Multiferroic nature of charge-ordered rare earth manganites

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Abstract
Charge-ordered rare earth manganites Nd$_{0.5}$Ca$_{0.5}$MnO$_3$, La$_{0.25}$Nd$_{0.25}$Ca$_{0.5}$MnO$_3$, Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ and Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ are found to exhibit dielectric constant anomalies around the charge-ordering or the antiferromagnetic transition temperatures. Magnetic fields have a marked effect on the dielectric properties, indicating the presence of coupling between the magnetic and electrical order parameters. The observation of magnetoferroelectricity in these manganites is in accord with the recent theoretical predictions of Khomskii and co-workers.

There has been intense interest in the study of multiferroics in recent years, and a few novel materials with multiferroic properties have indeed been discovered [1–5]. Multiferroics which exhibit coupling between the magnetic and electrical order parameters are of vital interest both academically and technologically. Coexistence of ferroelectricity and magnetism in transition metal oxide-based materials is generally not favoured since magnetism requires d-electrons and ferroelectricity does not. Magnetoelectric effects in many of the materials therefore occur by alternative mechanisms. Thus, magnetoelectric properties of rare earth manganates such as YMnO$_3$, TbMnO$_3$ and YMn$_2$O$_5$ arise due to the tilting of polyhedra or frustrated magnetism [6–8]. The 6s lone pair plays a crucial role in the magnetoelectric properties of bismuth-based materials such as BiFeO$_3$ and BiMnO$_3$ [9]. Recently, Khomskii and co-workers [10] have pointed out that coupling between magnetic and charge-ordering in charge-ordered and orbital-ordered perovskites can give rise to ferroelectric magnetism. Charge-ordering in the rare earth manganites, Ln$_{1-x}$Ca$_x$MnO$_3$, (Ln = rare earth) can be site-centred (SCO) or body-centred (BCO). The SCO behaviour occurs around $x = 0.5$ with a CE-type antiferromagnetic state while BCO can occur around $x = 0.4$ with a possible perpendicular spin structure. There is a report in the literature for the occurrence of a dielectric anomaly in Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ around the charge-ordering transition temperature [11]. Although magnetic
fields are noted to affect the dielectric properties of the manganites [12], there has been no definitive study of the effect of magnetic fields on the dielectric properties to establish whether there is coupling between the electrical and magnetic order parameters, especially in the manganite compositions corresponding to SCO and BCO. We have investigated the dielectric properties of Pr$_{0.7}$Ca$_{0.3}$MnO$_3$, Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ and Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ which have comparable radii of A-site cations, and exhibit charge-ordering in the 220–240 K region and an antiferromagnetic transition in the 130–170 K region. Electrical resistivity of these manganites is not affected significantly on application of magnetic fields up to 4 T.

Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ exhibits a charge-ordered transition at 240 K ($T_{CO}$), an antiferromagnetic transition at 140 K ($T_N$) and another transition to a canted antiferromagnetic state at around 50 K (figure 1(a)) [13]. The antiferromagnetic transition around 140 K, seen as a shoulder at low magnetic fields, cannot be easily discerned at higher fields. The transition around 50 K is also wiped out at high fields, the difference between the zero-field cooled and field-cooled data becoming negligible. The dielectric constant of Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ increases substantially in the region of $T_{CO}$ and $T_N$ showing a broad maximum, reaching a value of 500 or above. Application of a magnetic field of 3.3 T has a significant effect on the dielectric constant, showing an increase below $T_N$, as shown from figure 2. Pr$_{0.7}$Ca$_{0.3}$MnO$_3$, with a $T_{CO}$ of 225 K and $T_N$ of 130 K [14], shows a broad maximum in the dielectric constant around $T_{CO}$ with the value reaching 2000 or greater (figure 3). Application of a magnetic field of 2 T causes a marked increase in the dielectric constant below $T_{CO}$ as can be seen from figure 3. The results

Figure 1. Effect of magnetic fields on the magnetization behaviour of (a) Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ and (b) Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. Zero-field cooled and field-cooled data are shown as broken and full curves.
Figure 2. Temperature variation of the dielectric constant (1 MHz) of Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ in the absence and presence of a magnetic field ($H = 3.3$ T). The inset shows data at 30 kHz.

Figure 3. Temperature variation of the dielectric constant (1 MHz) of Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ in the absence and presence of a magnetic field ($H = 2$ T). The inset shows data at 30 kHz.

in figures 2 and 3 demonstrate that there is coupling between the electrical and magnetic order parameters in both Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ and Pr$_{0.7}$Ca$_{0.3}$MnO$_3$.

The case of Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ is of special interest because of the considerations mentioned earlier. This manganite exhibits a $T_{CO}$ of 240 K and $T_N$ of 170 K [14]. There is an additional magnetic transition around 50 K. With increasing field, the low-temperature transition is affected significantly, the material bearing exibitory greater ferromagnetic interactions. The dielectric constant of Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ shows a broad maximum around $T_N$ and the value is also high (figure 4). Application of a magnetic field of 2 T markedly affects the dielectric properties, as shown in figure 4. The sign of the magnetocapacitance effect changes with temperature, being negative near $T_N$, and positive near $T_{CO}$. We observe a crossing of the dielectric constant curves around a temperature between $T_{CO}$ and $T_N$. The magnetoelectric behaviour of this manganite is somewhat different from that of the Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ or Pr$_{0.7}$Ca$_{0.3}$MnO$_3$. The results, however, demonstrate the presence of magnetoelectricity in all the charge-ordered manganites studied by us as predicted by Khomskii and co-workers [10].
The present study of the charge-ordered manganites shows that many of the charge-ordered rare earth manganites are multiferroics showing magnetocapacitance. It is noteworthy that application of magnetic fields affects the magnetization behaviour of these materials, specially at low temperatures (figure 1). The manganites also exhibit certain other features. Thus, the broad maximum in the dielectric constant around $T_{CO}$ or $T_N$ becomes more prominent in the presence of the magnetic field in certain cases. The magnitude and sign of the magnetocapacitance effect depends on the frequency of measurement. It is generally better to employ a relatively high frequency, well above 10 kHz to obtain reliable data.

We have studied the dielectric properties of a few other charge-ordered rare earth manganites, $\text{La}_{0.25}\text{Nd}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ being one of them. This material exhibits a re-entrant ferromagnetic transition at a temperature lower than the charge-ordered transition. The charge-ordered transition is around 240 K and the ferromagnetic transition is at 150 K [15]. Interestingly, we find maxima in the dielectric constant at both $T_{CO}$ and $T_N$, the one at $T_{CO}$ being more prominent (figure 5).

Figure 4. Temperature variation of the dielectric constant (1 MHz) of $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ in the absence and presence of a magnetic field ($H = 2 \, \text{T}$). The inset shows data at 30 kHz.

Figure 5. Temperature variation of the dielectric constant of $\text{La}_{0.25}\text{Nd}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$. The hatched curve contains data taken in the 100 kHz–1 MHz range.
It is important to note some of the important characteristics of the charge-ordered manganites studied by us in order to fully understand their ferroic properties. The most important feature is that all the manganites exhibit electronic phase separation at low temperatures \( T < T_{CO} \) \[16\]. They exhibit a decrease in resistivity on application of large magnetic fields \( (> 4 \, T) \) \[16, 17\]. Application of electric fields also causes a significant decrease in the resistivity of the manganites \[17, 18\]. On the application of electric fields, the manganites show a magnetic response \[19\]. Such electric field-induced magnetization may also be taken as evidence for coupling between the electric and magnetic order parameters in the manganites. It is likely that grain boundaries between the different electronic phases have a role in determining the dielectric behaviour. The importance of grain boundaries in giving rise to high dielectric constants has indeed been recognized \[20, 21\]. In spite of the complexity of their electronic structure, the present study shows that the charge-ordered rare earth manganites possess multiferroic and magnetoelectric properties. Clearly, charge-ordering provides a novel route to multiferroic properties especially in the case of the manganites.

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