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Structure, transport and magnetic properties in $La_{2x}Sr_{2-2x}Co_{2x}Ru_{2-2x}O_6$

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ABSTRACT

The perovskite solid solutions of the type $La_{2x}Sr_{2-2x}Co_{2x}Ru_{2-2x}O_6$ with $0.25 \le x \le 0.75$ have been investigated for their structural, magnetic and transport properties. All the compounds crystallize in double perovskite structure. The magnetization measurements indicate a complex magnetic ground state with strong competition between ferromagnetic and antiferromagnetic interactions. Resistivity of the compounds is in confirmation with hopping conduction behaviour though differences are noted especially for $x=0.4$ and 0.6. Most importantly, low field (50 Oe) magnetization measurements display negative magnetization during the zero field cooled cycle. X-ray photoelectron spectroscopy measurements indicate the presence of Co^{2+}/Co^{3+} and Ru^{4+}/Ru^{5+} redox couples in all compositions except $x=0.5$. Presence of magnetic ions like Ru^{4+} and Co^{3+} gives rise to additional ferromagnetic (Ru-rich) and antiferromagnetic sublattices and also explains the observed negative magnetization.

1. Introduction

$LaSrCoRuO_6$ is a double perovskite whose magnetic properties critically depend on cationic order, charge balance and complex magnetic interactions between two transition metal ions [1–3]. Its crystal structure is composed of corner-shared CoO_6 and RuO_6 octahedra arranged in a pseudocubic array in the rocksalt arrangement. It is a semiconductor with ideal valence states HS Co^{2+} ($3d^7$ high-spin configuration) and Ru^{5+} ($4d^3$) [4]. Magnetically these compounds are reported to be antiferromagnetic with two magnetic face centered cubic (fcc) sublattices consisting of Co and Ru. Both the sublattices order with type II antiferromagnetic structure which would mean that the spins in [1 1 1] planes in succession Co–Ru–Co–Ru alternate as $+/+/-/-$. This marginalizes the Co–O–Ru nearest neighbour interactions and the ordering is governed by a competition between linear Co–O–Ru–O–Co and 90° Co–O–O–Co antiferromagnetic exchange paths [1,5]. The degree of ordering is known to affect the magnetic and transport properties due to changes in magnetic interactions and in cationic valence. Effects of anti-site disorder on the magnetic and transport properties due to La or Sr doping in $LaSrCoRuO_6$ have been investigated [1,5,6]. The change of composition (La or Sr doping) introduces mobile electrons in La richer samples or holes in Sr richer samples.

Another possible way of modifying magnetic and transport properties is by forming the solid solutions of antiferromagnetic $LaCoO_3$ and ferromagnetic $SrRuO_3$. These perovskite solid solutions of the form $Sr_{1-x}La_xRu_{1-x}Co_xO_3$ will have a strong interplay of cationic order, charge balance and complex magnetic interactions between the two B-site cations. In $SrRuO_3$ the 4d electrons of the low spin Ru^{4+} ions occupy the narrow π^* band near Fermi level [7]. The lower 3d energy levels of Co^{3+} causes a charge transfer from 4d Ru^{4+} to 3d Co^{3+} [2]. However, Co can have various electronic states including high spin (HS) Co^{2+}, Co^{3+} and Co^{4+}, intermediate spin (IS) Co^{3+} and Co^{4+} and low spin (LS) Co^{3+} and Co^{4+} [8–12]. This complicates the situation giving rise to properties like localized magnetic moment of Co [13], negative magnetoresistance [14]. In case of $Sr_{1-x}La_xRu_{1-x}Co_xO_3$, a complete charge transfer occurs at $x=0.5$. At this composition the CoO_6 and RuO_6 octahedra align themselves in a pseudocubic array in the rocksalt arrangement forming the archtype "double perovskite" structure.

The charge transfer between Ru and Co in $LaSrCoRuO_6$ is very sensitive to local atomic structure such as cation order [1,3,6]. Any disturbance in this cation order leads to compensation of antiferromagnetic interactions by the ferromagnetic interactions most likely associated with Ru–O–Ru interactions. The $LaCoO_3$ substituted $SrRuO_3$ has been known to exhibit large local magnetic moment arising due to Co spin polarizing the itinerant electrons of $SrRuO_3$ [2]. However, the delicate charge balance achieved in solid solutions by conversion of Co^{3+} to Co^{2+} and oxidation of Ru^{4+} to Ru^{5+} due to the formation of double perovskite structure has not been addressed. More importantly the magnetic interactions at play as the system transforms from a ferromagnetic ground state to an antiferromagnetic one are far from being clearly understood. It is with this aim the present investigation is proposed. This paper describes detailed investigations carried out on the structural, magnetic and transport properties of solid solutions of $SrRuO_3$ and $LaCoO_3$ which form double

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perovskite compounds of the type $La_{2x}Sr_{2-2x}Co_{2x}Ru_{2-2x}O_6$, where $0.25 \leq x \leq 0.75$.

2. Experimental

Polycrystalline samples of $La_{2x}Sr_{2-2x}Co_{2x}Ru_{2-2x}O_6$, $0.25 \leq x \leq 0.75$ were synthesized by solid state reaction method by taking pre-dried stoichiometric amounts of La_2O_3, $SrCO_3$, $Co(NO_3)_2 \cdot 6H_2O$ and RuO_2. These starting powders were ground thoroughly, pressed into pellets and heated for a total of 48 h, at 1300 °C with three intermediate regrinding steps. All samples were deemed to be phase pure, as X-ray diffraction (XRD) data collected on a Rigaku X-ray diffractometer in the range of $18^\circ \leq 2\theta \leq 80^\circ$ using CuK_α radiation showed no impurity reflections. The diffraction patterns were Rietveld refined using FULLPROF suite and structural parameters were obtained. DC magnetization (M) was measured, both as a function of temperature and magnetic field using the Quantum Design SQUID magnetometer (MPMS-5S). Magnetization as a function of temperature $M(T)$ was measured in an applied field of 50 and 1000 Oe in the temperature range of 5–300 K. The sample was initially cooled from 300 to 5 K in zero applied field and the data was recorded while warming up to 300 K in the applied magnetic field (referred to as ZFC curve) and subsequent cooling (referred to as FC curve) back to 5 K. Magnetization as a function of field was measured under sweep magnetic fields up to ±5 T at various temperatures. Before each $M(H)$ was recorded, the sample was warmed to 300 K and cooled back to the desired temperature. Neutron diffraction (ND) measurements were performed at room temperature (RT) and 20 K and a wavelength of 1.24 Å using powder diffractometer at Dhruva, Trombay. X-ray photoelectron spectra at Co (2p) and Ru (3d) levels were recorded using Thermo Fisher Scientific Multilab 2000 (England) instrument with AlK_α radiation (1486.6 eV). The binding energies reported here is with reference to graphite at 284.5 eV having an accuracy of ±0.1 eV.

3. Results

The Rietveld refined XRD patterns for all the compounds studied here are presented in Fig. 1. The samples crystallize in the $P2_{1/n}$ monoclinic structure with an initial increase followed by a decrease beyond $x = 0.5$ of cell volume as $LaCoO_3$ is added to $SrRuO_3$ to form a solid solutions. It may be mentioned here that the compounds with values of $x < 0.25$ and $x > 0.75$ have Pbnm and $R\overline{3}c$ structures respectively and hence were not studied as they cannot be classified as double perovskites. Rietveld refinement of the XRD patterns were carried out with the $P2_{1/n}$ space group wherein the La/Sr occupy the 4e site with the fractional coordinates (0.00125, 0.00774, 0.2463), Co is at 2c (0.5, 0, 0.5), Ru is at 2d (0.5, 0, 0) and the oxygen atoms occupy three sites, viz, (0.2491, 0.2566, 0.0295), (0.2207, −0.2233, 0.0295) and (−0.06418, 0.4995, 0.2507). The scale factor, back ground parameters, cell parameters, Co and Ru site occupancies along with instrumental broadening, totalling 17 parameters were refined in that order to obtain a good fit. As can be seen from Table 1 the B-site disorder was found to be least for $x = 0.5$ which also happens to be the stoichiometric double perovskite $LaSrCoRuO_6$. Interestingly the disorder or the deviation from expected occupancy is highest for $x = 0.4$ and 0.6. This aspect needs more attention and perhaps magnetic and transport properties will shed light on this. The crystallographic parameters obtained from the above refinements along with the Curie–Weiss parameters calculated from magnetization measurements are all summarized in Table 2.

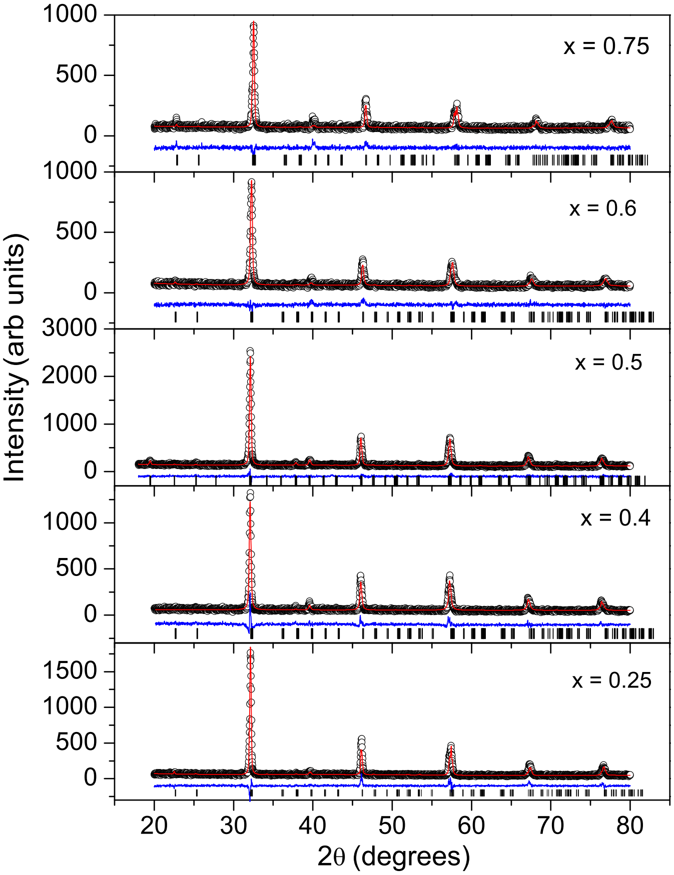

Fig. 1. Rietveld refined XRD patterns of $La_{2x}Sr_{2-2x}Co_{2x}Ru_{2-2x}O_6$. The open circles show the observed counts and the continuous line passing through these counts is the calculated profile. The difference between the observed and calculated patterns is shown as a continuous line at the bottom of the two profiles. The calculated positions of the reflections are shown as vertical bars.

Table 1
Expected (E) and refined (R) occupancies of Co and Ru for different values of $La_{2x}Sr_{2-2x}Co_{2x}Ru_{2-2x}O_6$.

$x \rightarrow$		0.25		0.4		0.5		0.6		0.75	
Sites	Atoms	E	R	E	R	E	R	E	R	E	R
$(\frac{1}{2},0,\frac{1}{2})$	Co	0.25	0.19	0.4	0.26	0.5	0.49	0.5	0.36	0.5	0.45
	Ru	0.25	0.31	0.1	0.24	–	0.01	–	0.14	–	0.05
$(\frac{1}{2}),0,0)$	Ru	0.5	0.44	0.5	0.36	0.5	0.49	0.4	0.26	0.25	0.20
	Co	–	0.06	–	0.14	–	0.01	0.1	0.24	0.25	0.30

Magnetization measurements performed in applied fields of 1000 and 50 Oe during the ZFC and FC cycles for $x = 0.25$, 0.4, 0.6 and 0.75 samples are presented in Fig. 2. In the case of $x = 0.25$, 0.4 and 0.6 there is a wide difference in magnetization recorded during the ZFC and FC cycles. The ZFC magnetization for these three samples, with increasing temperature increases sharply culminating into a broad hump centered around 50 K. It decreases slightly with further rise in temperature before increasing sharply resulting in a peak at about 150 K. The FC magnetization, on the other hand decreases continuously to about 167 K and then settles down into a low value giving an impression of a ferro to para transition. The wide difference in the magnetization between the ZFC and FC cycle indicates a complex magnetic ground state. It may also be noted that the magnetization (emu/mole) value at 5 K decreases with increasing La and Co contents. Further with increasing x the irreversibility between the ZFC and FC curves is also seen to decrease until at