Journal of Alloys and Compounds 709 (2017) 410–414

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Inverse and enhanced magnetocaloric properties of $HoCrO_3$

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A R T I C L E I N F O

Article history:
Received 5 December 2016
Received in revised form
9 March 2017
Accepted 12 March 2017
Available online 14 March 2017

Keywords:
Magnetocaloric effect
Magnetization crossover
Metamagnetic transition
Spin − re-orientation

A B S T R A C T

We report on the magnetic and magnetocaloric properties of 50% Fe^{3+} doped polycrystalline $HoCrO_3$ compounds in the vicinity of magnetic transitions. Due to complex magnetic interactions, we do see multiple transitions in χ *vs.* T graph pertinent to $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds related with Ho^{3+} ordering, Cr^{3+} ordering and spin − reorientation (SR). Due to re-orientation of spins, metamagnetic transitions are evident in low field regime of M *vs.* H. Quantified values of $-\Delta S_M$ around Ho^{3+} ordering infer that indeed Fe^{3+} substitution helped in enhancing magnetocaloric effect of $HoCrO_3$ compound. Such an enhanced $-\Delta S_M$ values are ascribed to increase in canting of Fe/Cr spins. Present results would be helpful in developing magnetic refrigerant materials for space applications particularly below 30 K.

1. Introduction

In recent years, refrigeration based on magnetic materials particularly using magnetocaloric effect (MCE) phenomenon has gained much attention in view of its application in future magnetic refrigeration technology due to its higher energy efficiency and environmental safety over the conventional gas compression refrigeration [1–3]. MCE is a magneto-thermal phenomenon, in which the temperature of a magnetic material changes when it is exposed to a magnetic field adiabatically [4]. A magnetic materials with a large change of magnetic entropy $\Delta S_M(T,H)$ or adiabatic temperature (ΔT) and a sufficiently large value of refrigeration capacity (RC) are promising candidates for magnetic refrigeration [5]. A plethora of compounds have been investigated to study the MCE in alloys like $Ni_{52.6}Mn_{23.1}Ga_{24.3}$ [6], $Gd_5(Si_2Ge_2)$ [7], $MnFeP_{0.45}As_{0.55}$ [8] as well as in oxide materials such as $Tb_{0.67}R_{0.33}MnO_3$ (R = Dy, Y and Ho) [9] and $La_{1-x}Ca_xMnO_3$ [10].

As far as oxide materials are concerned, distorted perovskite family of canted antiferromagnets, orthoferrites ($RFeO_3$) [11] and orthochromites ($RCrO_3$) [12] have attained much interest due to their unique physical properties and complex spin structure between the rare-earth (R) and the transition metal (TM) ions. $RFeO_3$ and $RCrO_3$ compounds have been explored for their MCE properties and suitability for magnetic refrigeration applications [13–15]. For example, a large MCE value of $-\Delta S$ ~8.4 J/kg-K and RC ~217 J/kg at 15 K and 4 T has been observed in $DyCrO_3$ due to ordering of Dy^{3+} at 2.3 K [14]. Yin et al., reported large MCE value of $-\Delta S$ ~10.5 J/kg-K at 4 T around Dy^{3+} ordering (14 K) in $DyFe_{0.5}Cr_{0.5}O_3$ compound [15]. Yet in another compound, $HoCrO_3$, large value of MCE has been reported and the values are $-\Delta S$ ~7.2 J/kg-K and RC ~408 J/kg at 20 K and at 7 T [16]. Although several reports have shown MCE on various magnetic materials like $Dy_{1-x}Sc_xNi_2$ [17], $R_{1-x}La_xNi_2$ (R = Tb, Dy, Ho) [18], Dy_2Cu_2Cd [19], TmAgAl [20], TmZn [21], Er_2Cu_2In [22], Eu_4PdMg [23], etc., as this field is highly demanding numerous new materials needs to be explored for various applications. Particularly, much attention is required to search for new materials with giant MCE below 30 K for utilization in space applications [1,24].

In this context, $HoCrO_3$ is a compound which shows large value of $-\Delta S$ (~7.2 J/kg-K) below 30 K. It is evident from the above discussion that substitution of Fe^{3+} in $DyCrO_3$ for Cr^{3+} has enhanced $-\Delta S$ values around Dy^{3+} ordering [15]. Hence, we believe that Fe^{3+} would play a crucial role in enhancing MCE in our present $HoCr_{0.5}Fe_{0.5}O_3$ compound around Ho^{3+} ordering. In addition, it also has been believed from neutron diffraction data that upon adding 50% of Fe to Cr, spin reorientation (SR) transition would be evident [25] due to an interaction between Ho^{3+} and Fe^{3+} moments. Such a SR transition would be associated with a change in magnetization direction from $G_xA_yF_z$ (Γ_4) to $F_xC_yG_z$ (Γ_2), where G_x, A_y, and F_z stand for spin component along x, y, and z axis in terms of Bertaut's notation, respectively [26], which can lead to large change in $-\Delta S_M$. Calculation of entropy change around SR transition is also aim of our present paper. Apart from the SR and Ho^{3+} ordering, indeed there exists a transition due to Cr^{3+}, which may also give large change in MCE. Hence, in the present work, we explored MCE properties of $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds around Ho^{3+}, Cr^{3+} and SR transition temperatures. In addition, we also studied

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http://dx.doi.org/10.1016/j.jallcom.2017.03.132

the nature of magnetic transition in aforesaid compounds through Arrott plots. Salient features of present manuscript are (a) upon adding 50% of Fe^{3+} to Cr^{3+}, enhanced value of MCE is evident in $HoCr_{0.5}Fe_{0.5}O_3$ compound (b) magnetization crossover is evident in $HoCrO_3$ compound and metamagnetic transition prevails around Ho^{3+} ordering in both $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds (c) Spin reorientation (SR) transition is apparent in $HoCr_{0.5}Fe_{0.5}O_3$ compound around 150 K.

2. Experimental details

Polycrystalline $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds were prepared by conventional solid state reaction method using High purity oxide powders of Ho_2O_3, Fe_2O_3, and Cr_2O_3 (purity > 99.9%) (Sigma-Aldrich chemicals India) as starting raw materials. The temperature (T) dependent magnetization (M) (M *vs.* T) and magnetic field (H) dependent magnetization (M *vs.* H) measurements were performed using a Quantum Design magnetic property measurement system (MPMS) in the temperature range of 5–300 K. Magnetization isotherms (M *vs.* H) were measured at different temperature ranges and up to a maximum magnetic field of 6 T. Before we perform each measurement of M *vs.* H, the sample was warmed up to a temperature greater than ordering temperature of transition metal to remove the magnetic history.

3. Results and discussion

The phase purity of $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds was confirmed [27] at room temperature using powder x - ray diffraction (XRD) (PANalytical X-ray diffractometer) with Cu - K_α radiation ($\lambda = 1.5406$ Å) and with a step size of 0.017° in the wide range of the Bragg angles 2θ (20°–80°) as shown in Fig. 1. From the Fig. 1, it is observed that the indexed reflections are allowed for a compound with $GdFeO_3$ type distorted perovskite structure with a space group of *Pbnm*. We do not see any impurity phase within the detectable limits of the XRD. The structural parameters obtained from the Rietveld refinement has been published elsewhere [27]. The increase in the lattice parameter is evident from the refinement with increasing Cr^{3+} content, which is consistent with the fact that ionic radius of Cr^{3+} (0.615 Å) is smaller than that of Fe^{3+} (0.645 Å).

Fig. 2(a) shows the temperature (T) *vs.* susceptibility (χ) graph in zero field cooled (ZFC) conditions. It is evident from the figure that the Cr^{3+} moments ordered antiferromagnetically (AFM) at 142 K. Such AFM is believed to have canting nature with AFM axis at 142 K (T_N). On the other hand, transition due to Ho^{3+} moments is evident at 8 K (T_N^{Ho}) [28]. Fig. 2(b) shows χ *vs.* T graph for $HoCr_{0.5}Fe_{0.5}O_3$ compound. In 50% Fe substituted compound, in addition to AFM and Ho^{3+} (13 K) ordering, we also could able to realize a transition due to SR [25]. The origin of such SR is due to change in magnetization from $G_xA_yF_z$ (Γ_4) to $F_xC_yG_z$ (Γ_2), where G_x, A_y, and F_z stand for spin component along x, y, and z axis in terms of Bertaut's notation, respectively. Such a SR transition is evident around 150 K (T_{SR}) and we also ascribe such SR in $HoCr_{0.5}Fe_{0.5}O_3$ compounds to complex exchange interaction between the Fe^{3+} and the Ho^{3+} ions [29]. Indeed, there is a shift for Ho^{3+} ordering from 8 to 13 K and T_N from 142 to 273 K upon adding 50% Fe to Cr. The obtained T_N and T_{SR} values are in good agreement with the literature [25,28].

As there are multiple transitions in both the compounds, we do expect a large change in entropy around these transitions. Hence, in order to quantify the change in entropy we performed the M *vs.* H measurements in the vicinity of the magnetic transitions for both the $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$compounds. Fig. 3(a)-(d) shows first quadrant magnetization isotherms of $HoCrO_3$ (at 2–10 K and 136–146 K with an interval of 2 K) and $HoCr_{0.5}Fe_{0.5}O_3$ (at 5–20 K with an interval of 3 K and 120–200 K with an interval of 10 K) compounds with a maximum magnetic field of 6 T. A field induced metamagnetic transition is evident in the low magnetic field region for all M *vs.* H graphs pertinent to $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds as shown in Fig. 3(a) and 3(b). Now we define the critical field (H_C) as the field below which the material shows AFM behaviour and exhibits ferromagnetic (FM) behaviour above this field. Such a field induced transition in low field region can be ascribed to the onset of a first order metamagnetic transition (from original AFM state to FM state). Evidenced metamagnetic transition may be due to the magnetization reversal of those ions whose

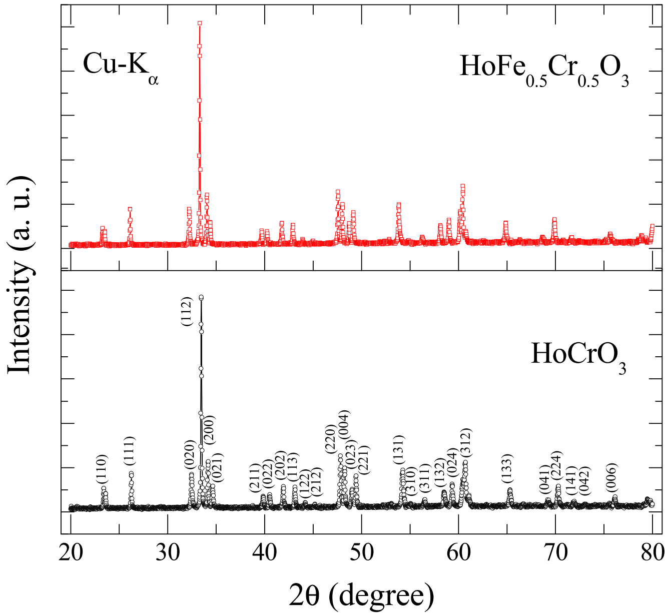

Fig. 1. Powder x-ray diffraction patterns pertinent to $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ recorded at room temperature.

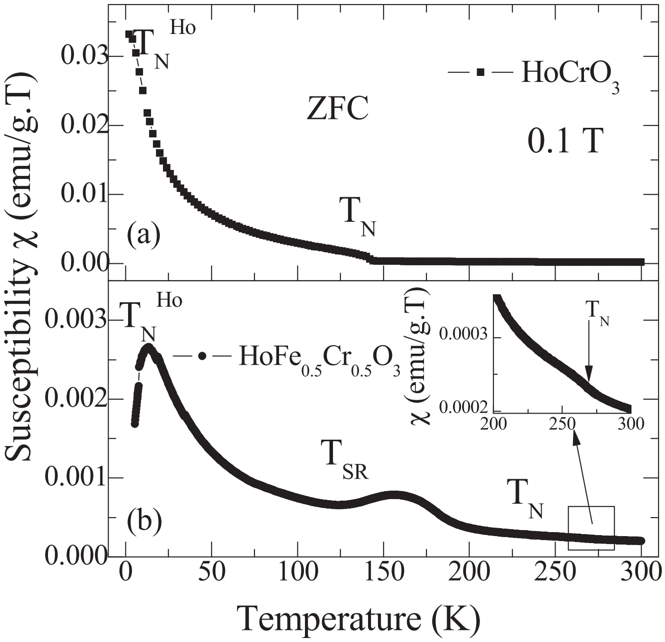

Fig. 2. Temperature (T) dependence of susceptibility (χ) pertinent to $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds measured at 0.1 T under zero field cooled condition (ZFC).