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Exchange bias in a mixed metal oxide based magnetocaloric compound $YFe_{0.5}Cr_{0.5}O_3$

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ABSTRACT

We report a detailed investigation of magnetization, magnetocaloric effect and exchange bias studies on a mixed metal oxide $YFe_{0.5}Cr_{0.5}O_3$ belonging to perovskite family. Our results reveal that the compound is in canted magnetic state (CMS) where ferromagnetic correlations are present in an antiferromagnetic state. Magnetic entropy change of this compound follows a power law ($\Delta S_M \sim H^m$) dependence of magnetic field. In this compound, inverse magnetocaloric effect (IMCE) is observed below 260 K while conventional magnetocaloric effect (CMCE) above it. The exponent 'm' is found to be independent of temperature and field only in the IMCE region. Investigation of temperature and magnetic field dependence studies of exchange bias, reveal a competition between effective Zeeman energy of the ferromagnetic regions and anisotropic exchange energy at the interface between ferromagnetic and antiferromagnetic regions. Variation of exchange bias due to temperature and field cycling is also investigated.

1. Introduction

Mixed metal oxides belonging to perovskite structure have attracted considerable attention in recent years by virtue of their interesting magnetic properties, which can be useful from the viewpoint of technological application and fundamental physics. The combination of 3d–3d or 3d–4d/5d element in a perovskite structured oxide of the form $AB'_{1-x}B''_xO_3$ (A=rare-earth ions, B′/B″=transition metal ions) forms one such mixed metal oxides. Investigations are being carried out on this new kind of half doped chromites and ferrites, $LnFe_{0.5}Cr_{0.5}O_3$, where Ln=La, Y and Dy [1–7]. Combining the two transitions metal within the perovskite structure can be an effective approach of enhance the magnetic property and at the same time tune/induce functional properties as compared to their parent compounds. For example $DyCrO_3$ shows large magnetocaloric effect (MCE) while $DyFeO_3$ shows magnetic field induced multiferroicity below Dy ordering temperature. However, $DyFe_{0.5}Cr_{0.5}O_3$ is significantly different showing a large magnetization and MCE enhanced by magnetoelectric coupling [6]. The compound $YFeO_3$ [8] and $YCrO_3$ [9] exhibit antiferromagnetic ordering around 640 and 140 K respectively along with a weak ferromagnetic behavior with no functional properties. In contrast, $YFe_{0.5}Cr_{0.5}O_3$ shows the phenomenon of magnetization reversal with a high compensation temperature [2].

Materials exhibiting magnetocaloric effect (MCE) is an active area of research in the area of magnetic condensed matter physics [10], as such materials can be used for solid-state cooling techniques. Such techniques offer a smart solution to the issues related to gas compression/expansion cycle. Additionally, a detailed study of the temperature and field dependence of MCE is helpful in gaining insight about the magnetic phase in a magnetic material and can also provide information about the performance of the material as a magnetic refrigerant.

In magnetic materials, presence of simultaneous ferromagnetic (FM)/antiferromagnetic(AFM) coupling results in the shift of magnetic hysteresis loop away from the centre of symmetry from its normal position when the loop taken in the different cooling field with respect to that taken in zero cooling field [11]. This phenomenon is known as Exchange bias (EB). EB has already been reported in some phase-separated bulk materials, FM/AFM multilayers and magnetic nanoparticles [12–15]. FM/AFM systems are important in understanding the core issues related to exchange bias such as possible origins of the hysteresis loop asymmetry [16–18]. Investigations of EB and its variation with physical parameters have attracted considerable attention in the field of magnetism due to their application in the fundamental science, ultrahigh density magnetic recording, giant magnetoresistance, spin valve, magnetic storage devices, magnetic switches, and magnetic random access memories [2,19–22]. Systems showing magnetization reversal are also useful for such applications. Recent studies have reported the coexistence of magnetization reversal and exchange bias in some transition metal oxides with the perovskite structure,

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e.g., $La_{0.2}Ce_{0.8}CrO_3$, Sr_2YbRuO_6, and $YbCrO_3$, [23–25]. It would be of great interest to study a compound, where, there is a coexistence of magnetization reversal and EB.

In this context, $YFe_{0.5}Cr_{0.5}O_3$ is an interesting system. Along with magnetization reversal at low applied field this compound shows the phenomenon of magnetic switching [2]. Observation of ferroelectricity and magnetoelectric effect at the magnetic ordering temperature (~260 K) is reported in compound [7]. Other studies suggest a relaxor-like dielectric behavior around 507 K, attributed to the disordered nature arising from random distribution of Fe^{3+} and Cr^{3+} ions [4]. However, to the best of our knowledge, a detailed and systematic analysis of the low field magnetic study of this compound under different temperature and magnetic field protocol is lacking in literature. Low field magnetic measurements are useful to identify the intrinsic signature of inhomogeneously magnetized system as high magnetic field can mask it. Even though some of the functional properties like observation of magnetocaloric effect [2] and exchange bias [26] is reported in literature, a detailed analysis of these properties are yet to be carried out.

In this work, through bulk magnetization measurements we investigate magnetic state of the sample $YFe_{0.5}Cr_{0.5}O_3$. Our results reveal that the compound is in a canted magnetic state (CMS) where ferromagnetic correlations coexist with antiferromagnetic correlations. Magnetocaloric properties of the compound is also studied which reveals that magnetic entropy change of this compound follows a power law dependence of magnetic field of the form $\Delta S_M \sim H^m$. This compound exhibited inverse magnetocaloric effect (IMCE) below 260 K while conventional magnetocaloric effect above it (CMCE). The exponent m is found to be independent of temperature and field only in the IMCE region. Additionally, temperature and magnetic field dependence studies of exchange bias reveal a competition between effective Zeeman energy of the FM regions and anisotropic exchange energy between FM/AFM interfaces. Effects of temperature and field cycles on exchange bias field are also investigated

2. Experimental

The compound $YFe_{0.5}Cr_{0.5}O_3$ (YFCO) is prepared by solid state reaction method. Y_2O_3, Fe_2O_3 and Cr_2O_3 procured from Sigma-Aldrich (purity > 99.9%) were taken in stoichiometric amount. After mixing, the powder is subjected to a heat treatment of 900 °C for 24 h. After that powder is regrind and heated at 1200 °C for 24 h. The resulting powder pressed in to pellets and sintered at 1300 °C for 24 h. The x-ray diffraction measurement at room temperature is carried out using Rigaku Smart Lab diffractometer with CuKα radiation (data is taken in angular step 0.02). The Rietveld refinement of the powder diffraction data of YFCO is performed by FullProf Suite software [27]. Temperature and magnetic field dependent magnetization data in the temperature range 2–390 K and magnetic field upto 50 kOe is collected by the Magnetic Property Measurements System (MPMS) from Quantum design, USA. Heat capacity measurement is performed using Physical Property Measurements System (PPMS) from Quantum design in zero magnetic field in temperature range 2–270 K.

3. Results and discussions

Fig. 1 shows the representative XRD pattern of YFCO. The sample is seen to be single phase and the XRD pattern is analysed by Rietveld profile refinement [28]. The analysis reveals that YFCO has orthorhombic crystal structure with Pnma space group. The lattice parameters, unit cell volume and atomic positions obtained

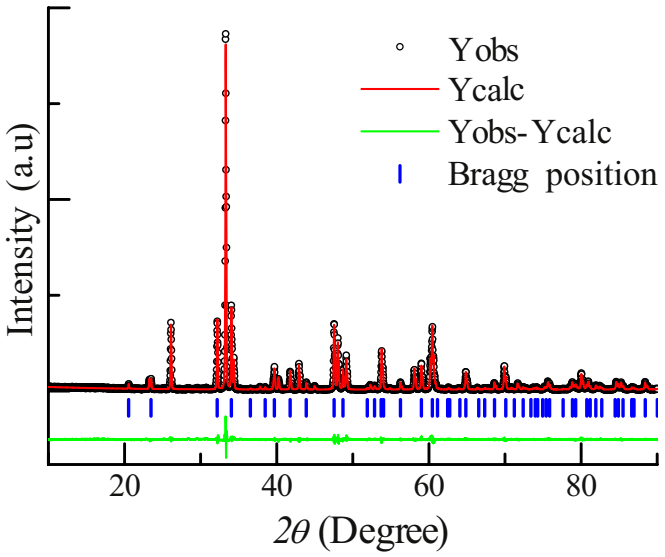

Fig. 1. X-ray diffraction patterns (Cu K_α) for $YFe_{0.5}Cr_{0.5}O_3$. The result of Rietveld analysis of the XRD pattern is also shown.

Table 1
Unit cell parameter and atomic positional parameter for $YFe_{0.5}Cr_{0.5}O_3$.

Lattice parameters			
a (Å)	b (Å)	c (Å)	V (Å^3)
5.5574 (3)	7.5689 (7)	5.2628 (2)	221.380 (9)
Bragg R-factor = 2.93	R_f-factor = 2.54		χ^2 = 2.11

Atomic positions				
	Site	x	y	z
Y	4c	0.0666	0.2500	0.9832
Fe	4b	0.5000	0.0000	0.0000
Cr	4b	0.5000	0.0000	0.0000
O1	4c	0.4638	0.2500	0.1071
O2	8d	0.3040	0.0551	0.6924

from Rietveld refinement of powder XRD data is tabulated in Table 1. The obtained lattice parameters match well with the reports on YFCO [2,4].

Even though there are couple of reports [2,7] about the temperature response of magnetization of this compound, we repeat this measurement under different temperature and field protocols. In Fig. 2, magnetization plot of YFCO in the temperature range 2–395 K under the Zero Field Cooling (ZFC), Field Cooled Cooling (FCC) and Field Cooled Warming (FCW) condition, at 100 Oe field is shown. In this compound magnetic ordering starts ~275 K [obtained from d(M/H)/dT vs. T plot (not shown)]. The ordering temperature is in analogy with Ref. [2]. It is observed that under ZFC condition, the magnetization decreases as temperature is decreased, goes through a minimum ~267 K and then increases with decreasing temperature. At small applied field the minimum occur with a negative magnetization. Bifurcation between ZFC and FCC curve starts around 380 K. FCC curve increases with decreasing temperature and attains a maximum value at ~267 K. Then it decreases and attains a zero value of magnetization at the compensation temperature (T_{comp}). Below T_{comp}, magnetization is negative down to 2 K. Such behavior arises due to the fact, that, the net magnetization arising out of coupling between Fe–O–Fe, Cr–O–Cr and Fe–O–Cr is aligned opposite to the applied field. FCC curve obtained under −100 Oe is exactly the mirror image of that