Investigation on the structural, electrical and magnetic properties of layered perovskite manganite DySr$_2$MnCrO$_7$

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The layered perovskite oxide DySr$_2$MnCrO$_7$ has been prepared by the standard ceramic method. The powder X-ray diffraction studies suggest that the phase crystallizes with tetragonal unit cell in the space group I4/mmm. The electrical transport properties show that the phase is an electrical insulator and the electrical conduction in the phase occurs by a 3D variable range hopping mechanism. The magnetic properties suggest that the ferromagnetic interactions are dominant.

Keywords: DySr$_2$MnCrO$_7$, Structure, Electric transport properties, Magnetic properties

In the past few years, the bilayered manganites La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ of Ruddlesden-Popper (RP) phases ($n$=2) continue to offer a rich display of a variety of physical phenomena attracting physicists, chemists and materials scientists. Ever since Moritomo et al.\textsuperscript{1} discovered colossal magnetoresistance (CMR) properties in the layered La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ system akin to their three-dimensional counterparts (cubic perovskites), there followed a flurry of activity on the layered manganites especially with the $n=2$ structure.\textsuperscript{1-4} The most important one is that they exhibit a property known as CMR, which not only has a tremendous potential for applications but also is the starting point for the development of many theories attempting to interpret the voluminous experimental data. Then, there are phase transitions from a ferromagnetic metallic state to either an antiferromagnetic insulating state or to a paramagnetic insulating state. In some compounds, the strong competition between the ferromagnetic (FM) and the antiferromagnetic phases, below $T_c$, drives the system to a host of other new magnetic orders, such as a cluster glass, spin glasslike state or to a charged-orbital ordered state. These provide an opportunity to understand the phenomena caused by the complex interplay among the spin, charge and orbital orderings and the lattice degrees of freedom.\textsuperscript{5,6}

It is well known that the correlation between the magnetic and the electrical properties in the mixed-valence manganites is generally understood in terms of the double exchange (DE) interaction mechanism.\textsuperscript{7} Besides the DE mechanism, the Jahn-Teller effect, phase separation (PS)\textsuperscript{8} and antiferromagnetic (AFM) superexchange and charge-orbital ordering interactions also play an important role. The saturation magnetization decreases with decrease in grain size. The decreasing grain size causes an increase in the proportion of non-collinear magnetic structure, in which magnetic moments are not aligned with the direction of external magnetic field. This increase in the proportion of non-collinear structure decreases the saturation magnetization.\textsuperscript{9-11} The bilayer manganites, La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$, offer another unique opportunity to investigate the generic features of the mixed-valence manganites. Mn-site doping in the bilayer manganites can dramatically change the magnetic and electrical properties. Some such studies have been undertaken during the past few years.\textsuperscript{12-18} Cr is a very interesting substitution ion for Mn site, because Cr$^{3+}$ (ionic radius = 0.62 Å) has the same electronic configuration ($t^3_{2g} e^0_{g}$) as that of Mn$^{4+}$, and closely identical ionic radius as that of Mn$^{3+}$ (ionic radius = 0.65 Å). There may be FM DE interaction between Cr$^{3+}$ and Mn$^{3+}$ just as between Mn$^{4+}$ and Mn$^{3+}$. Some reports on the effect of Cr doping in the cubic perovskite manganites have appeared, and several reports on such studies have also appeared in case of bilayer manganites.\textsuperscript{19-23} But there are a few reports on the effect of Cr doping in the bilayer manganite LaSr$_2$Mn$_2$O$_7$\textsuperscript{24} and there is hardly any
report of Cr doping in the phase containing rare-earth ion other than La.

In the present work, a new RP-type phase \((n=2)\) containing rare earth Dy and 50% substitution of Cr at Mn site with composition DySr\(_2\)MnCrO\(_7\) has been synthesized and its crystal structure has been determined by powder X-ray diffraction studies. The electrical resistivity and magnetic susceptibility of the phase have been studied as functions of temperature.

**Experimental Procedure**

DySr\(_2\)MnCrO\(_7\) was prepared by the standard ceramic method by heating the stoichiometric amounts of Dy\(_2\)O\(_3\) (Aldrich 99.9%), SrCO\(_3\) (Aldrich 99.9%), MnO\(_2\) (Aldrich 99.9%) and Cr\(_2\)O\(_3\) (Aldrich 99.9%). Prior to use, Dy\(_2\)O\(_3\) was heated at 1000°C to remove moisture. Before heating, the mixtures were homogenized by grinding with an alumina mortar and pestle. The mixtures were then pressed into pellets 10 mm in diameter and 1 mm thick by hydraulic press under 20 MPa, and then calcined at 1200 K in static air atmosphere in an electric tube furnace for about 36 h. The calcined pellets were ground, and again pressed into pellets by hydraulic press under 20 MPa, and then calcined at 1583 K for about 72 h in static air atmosphere with a number of intermediate grindings and pelletizings. The sample was then cooled down slowly to room temperature in the electric furnace. The final black coloured product, after pulverization, was used for further investigations.

The total amount of various constituent cations was estimated by Perkin Elmer atomic absorption spectrometer 700. The oxygen content in the sample was determined by the oxidation-reduction method described elsewhere.\(^{25,26}\) The precise chemical composition was determined to be DySr\(_2\)MnCrO\(_6\)\(_{0.93}\).

The room temperature X-ray diffraction data of the phase was recorded on Bruker AXS diffractometer type D 76181 (Karlsruhe, Germany) using CuK\(_\alpha\) radiations. The data were collected at scanning speed of 1°/min in the 2\(\theta\) range of 10-80°. The experimental XRD data is given in Table 1, while the pattern is plotted in Fig. 1.

The electrical resistivity measurements of the pellet of the product, sintered at 1400 K for about 12 h before use, were carried out with four probe method in the temperature range 150-300 K. For the electrodes, thin copper wires were attached to the surface of the pellet with silver paste. The magnetic susceptibility of the polycrystalline sample was measured by means of the Faraday technique in the temperature range 100-300 K using Hg[Co(SCN)]\(_4\) as calibrant in an external field of 3,700 gauss. All the magnetic susceptibility values were corrected for diamagnetism of the constituent atoms.

**Results and Discussion**

All the peaks of X-ray diffraction pattern of polycrystalline sample DySr\(_2\)MnCrO\(_7\) were successfully indexed on the tetragonal Sr\(_3\)Ti\(_2\)O\(_7\)-type structure of space group \(I4/mmm\). The unit cell parameters and space group were determined and tested by using program “Checkcell”\(^{27}\) and are given in Table 1. The atomic positions of Dy/Sr, Mn/Cr and O for DySr\(_2\)MnCrO\(_7\) have been estimated from analogy with of Sr\(_3\)V\(_2\)O\(_7\) without refinement.\(^{28}\) The theoretical diffraction intensities (Table 1) of the phase were generated with programs “Diamond” (Method of Klaus Brandenburg 1998) and “Mercury 2.3” based on the atomic positions, cell parameters and space group \(I4/mmm\). The agreement between the theoretical and experimental intensities for the phase is in general satisfactory considering that the atomic positions are not refined and that, any preferred orientation effects are neglected. The XRD results confirmed that the phase with composition DySr\(_2\)MnCrO\(_7\) having Sr\(_3\)Ti\(_2\)O\(_7\) type structure has been formed. The crystallite size \((P)\) has been calculated from the strong reflection peak using the following Scherrer’s equation\(^{29}\)

\[
P = \frac{K\lambda}{\beta_{1/2} \cos \theta}
\]

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where $K = 0.89$ and $\beta_{1/2}$ = full width at half maxima. The value of particle size comes to be 163 nm.

The temperature dependence of electrical resistivity is given in Fig. 2, where $\rho$ is plotted against temperature ($T$). The plot shows that the temperature co-efficient of resistivity is negative suggesting that the material is an insulator in the temperature range 150-300 K. The insulating behaviour of phase $\text{DySr}_2\text{MnCrO}_7$ is due to the localization of charge carriers. The similar results were also reported earlier in such RP-type phases containing Mn and Cr ions at B site.\textsuperscript{22,24} Such type of manganites show insulator-metal (I-M) transition at very low temperatures but our study is, however, limited to resistivity measurements in the temperature range 150-300 K. Various equations based upon different mechanisms of conduction, such as those applicable in case of Arrhenius model, polaron hopping model and variable range hopping model have been applied to the data of electrical resistivity of the phase.\textsuperscript{30-32} We find, the conduction process in the phase is best described using the Mott’s variable range hopping (VRH) model. In this model $\rho(T)$ is expressed as\textsuperscript{32}

$$\rho = \rho_0 \exp(BT^{-1/4})$$

where $B$ is characteristic energy of hopping. The linearity of plot between log $\rho$ and $T^{-1/4}$ (Fig. 3) shows that the electrical conduction occurs by Mott’s variable range hopping mechanism which is generally observed in such perovskite-related phases.\textsuperscript{33,34}

The temperature dependence of the inverse molar magnetic susceptibility for $\text{DySr}_2\text{MnCrO}_7$ is shown in Fig. 4. The effective magnetic moment ($\mu_{\text{eff}}$) has been calculated from the $\chi^{-1}$ versus $T$ plot and leads to the value 12.06 BM The contribution of the manganese
ion (µMn) to the magnetic moment has been calculated from the effective moment (µeff) and the theoretical moments of Dy3+ and Cr3+ ions from the relation

\[ \mu_{\text{eff}} = n_1 \mu_{\text{Dy}^{3+}} + n_2 \mu_{\text{Mn}^{3+}} + n_3 \mu_{\text{Cr}^{3+}} \]

where \( n_1, n_2 \) and \( n_3 \) are the number of Dy, Mn and Cr ions respectively, \( \mu_{\text{Dy}^{3+}} \) is the theoretical magnetic moment of the Dy3+ ion (10.63 BM) and \( \mu_{\text{Cr}^{3+}} \) is that of Cr3+ ion, assuming it to be in the high spin state \( (t_{2g}^3 e_g^0) \). For \( \mu_{\text{Mn}^{3+}} \), we obtain the value 4.18 BM. This value is larger than the theoretical magnetic moment of high spin Mn4+ ion (3.87 BM) which suggests that manganese ion is partly present in the 3+ oxidation state. The stoichiometry of the phase (DySr2MnCrO6.93) also suggests the presence of manganese ion in mixed valence state 4+ and 3+, assuming Dy in 3+, Sr in 2+ and Cr in 3+ oxidation states. It has been observed from the \( \chi^{-1} \) versus \( T \) plot (Fig. 4) that the Weiss constant (θ) is 28 K. The positive (θ) value suggests that ferromagnetic interactions are dominant in the magnetic structure of DySr2MnCrO7. The similar results were also reported earlier in such type of manganites.24,33

The ferromagnetic interactions could be due to double exchange (DE) interaction between Mn3+ and Mn4+ ions. Since the Cr3+ ion has the same electronic configuration \( (t_{2g}^3 e_g^0) \) as the Mn4+ ion, there may exist a ferromagnetic DE interaction between Cr3+ and Mn3+ ions just as between Mn4+ and Mn3+ ions. The proposal has been proved by some experimental results.36

Conclusions

A new RP-type phase of composition DySr2MnCrO7 has been synthesized by standard ceramic method. Its structure has been determined by X-ray diffraction studies. The results show that the phase crystallize in the I4/mmm space group with tetragonal unit cell. The electrical resistivity studies show that the material is an electrical insulator and conduction occurs by a 3D variable range hopping mechanism. The magnetic studies suggest that the ferromagnetic interactions are dominant and manganese ion in the phase is present in mixed valence state (Mn4+/Mn3+).

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References

SINGH et al.: LAYERED PEROVSKITE MANGANITE DySr$_2$MnCrO$_7$