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Study of electrical transport and magnetic properties in $CaMn_{1-x}Cu_xO_3$

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Abstract

Copper doped, $CaMn_{1-x}Cu_xO_3$ compounds have been prepared in single phase form for $x = 0$–0.20. XRD patterns could be analyzed using *Pbnm* space group with typical lattice parameters $a = 5.276$ Å, $b = 5.259$ Å and $c = 7.459$ Å. All samples exhibit antiferromagnetic transitions with Neel temperatures around 124 K. The temperature variations of electrical resistivity follow the semi-conducting behaviour and they could be analyzed using variable range hopping with Coulomb interaction (ES-VRH) model. The Cu doping is found to enhance the antiferromagnetic interactions.
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1. Introduction

The rare earth manganites with perovskite structure exhibit interesting electrical and magnetic properties and they have potential applications in magnetic recording [1,2]. There are several reports on colossal magneto resistivity (CMR) in $La_{1-x}D_xMnO_3$ (D = Ca, Sr, Ba, Pb) compounds [3]. Recently there are a few reports of metal–insulator transitions and CMR in Mn^{4+} rich electron doped manganites [4–6]. $CaMnO_3$ is one of the parent compounds of CMR materials and its preparation and electrical transport studies are reported by several groups [7–10]. CMR and reduction in electrical resistivity have been observed in $CaMnO_3$ by oxygen reduction or by partial doping of rare earth ion in place of Ca [11–15]. The above process leads to mixed valency of Mn^{3+} and Mn^{4+} ions, which play a major role on CMR behaviour due to their double exchange interaction [16].

The Mn atoms play a major role in CMR behaviour and there are several reports on the study of structural, electrical and magnetic properties by doping Cu in place of Mn, especially in La–Mn–O series [17–21]. It has been found that Cu doping enhances the antiferromagnetic interaction by reducing the ferromagnetic Curie temperature and increases the electrical resistivity by localizing the charge carriers. The electrical resistivity of $CaMnO_3$ and $LaMnO_3$ based materials mostly follow the small polaron hopping and/or variable range hopping mechanism [11,13,19]. The physical properties of $CaMnO_3$ is comparable to that of $CaCuO_2$, the parent compound of high T_C superconductors [22]. In general, the CMR and high T_C superconducting materials have several similarities [23]. To study the possible superexchange magnetic interaction between Cu and Mn ions, we have prepared $CaMn_{1-x}Cu_xO_3$ compounds ($x \leq 0.20$) and carried out X-ray diffraction, electrical resistivity and ac susceptibility measurements. The resistivity data have been analyzed in detail to understand the conduction mechanism.

2. Experimental details

$CaMn_{1-x}Cu_xO_3$ compounds for $x = 0$, 0.10 and 0.20 have been prepared by solid-state route. Stoichiometric ratio of $CaCO_3$, $MnCl_2{\cdot}4H_2O$ and $(CH_3COO)_2Cu{\cdot}H_2O$ with 99.9% purity were weighed and ground under acetone. The mixture of the above compounds were presintered in the temperature range 850–950 °C for over 50 h with several intermediate grindings. The presintered powder was pressed into cylindrical pellet form and was annealed in the temperature range 1000–1100 °C for 50 h with intermediate grindings and repelletising. X-ray diffraction (XRD) patterns were recorded at room temperature by using Seifert-3003TT XRD machine with Cu Kα radiation.

The temperature variation of dc electrical resistivity was measured by employing linear four probe technique and by using a

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constant current source and nanovoltmeter. Temperature variation of ac susceptibility was measured by employing mutual induction bridge method. The primary coil was energized using a sinusoidal signal of 233 Hz and the amplitude of ac magnetic field was 12.3 Oe. The susceptibility signal was measured using a dual phase lock-in amplifier. The temperature variation was achieved using a closed cycle Helium refrigerator equipped with a temperature controller. The oxidation state of Mn was determined by a chemical titration method, in which the samples were dissolved in dilute sulphuric and phosphoric acids with an addition of excess amount of $Fe(NH_4)_2(SO_4)_2$ and were titrated against self indicating $KMnO_4$ solution.

3. Results and discussions

The XRD patterns recorded for $CaMn_{1-x}Cu_xO_3$ with $x = 0$, 0.10 and 0.20 are shown in Fig. 1. We can see that the samples are essentially in single phase form with orthorhombic symmetry. The XRD patterns were analyzed using fullproof program by employing Rietveld refinement technique [24]. The patterns could be refined by using *Pbnm* space group in orthorhombic system. Typical plot of XRD pattern along with Rietveld refinement are shown in Fig. 2 for $x = 0.20$. The experimental data are shown as crosses (+) and the calculated intensities (solid lines) closely follow the experimental data. The dotted lines represent the difference between measured and calculated intensities. The typical values of reliability factors are $R_p = 9.0\%$ and $\chi^2 = 1.2\%$. The typical values of lattice parameters for $x = 0$ sample are $a = 5.276$ Å, $b = 5.259$ Å and $c = 7.549$ Å and these values are comparable to those reported by Zeng et al. [14] for $CaMnO_3$.

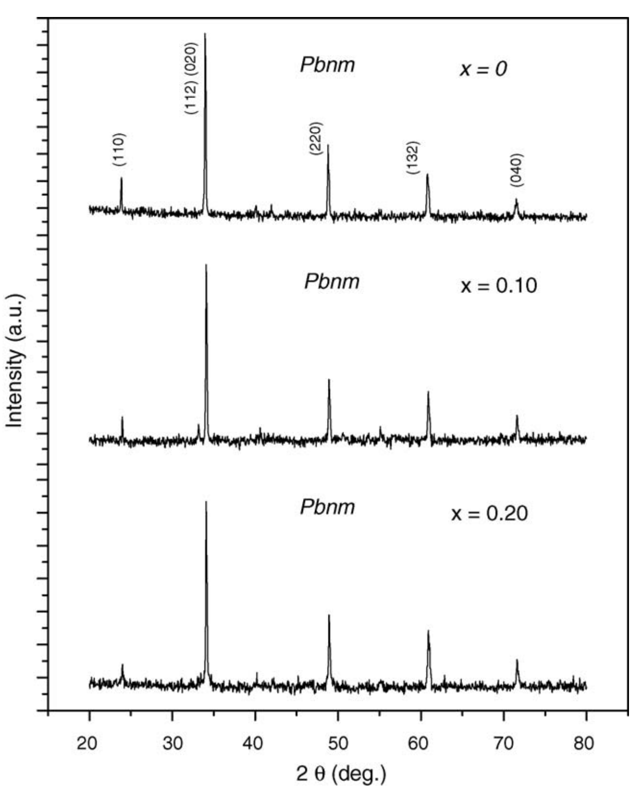

Fig. 1. XRD patterns of $x = 0$, 0.10 and 0.20 samples in $CaMn_{1-x}Cu_xO_3$.

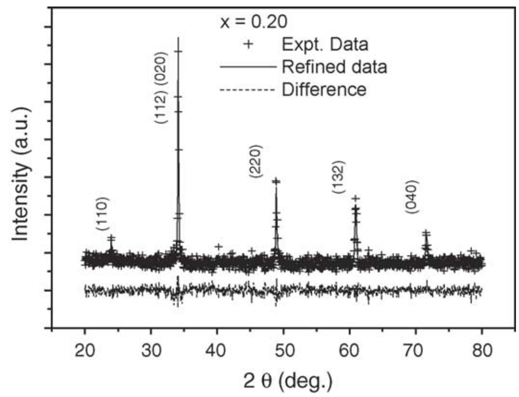

Fig. 2. XRD pattern for $x = 0.20$ sample. The '+' signs represent experimental data points and solid line represents Rietveld refined data. The dotted lines show the difference between experimental and refined data.

The lattice parameters, ⟨Mn–O⟩ bond length and Mn valency are tabulated in Table 1. The lattice parameters marginally increase with doping and this could be mainly due to larger ionic size of Cu^{2+} or Cu^{3+} compared to Mn^{4+}. The average Mn valency increases with Cu doping as expected. The values of ⟨Mn–O⟩, the bond lengths are comparable to those reported by Melo Jorge et al. [10] for $CaMnO_3$. The occupancy values of Ca, Mn, Cu were taken as free parameter during the Rietveld analysis and these values are listed in Table 1. One can find that the occupancy of Mn and Cu are close to the expected values. We could not determine the 'O' concentration unequivocally.

Typical plots of temperature variations of ac susceptibility (χ') are shown in Fig. 3 for samples with $x = 0$ and 0.20. One can observe the antiferromagnetic transitions. The Neel temperature (T_N) was determined from the temperature corresponding to $d\chi'/dT = 0$ followed by a positive peak in $d\chi'/dT$ versus temperature plot. These values are in good agreement with values determined from the peak of the χ' versus temperature plot. The values of Neel temperature, T_N and $\chi'(T_N)$ for different samples are tabulated in Table 1. These values are comparable to those reported in literature for $CaMnO_3$ based compounds [13,25]. For $x = 0$, the parent compound, a weak ferromagnetic signal of magnitude $\chi' \cong 3 \times 10^{-4}$ emu/gmOe is observed below the anti-

Table 1
Parameters obtained from ac susceptibility measurement and XRD analysis

Parameters	Samples		
	$x = 0$	$x = 0.10$	$x = 0.20$
a (Å)	5.276	5.278	5.278
b (Å)	5.259	5.261	5.260
c (Å)	7.459	7.464	7.462
G_{Ca}	0.905	0.990	0.984
G_{Mn}	0.922	0.859	0.765
G_{Cu}	–	0.092	0.197
⟨Mn–O⟩ (Å)	1.866	1.867	1.884
Mn valency	4.07	4.10	4.19
T_N (K)	124.2 ± 0.5	124.6 ± 0.5	125 ± 0.8
$\chi'(T_N)$ (10^{-3} emu/gmOe)	1.27 ± 0.01	1.27 ± 0.01	2.30 ± 0.01

The Mn valency determined from chemical titration is also given. G_{Ca}, G_{Mn} and G_{Cu} are the occupancy of respective elements obtained form the Rietveld analysis.

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