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Structural and magnetic properties of layered perovskite manganite $LaCaBiMn_2O_7$

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Abstract. The layered perovskite oxide, $LaCaBiMn_2O_7$, has been prepared by the conventional aqueous solution precipitation method. The powder X-ray diffraction studies suggest that the phase crystallizes with tetragonal unit cell in the space group I4/mmm. The magnetic properties suggest that the ferromagnetic interactions are dominant and manganese ion in the phase is present in mixed valence states $Mn^{3+}$and Mn^{4+}. The thermomagnetization curve is found to obey the Bloch law. Spin wave stiffness constant D and the approximate value for J_{MnMn}exchange interaction were estimated from the experimental results.

1. INTRODUCTION

Perovskitemanganites represent nowadays one of the most intensively studied research topic in the fields of solid state chemistry and physics [1–3]. The discovery of the colossal magnetoresistance effect in the $La_{2-2x}Sr_{1+2x}Mn_2O_7$ manganite, which represents the n = 2 member of the Ruddlesden-Popper series of manganites, has attracted special interest due to its crystal structure forming a naturally layered system [4–8]. In particular, distinct features of the bilayeredmanganites are the anisotropic characteristics in both charge-transport and magnetic properties and the reduced dimensionality of the Mn-O-Mn networks which leads to several intriguing changes including enhanced MR effects, large magneto-caloric effects, unconventional magnetostriction, and anisotropic transport in charge carriers. Moreover, these layered systems exhibit a variety of both ferromagnetic and antiferromagnetic structures.

In this paper we present the result of the synthesis and characterization of the $LaCaBiMn_2O_7$ compound. The Sample so prepared has beenfully characterized for what concerns their structure, by means of X-ray diffraction (XRD), and static magnetization (M) measurements have been carried out to complete the samples characterization.

2. EXPERIMENTAL

Crystalline powders of $LaCaBiMn_2O_7$ have been prepared from aqueous solutions of $La(NO_3)_3, 6H_2O$; $Ca(NO_3)_2, 4H_2O$; $Bi(NO_3)_3, 5H_2O$ et $Mn(NO_3)_2, 4H_2O$ as starting materials. The mixture (precipitate + solution) was dried at about 60 °C to remove the liquid. The resulting powder was placed in platinum crucible and heated at 1173 K for 24 h in air atmosphere with intermediate regrinding. We characterized the sample using X-ray diffraction (Cu-Kα radiation $\lambda_{Cu} = 1.5406$ Å). Magnetic measurements were carried out on a superconducting quantum interference device (SQUID) magnetometer.

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3. RESULTS AND DISCUSSION

3.1. X-ray powder diffraction

Figure 1 shows the X-ray diffraction pattern for a bulk sample of $LaCaBiMn_2O_7$. All the diffraction peaks are indexed with the $Sr_3Ti_2O_7$-type perovskite indicates that the sample is nearly single phase of the $Sr_3Ti_2O_7$-type structure. In figure 2, we show the crystal structure of $LaCaBiMn_2O_7$, which is the tetragonal structure with $Sr_3Ti_2O_7$-type perovskite ABO_3. The space group is I4/mmm. The lattice parameters of the tetragonal unit cell for this sample are a = 3.824 Å and c = 19.183 Å. In this system, the double perovskite layers are interleaved with La(Ca, Bi)O layers and Mn-O-Mn bonds in the c-axis direction are separated from one another by the La(Ca, Bi)O layers. Thus, the Mn-O-Mn exchange interaction can take place between the Mn ions in the a-b plane of the perovskite layers, whereas the exchange interaction between the double perovskite layers (in the c-axis direction) must be through O^{2-}ions.

Therefore, it is likely that the physicalproperties of $LaCaBiMn_2O_7$ are inherently two dimensional or quasi-two dimensional.

Average grain size t was calculated from XRD peaks using the Scherer formula:

$$t = \frac{0.9\lambda}{\beta \cos\theta}, \quad (1)$$

where λ is X-ray wavelength employed, θ is the diffraction angle and β is the experimental full with at half maximum. The obtained t value is about 30 nm.

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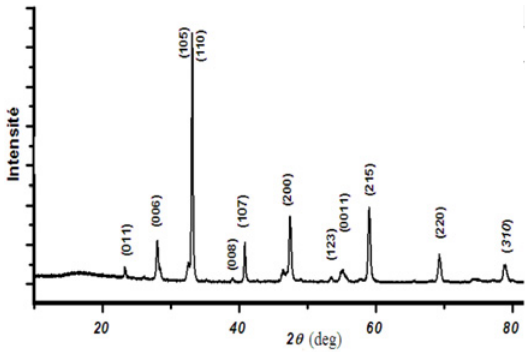

Figure 1. X-ray diffraction pattern of $LaCaBiMn_2O_7$ sample.

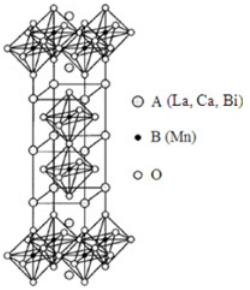

Figure 2. Crystal structure of $LaCaBiMn_2O_7$ with the tetragonal $Sr_3Ti_2O_7$-type Perovskite (ABO_3).

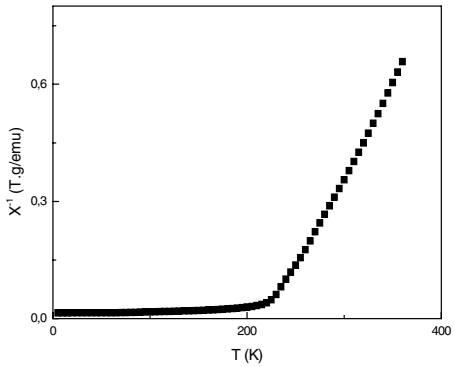

Figure 3. Inverse susceptibilities of $LaCaBiMn_2O_7$ against temperature obtained at an applied of 1T.

3.2. The temperature dependence of the inverse magnetic susceptibility

The temperature dependence of the inverse magnetic susceptibility for $LaCaBiMn_2O_7$ is shown in Fig. 3. The effective magnetic moment (μ_{eff})has been calculated from the high temperature linear region of the χ^{-1} versus T plot and leads to a value of 9.7 μ_B. The contribution of the manganese ion ($\mu_{eff,Mn}$)to the magnetic moment has been calculated from the effective moment (μ_{eff}). For $\mu_{eff,Mn}$, we obtain a value of 4.85 μ_B. From the Curie-Weiss plot the paramagnetic Curie temperature is found to be 230K indicating strong ferromagnetic exchange interactions between Mn ions.

In this case, using the ionic magnetic moment values $\mu_{Mn}^{3+} = 4.9\mu_B$ and $\mu_{Mn}^{4+} = 3.87\mu_B$, we have estimated the molar fraction of these ions in the compound from relation

$$(\mu_{eff,Mn})^2 = x(\mu_{Mn}^{3+})^2 + (1-x)(\mu_{Mn}^{4+})^2, \qquad (2)$$

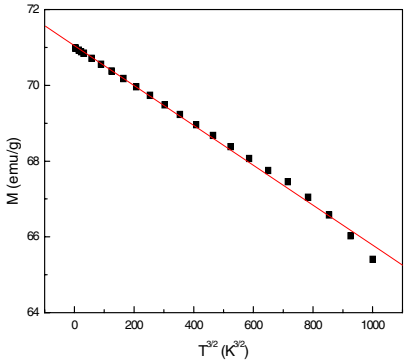

Figure 4. Magnetization versus $T^{3/2}$.

Table 1. Some magnetic parameters of $LaCaBiMn_2O_7$ sample.

M (emu/g)	B(10^{-5} $K^{-3/2}$)	D (meV.Å^2)	J_{MnMn} (10^{-23} J)	k_F (Å^{-1})
71	7.1	89	15	0.49

where x and (1−x) the molar fraction of manganese in Mn^{3+} and Mn^{4+} valence states. We obtain a x value of 0.9 (90% of Mn^{3+}).

Value for the Mn-Mn exchange interaction constant J_{Mn-Mn} was derived from the measured Curie temperature (T_C) in the mean field approximation:
$3k_BT_C = 2zJ_{Mn-Mn}S(S+1)$, where we have assumed z=4 nearest neighbors (Table 1).

3.3. Exchange constant

The temperature dependence of magnetization M follows Block's $T^{3/2}$ Low and is therefore due to the thermal excitation of spin waves. According to the spin wave theory, the temperature dependence of the magnetization of ferromagnetic materials is given by

$$\frac{M(3K) - M(T)}{M(3K)} = BT^{3/2}, \qquad (3)$$

Eq. (1) is a good approximation of low temperature magnetization in polycrystalline ferromagnets [9]. The parameter B introduced in eq. (3) is related to the spin wave stiffness constant D by the following relation:

$$B = 2.612\frac{g\mu_B}{M(3K)}\left(\frac{k_B}{4\pi D}\right)^{3/2}, \qquad (4)$$

where g is the spectroscopic g-factor ($g_{Mn} = 2$), k_B is the Boltzmann's constant and μ_B is the Bohr magneton. From the magnetization versus magnetic field curves we have deduced the spontaneous magnetization values M_S at each measurement temperature and reported the temperature dependence of the spontaneous magnetization in Fig. 4. The curve is plotted versus $T^{3/2}$. These experimental data have been adjusted by using the Eq. (2) giving rise to B parameter (Table I). Finally, knowing B and using Eq. (3), D was calculated (Table 1).

Katsuki and Wolhfarth [10] have discussed the correlation between D and the T_C on the basis of itinerant electron model. Using the effective mass approximation they have obtained the following relationship:

$$D = \frac{\pi k_B T_C}{6\sqrt{2}k_F^2}, \quad (5)$$

where k_F is the Fermi wave-vector and the k_F value obtained was listed in Table 1.

4. CONCLUSIONS

Layered perovskite manganite $LaCaBiMn_2O_7$, has been synthesized by the conventional aqueous solution precipitation method. Its structure has been determined by X-ray diffractometry. The results show that the phase crystallizes in the I4/mmm space group with tetragonal unit cell. The magnetic studies suggest that the ferromagnetic interactions are dominant and manganese ion in the phase is present in mixed valence states (Mn^{3+}/Mn^{4+}). We have studied the magnetization of our sample in terms of the spin wave theory which allowed us to determine the spin wave stiffness constants D. From T_C in the mean field approximation, the exchange interaction J_{Mn-Mn} was estimated.

References

[1] K.H. Ahn, T. Lookman, and A.R. Bishop, Nature, 428, 401 (2004).

[2] L. Malavasi, M.C. Mozzati, C.B. Azzoni, G. Chiodelli, and G. Flor, Solid State Commun., 123, 321 (2002).

[3] L. Malavasi, M.C. Mozzati, P. Ghigna, C.B. Azzoni, and G. Flor, J. Phys. Chem. B, 107, 2500 (2003).

[4] T. Kimura, Y. Tomioka, H. Kuwahara, A. Asamitsu, M. Tamura, Y. Tokura, Science, 274, 1698 (1996).

[5] T. Kimura, and Y. Tokura, Annu. Rev. Mater. Sci., 30, 451 (2000).

[6] M. Kubota, H. Fujioka, K. Hirota, K. Ohoyama, Y. Moritomo, H. Yoshizawa, and Y. Endoh, J. Phys. Soc. Jpn., 69, 1606 (2000).

[7] C.D. Ling, J.E. Millburn, J.F. Mitchell, D.N. Argyriou, J. Linton, and H.N. Bordallo, Phys. Rev. B, 62, 15096 (2000).

[8] J.F. Mitchell, D.N. Argyriou, A. Berger, K.E. Gray, R. Osborn, and U. Welp, J. Phys. Chem. B, 105, 10731 (2001).

[9] F. Keffer, Handbuch der Physik, vol. XVIII/2. Eds. F. Flügge, H.P.J. Wijin, Springer-Verlag, Berlin, (1966) 50.

[10] A. Katsuki and E.P. Wolhfarth, Proc. Roy. Soc. A 295 182 (1966).