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ORIGINAL PAPER

Magnetic State and Magnetocaloric Effect of $SmMnO_3$

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Abstract We present a study of magnetization and magnetocaloric effect for the $SmMnO_3$ compound. This compound was synthesized by combustion reaction and its magnetic and structural properties studied by X-ray powder diffraction (XRD) and magnetization (M) measurements as a function of temperature and under magnetic fields The XRD pattern at room temperature confirme the presence of a single phase with orthorhombic structure. From magnetization versus temperature, we observe two magnetic orderings, the firs one at 6 K due to Sm^{3+}, and the other one at $T_N = 57(2)$ K is the anti-ferromagnetic long-range ordering. The magnetic entropy change, ΔS_M, was obtained from magnetization isotherms close to T_N where it reaches a maximum value of about 8.0 J/kg K for an applied fiel of 7 T.

Keywords $SmMnO_3$ · Magnetocaloric effect · Multiferroic

1 Introduction

Multiferroics are materials having two or more states with spontaneous ordering, for instance of magnetization, polarization, or strain. They are among the most investigated materials in recent years probably due to their potential for applications in technology as well as interesting physics responsible for this behavior [1].

From a diversity of materials which exhibit coupling between magnetic and ferroelectric properties, the manganite compounds $RMnO_3$ (R = rare earth) have attracted lot of interest. The dielectric properties of these materials are highly sensitive to applied magnetic fields as the ferroelectricity is induced by the complex magnetic ordering, typical of a frustrated magnet. The crystal structure of $SmMnO_3$ (space group *Pnma*) has an orthorhombic perovskite structure [2] with four formula units per unit cell and four 3d electrons: three t_{2g} and one e_g.

The application of magnetic fiel decreased magnetic entropy of the material (S_M). Under adiabatic conditions, the entropy change (ΔS_M) will be offset by a shift equal to the entropy, associated with the lattice, resulting in a change in temperature of the material ΔT_{ad}. Both quantities, ΔS_M and ΔT_{ad} characterize the Magnetocaloric Effect (MCE).

The change in the magnetic entropy, ΔS_M and hence the MCE is maximum close to the temperature of magnetic transition. Most of the materials present second order magnetic transition (T_C), with a moderate change of entropy. However, some compounds as $Gd_5Si_2Ge_2$ [3], $MnFeP_{0.45}As_{0.55}$ [4], and Ni_2MnGa [5] have an abrupt change in the magnetization around T_C (first-orde transition) and, therefore, a giant MCE.

The manganites exhibit f rst- or second-order transition, depending on the composition ratio and of atomic radius [6, 7]. In some cases, a structural transition close to the temperature of magnetic transition can influenc the MCE for the coupling between the lattice and the magnetic degrees of freedom [8]. The application of high external magnetic fiel can also change the symmetry of the structure and volume modifying the magnetic entropy, as in the $Pr_{0.46}Sr_{0.54}MnO_3$ compound. Here, we present a preliminary study of magnetocaloric properties of $SmMnO_3$ from magnetization data as a function of temperature under field up to 7 Tesla.

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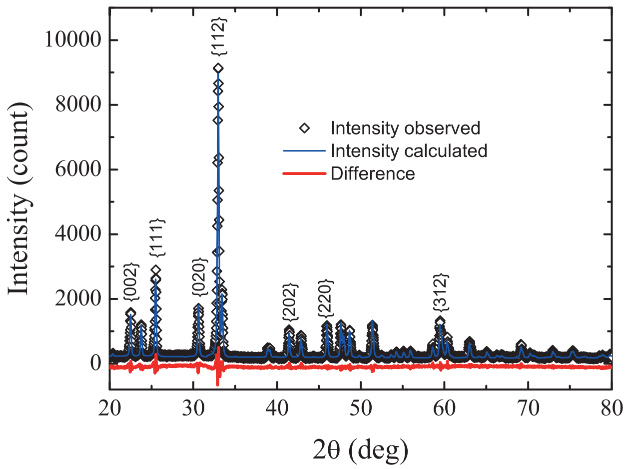

Fig. 1 X-ray diffraction pattern for polycrystalline $SmMnO_3$

2 Experimental Details

The $SmMnO_3$ compound was obtained by combustion reaction with starting salts reagents: Samarium nitrate ($Sm(NO_3)_3{\cdot}6H_2O$) and manganese chloride ($MnCl_2{\cdot}4H_2O$) with purity 99.9 % and urea used as fuel. The mixture was heated at 350 °C until the combustion reaction is carried out. The resulting power was calcined at 1300 °C for 12 hours in a furnace with the open atmosphere. The X-ray powder diffraction data were collected at room temperature using a Dmax2500 Rigaku diffractometer with radiation CuK_α ($\lambda = 1.5418$ Å). The magnetic measurements were made on a commercial magnetometer MPMS (of Quantum Design) with SQUID detection operating in temperature range $2 \le T \le 300$ K and external magnetic fiel $0 \le H \le 7$ T.

3 Results

The X-ray pattern taken on the polycrystalline sample at room temperature was indexed on the orthorhombic space group *Pnma*; no impurity phases such as Sm or Mn binary oxides were detected. The lattice parameters obtained by least squares refinemen of powder data are $a = 5.358$ Å, $b = 5.825$ Å, and $c = 7.483$ Å. Figure 1 shows the X-ray diffraction pattern which we identify the planes of diffraction.

The temperature dependence of magnetization is presented in Fig. 2. As shown in that figure at high temperatures ($T > 70$ K), the susceptibility follows Curie–Weiss behavior with $\mu_{\mathrm{eff}} = 5.40\ \mu_B$/formula unit which is close to the value expected for Sm^{3+} and Mn^{3+} free ions [9]. The paramagnetic Curie temperature (θ) was found to be −64 K. By the f rst derivative of its magnetization curve as shown in Fig. 2, two peaks at 6 K and 57 K are observed, indicating an anti-ferromagnetic transition. The isothermal magnetization

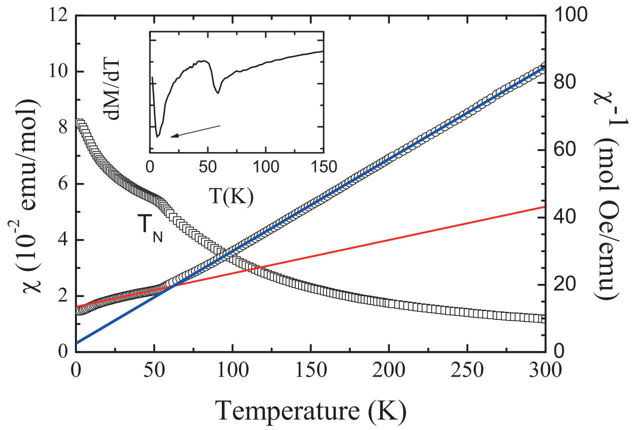

Fig. 2 Susceptibility as a function of temperature for 5 T magnetic fiel and inverse of susceptibility vs. T. *Inset* shows f rst derivative of magnetization for $SmMnO_3$

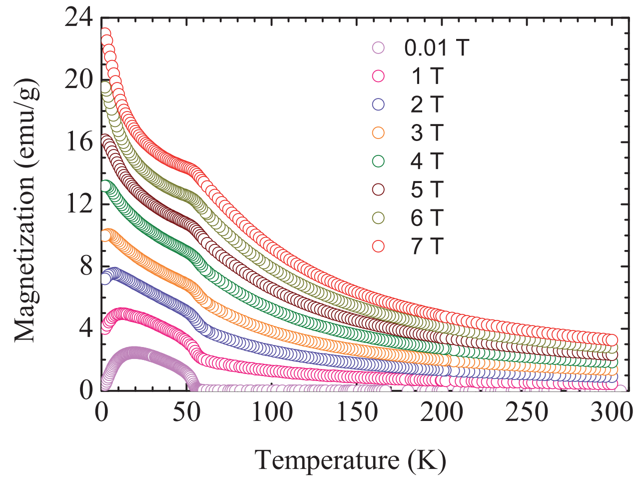

Fig. 3 Magnetization vs. T curves for $SmMnO_3$ in a interval of external applied f eld of 0,01 T to 7 T for $SmMnO_3$

(not shown here) at 2 K is linear and reversible up to 7 T, which is consistent with the antiferromagnetic nature of the magnetic ordering.

In order to evaluate the magnetocaloric effect for the $SmMnO_3$ compound, we calculated the entropy changes associated with an applied magnetic fiel variation (0.01 T to 7 T) from the isofiel curves of magnetization versus temperature. The curves are shown in Fig. 3. Measurements were performed in two modes: In field-cooled cooling (FCC) and field-cooled- arming (FCW) modes, the fiel was applied at room temperature, and data were taken during cooling and warming, respectively in a field

The variation of entropy (S) of a magnetic material on the application of a magnetic fiel (H) is related to that of magnetization (M) with temperature (T) by the thermodynamic Maxwell relation: $\frac{\partial S(T,H)}{\partial H} = (\frac{\partial M(T,H)}{\partial T})_H$. By integrating this expression in a reversible process, we obtain the isothermal entropy change $\Delta S_M = S_M(H) - S_M(0)$ by

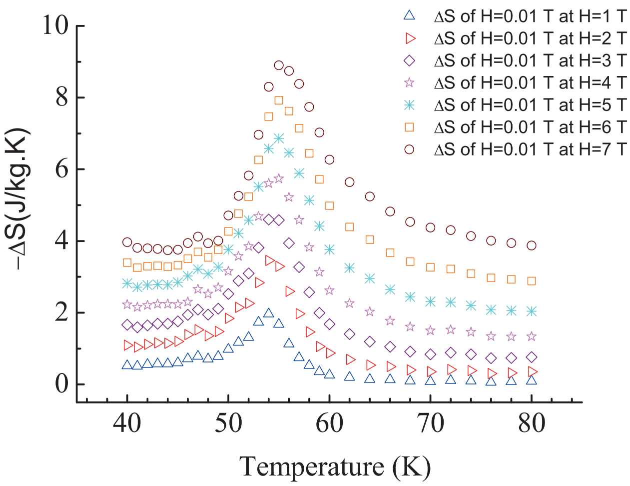

Fig. 4 Isothermal curves of entropy change to applied external f eld ranging of 0.01 T to 7 T in the temperature range from 2 K to 80 K for $SmMnO_3$

$\Delta S_M = \int_{H_0}^{H} (\frac{\partial M}{\partial T})_H \, dH$. Figure 4 shows the curves of entropy change obtained for the $SmMnO_3$ in different applied field of 0.01 T to 7 T.

The expected behavior of change of entropy is observed, which is the increased reduction in entropy with increasing applied field The change in entropy around T_C was 8.9 $\mathrm{J\,Kg^{-1}K^{-1}}$ at the temperature of 56 K under external fiel of 7 T. At low temperatures, we also observed a signifi cant change in entropy, 9.6 $\mathrm{J\,Kg^{-1}K^{-1}}$ in 9 K, in a variation of the applied fiel 7 T. This indicates you may be experiencing some magnetic ordering below T_N, which is also suggested by the magnetization curves as a function of temperature.

An anti-ferromagnetic coupling at low temperatures survives up to ∼6 T and a forced anti-ferromagnetic coupling between Sm^{3+} and Mn^{3+} seems to appear above ∼7 T field

The behavior of the peak at $T_S \sim 10$ K suggests short-range Sm^{3+} spin ordering. A shift of the peak position towards low temperatures is observed at increasing fiel due to spin reorientation. The loss of short-range Sm^{3+} spin order and the development of long-range Mn^{3+} spin order explain the very weak peak at $T_N \sim 57$ K. It is a well-known fact that Mn–Mn exchange is very sensitive to distance and it plays an important role mainly due to Sm–Mn coupling. As a result of this interplay, one observes at 7 T that the entropy change at T_S overcome the peaks associated to the lost of anti-ferromagnetic order at T_N.

4 Conclusions

In the study of magnetic properties of polycrystalline $SmMnO_3$, we observed an anti-ferromagnetic transition around 57 K and a transition at 6 K to be understood. From the Curie–Weiss fi to the inverse of susceptibility the effective moment $\mu_{\mathrm{eff}} = 5.40\ \mu_B$/formula unit. was determinate, which is close to the contribution of Sm^{3+} and Mn^{3+} free ions.

The magnetocaloric properties of this compound indicated usual MCE, because it has maximum value of the entropy isothermal change smaller than that of Gd, which under a variation of a fiel of 2 T shows a maximum around 5 $\mathrm{J\,kg^{-1}K^{-1}}$ to temperature of 292 K.

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