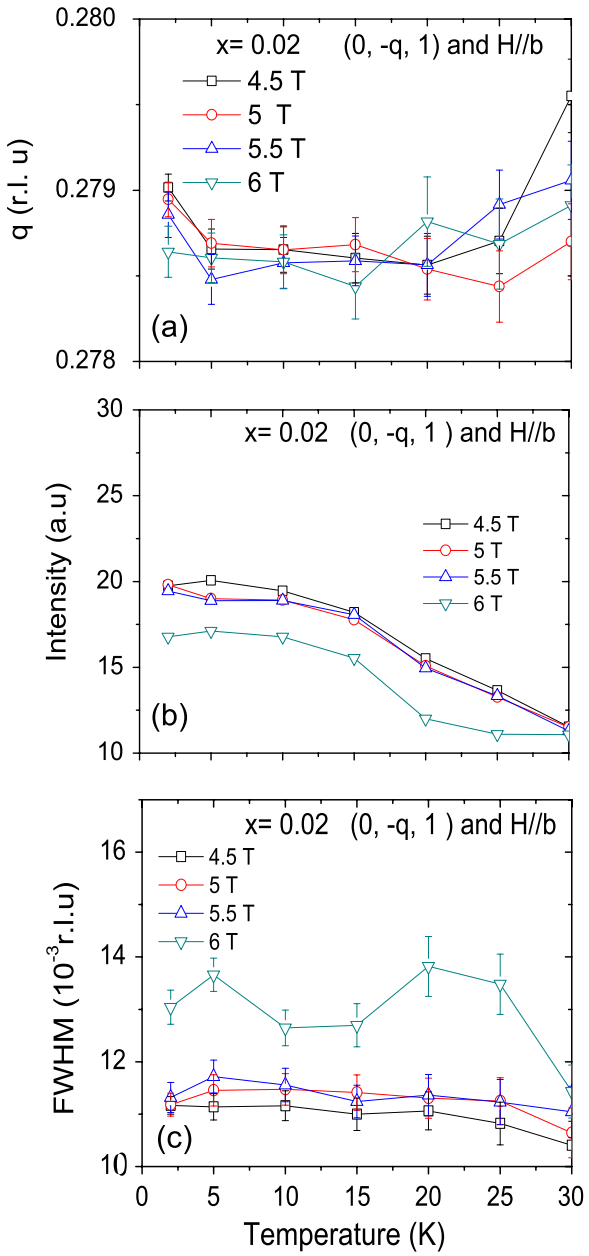

Figure 4. Temperature dependence of the (a) Mn-spin incommensurability (q_{Mn}) in reciprocal lattice units, (b) integrated intensity and (c) full width at half-maximum of the $(0, -q_{Mn}, 1)$ reflection of $Tb_{0.98}Ca_{0.02}MnO_3$ in magnetic fields applied along the b-axis.

and Tb-spin reflections are accessible: A-type ($h + k$ = even and l = odd), G-type ($h + k$ = odd and l = odd), C-type ($h + k$ = odd and l = even), and F-type ($h + k$ = even and l = even) [13]. We were only able to observe A-type reflections due to the large area of reciprocal space that was blocked by the bulky horizontal magnet. For $H \parallel b$, we followed the position, intensity and width of the first-harmonic A-type reflection $(0, -q_{Mn}, 1)$ in the range $q_{Mn} = 0.23$–0.31, collecting data at intervals of 0.002 reciprocal lattice units. We applied magnetic fields of between 4.5 and 6 T in steps of 0.5 T at various temperatures. The maximum of the A-type reflection lies at $q_{Mn} \sim 0.28$, which is similar to the value of q_{Mn} for

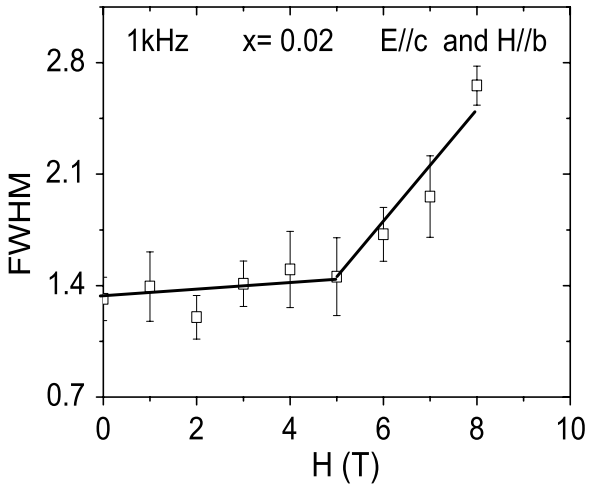

Figure 5. Full width at half-maximum of the dielectric peak at the ferroelectric transition temperature of $Tb_{0.98}Ca_{0.02}MnO_3$ as a function of the magnetic field applied along the b-axis.

undoped $TbMnO_3$ [1, 3]. In figure 4, we plot the temperature dependence of the incommensurability q_{Mn} and the integrated intensity and peak width of the $(0, -q_{Mn}, 1)$ reflection at various magnetic fields, obtained by fitting the peaks with a Gaussian function. We find that the incommensurability of $q_{Mn} \sim 0.28$ does not change in magnetic fields of up to 6 T applied along the b-direction. This behavior is in contrast to that of undoped $TbMnO_3$, in which the polarization flop is accompanied by a discontinuous change from $q_{Mn} = 0.28$ to 0.25 for both $H \parallel b$ and $H \parallel a$ [5]. The polarization flop in our $x = 0.02$ sample takes place at approximately $H = 6$ T, as shown in the dielectric and polarization measurements in figure 1. In figures 4(b) and (c) we observe that the integrated intensity decreases at $H = 6$ T while the peak width increases. This behavior indicates that the coherence length of the Mn-spin-spiral structure begins to decrease at 6 T, which is the maximum magnetic field obtainable with the horizontal-field magnet.

4. Discussion

The ferroelectric behavior of our $x = 0.02$ sample is similar to that of undoped $TbMnO_3$, where a magnetic field applied along the b-axis induces a polarization flop from the c-axis to the a-axis. However, the critical field required to flop the polarization is slightly higher for the $x = 0.02$ sample. The critical field depends on the magnetic exchange interactions and the magnetic anisotropy. If we assume that the contribution from the Tb^{3+} sublattice is the same as that in undoped $TbMnO_3$, the higher critical field for $x = 0.02$ might be associated with a weakening of the Mn next-nearest-neighbor superexchange interaction and decreasing magnetic anisotropy due to the existence of Mn^{4+}. As discussed in our previous study of this system [10], the Mn–O–Mn bond angle increases with increasing Ca concentration.

More information on the nature of the polarization flop in the $x = 0.02$ sample can be obtained by studying the behavior

of the dielectric constant close to the onset of ferroelectricity at T_c. The dielectric peak becomes broader and shifts to lower temperature as the magnetic field is increased above 5 T, as seen in figure 1(a). We fitted the dielectric peak using a Gaussian function and the resulting full width at half-maximum (FWHM) is shown as a function of field in figure 5. The FWHM is almost constant below 5 T and then increases with magnetic field above 5 T. This is different to the situation for undoped $TbMnO_3$, where the dielectric peak at the ferroelectric transition does not change in width with the magnetic field. We suggest that a transformation from the ferroelectric state to a relaxor state occurs at 5 T in the $x = 0.02$ sample. In other words, a magnetic field applied along the b-axis induces a ferroelectric to relaxor crossover. This hypothesis is supported by the frequency dependence of the dielectric constant shown in figure 2, where the dielectric peak remains sharp and almost frequency independent in the absence of magnetic field but is broader and frequency dependent in a field of 8 T. The relaxor behavior at high field might be related to a decrease of the coherence length of the spin spiral, as suggested by our neutron diffraction data at 6 T. Ferroelectric–relaxor crossover phenomena have previously been induced in conventional ferroelectrics, such as $KTaO_3$ doped with 1.2% Nb and $Pb(Zn_{1/3}Nb_{2/3})O_3$ doped with 5% of $PbTiO_3$, by the application of hydrostatic pressure. In these examples pressure causes a decrease in the correlation length of the dipolar interaction [11, 12]. A similar argument can be used to explain the magnetic field induced crossover in $Tb_{0.98}Ca_{0.02}MnO_3$. Doping with Ca leads to the presence of Mn^{4+} on the perovskite B site, which introduces double-exchange interactions with Mn^{3+}. When the magnetic field is increased, the electron hopping rate also increases. The electron hopping rate is proportional to $\cos(\theta/2)$, where θ is the misalignment angle between neighboring spins [14]. The increased occurrence of double exchange at high magnetic fields then causes a decrease in the coherence length of the spiral structure.

The second peak in ε_c at $T \sim 13$ K in a field of 8 T (see figure 2) corresponds to the temperature at which the c-axis polarization disappears and the a-axis polarization appears. Our neutron diffraction results show that the incommensuration of the $x = 0.02$ Mn spiral does not change (q_{Mn} remains at a value of 0.28) as the magnetic field is increased up to the critical field of 6 T. This is in contrast to the case for undoped $TbMnO_3$, where the polarization flop is accompanied by a first-order transition from an incommensurate spin structure with $q_{Mn} = 0.28$ to a commensurate structure with $q_{Mn} = 0.25$ [5]. These results support the scenario in which the mechanism of the polarization flop in multiferroic $RMnO_3$ involves a rotation of the spin-spiral plane and are in good agreement with the recent neutron diffraction study of Aliouane *et al* [9].

For the $x = 0.05$ sample, the application of a magnetic field along the b-axis gives rise to a suppression of the broad peak in ε_c (see figure 3). As reported in [10], the $x = 0.05$ sample displays behavior characteristic of a relaxor–ferroelectric even in zero field. Increasing the magnetic field will again lead to an increased occurrence of electron hopping associated with double exchange, thus decreasing the coherence length of the Mn-spin spiral further and hence decreasing T_m. Moreover, this field induced suppression of the relaxor–ferroelectric state leads to a new mechanism of magnetocapacitance; as shown in figure 3, the magnitude of the large negative magnetocapacitance is greatest at T_m.

5. Conclusion

We have investigated the behavior of $Tb_{1-x}Ca_xMnO_3$ with $x = 0.02, 0.05$ and 0.1 under a magnetic field. For $x = 0.02$, the application of magnetic fields greater than 5 T along the b-axis at temperatures close to the ferroelectric transition induces a crossover from ferroelectric to relaxor behavior. The mechanism of this crossover involves a decrease in the coherence length of the Mn-spin-spiral structure. For the $x = 0.05$ sample, the application of a magnetic field along the b-axis gives rise to large negative magnetocapacitance with a novel mechanism, in which the relaxor–ferroelectric state is suppressed by the field due to a decreasing coherence length of the Mn-spin-spiral structure.

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