Structural and magnetic properties of layered perovskite manganite LaCaBiMn$_2$O$_7$

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Abstract. The layered perovskite oxide, LaCaBiMn$_2$O$_7$, 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$_{2−x}$Sr$_x$MnO$_3$ 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 magnetostriiction, 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$_2$O$_7$ compound. The Sample so prepared has been fully 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$_2$O$_7$ have been prepared from aqueous solutions of La(NO$_3$)$_3$, 6H$_2$O; Ca(NO$_3$)$_2$, 4H$_2$O; Bi(NO$_3$)$_3$, 5H$_2$O et Mn(NO$_3$)$_2$, 4H$_2$O 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-K$_\alpha$ radiation $\lambda_{Cu} = 1.5406$ Å). Magnetic measurements were carried out on a superconducting quantum interference device (SQUID) magnetometer.

3. RESULTS AND DISCUSSION

3.1. X-ray powder diffraction

Figure 1 shows the X-ray diffraction pattern for a bulk sample of LaCaBiMn$_2$O$_7$. All the diffraction peaks are indexed with the Sr$_3$Ti$_2$O$_7$-type perovskite indicates that the sample is nearly single phase of the Sr$_3$Ti$_2$O$_7$-type structure. In figure 2, we show the crystal structure of LaCaBiMn$_2$O$_7$, which is the tetragonal structure with Sr$_3$Ti$_2$O$_7$-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 physical properties of LaCaBiMn$_2$O$_7$ are inherently two dimensional or quasi-two dimensional.

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

$$t = \frac{0.9\lambda}{\beta \cos \theta},$$

where $\lambda$ is X-ray wavelength employed, $\theta$ is the diffraction angle and $\beta$ 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$_2$O$_7$ sample.

Figure 2. Crystal structure of LaCaBiMn$_2$O$_7$ with the tetragonal Sr$_3$Ti$_2$O$_7$-type Perovskite (ABO$_3$).

Figure 3. Inverse susceptibilities of LaCaBiMn$_2$O$_7$ against temperature obtained at an applied of 1T.

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

Table 1. Some magnetic parameters of LaCaBiMn$_2$O$_7$ sample.

<table>
<thead>
<tr>
<th></th>
<th>B($10^{-23}$ J)</th>
<th>D (meVÅ$^2$)</th>
<th>$J_{MnMn}$ ($10^{-23}$ J)</th>
<th>$k_f$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71</td>
<td>7.1</td>
<td>89</td>
<td>15</td>
<td>0.49</td>
</tr>
</tbody>
</table>

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

$$M(3K) - M(T) = B T^{3/2},$$

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:

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

where $g$ is the spectroscopic g-factor ($g_{Mn} = 2$), $k_B$ is the Boltzmann’s constant and $\mu_B$ 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 $T^{5/2}$. 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:

\[ D = \frac{\pi k_B T_C}{6\sqrt{2} k_F^2}, \]  

(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 (\( \text{Mn}^{3+}/\text{Mn}^{4+} \)). 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 \( J_{\text{Mn}--\text{Mn}} \) was estimated.

References