

Structural & physical properties of the binary transition metal- containing perovskite $\text{La}_2\text{CoMnO}_6$

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Abstract

We are currently developing binary transition metal containing perovskite type materials, which potentially possess novel temperature-induced structural and electronic transitions. Infrared, structural and electrical data for the $\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$ ($x=0.5$) system are reported revealing some interesting features including an insulator metal transition, charge ordering and charge disproportionation.

Keywords: (Infrared spectroscopy, X-ray absorption spectroscopy, Neutron diffraction, Metal-insulator phase transition, Order-disorder phase transition)

1. Introduction

LaCoO_3 has been extensively studied in the past because of its novel electronic properties. Below 77K the Co^{3+} ions exist in a diamagnetic low spin state. In the temperature range 77 – 200K there is a thermally driven spin state transition. In the temperature region 200 – 400K, the high spin and low spin Co^{3+} pairs transform to Co^{2+} and Co^{4+} . At 700K, LaCoO_3 becomes metallic [1].

Another interesting perovskite is LaMnO_3 , which at room temperature is a semiconductor. A Jahn Teller distortion - necessitating the lifting of e_g orbital degeneracy (in octahedral symmetry) gives rise to irregular MnO_6 octahedra. This distortion decreases in magnitude with increasing temperature and LaMnO_3 becomes metallic at 800K [2].

Of interest to us is what are the consequences for the electronic properties of LaMnO_3 and LaCoO_3 in the single-phase material $\text{La}_2\text{CoMnO}_6$.

2. Experimental

The material was synthesised by nitrate decomposition at 800K, followed by annealing in air at 1400 K for 16 hours with intermittent grinding. The material was finally cooled at a rate of 1K min^{-1} to 290K. Ambient and high temperature powder X-ray diffraction patterns were recorded using Philips diffractometers, one of which was modified for high temperature measurements. Mn and Co K-edge EXAFS were measured on station 8.1 at the SRS

facility Daresbury, UK. Infrared properties were measured using a Nicolet Instruments 760 IR spectrometer using a modified Oxford Instruments cryostat with an operating temperature of 12-700K. Electrical measurements were performed using a 4-wire technique on pressed pellets. The samples were cooled and heated in the modified cryostat. Neutron time-of-flight data was obtained using HRPD at the Rutherford Appleton Laboratory, UK.

3 Results

3.1 Ambient Temperature Structure

Ambient temperature X-ray diffraction (XRD) confirmed a single-phase material, which could be indexed to the orthorhombic space group Pnma . The XRD pattern contained superlattice reflections which could be indexed by doubling of the c-axis. EXAFS measurements indicated that the Co and Mn to oxygen bond distances at room temperature were significantly different being 1.99\AA and 1.86\AA respectively. Shannon [3], suggested that by comparing the interatomic transition metal (TM) to oxygen distances of materials where the TM oxidation state is unknown with materials containing the same ions with the TM in known oxidation states, it would be possible to infer the unknown oxidation state of the TM ion. This approximation is valid as long as similar bonding is found

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in the unknown and reference systems. We have used a similar procedure for our system (table 1).

Table 1 TM-O Bond distances obtained from EXAFS

Material	K-Edge	TM-O Distance/Å
La ₂ CoMnO ₆	Co	1.99
La ₂ CoMnO ₆	Mn	1.86
LaCoO ₃	Co	1.93
La ₂ CoO ₄	Co	1.99
LaMnO ₃	Mn	1.92
CaMnO ₃	Mn	1.86

3.2 Temperature Dependence of Structure

The temperature dependence of the XRD pattern shows two discontinuities in the cell volume one at 400K and the other at 600K (figure 1). The transition at 600K is associated with the loss of the superlattice reflections in the XRD pattern whilst, interestingly, the 400K anomaly is associated with an electrical transition (vide infra).

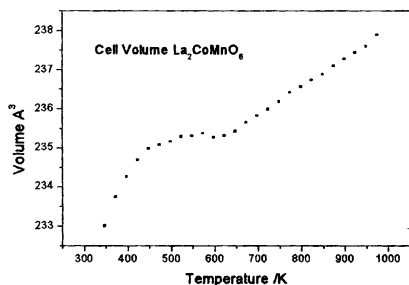


Figure 1 Temperature dependence of cell volume of La₂CoMnO₆

Refinement of neutron diffraction data obtained at 300K reveals a monoclinic distortion (P21/m) with ordering of the cobalt and manganese ions. Refinement of the patterns above 400K indicates the TM site preference begins to decrease. Just above the transition at 400K, a change is observed in the profile and intensity of the superlattice reflections. Upon further heating to 625K, there is a change of structure from monoclinic to rhombohedral. Refinement of the neutron diffraction data confirms unambiguously the superlattice reflections to be result of charge ordering and not octahedral tilting something that XRD is unable to do. Further details of this work will be reported subsequently.

3.3 Infrared and Electrical Properties

The relationship between infrared absorption and resistivity is shown in figure 2. A dramatic change in infrared absorption is observed at the point where an electrical transition is seen (400K). The changes were followed at an arbitrary point of 1000 cm⁻¹. Although the magnitudes of the changes are not as large at shorter

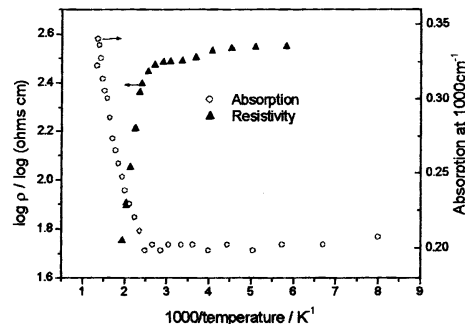


Figure 2 Temperature dependence of the electrical properties and infrared absorption of La₂CoMnO₆

wavelengths, they are still evident.

4 Discussion

The structure determined by the neutron diffraction data of La₂CoMnO₆ is similar to that of YNiO₃ [4] where the Ni ions are suggested to exist as Ni^{3+(+δq)} + Ni^{3+(-δq)} with δq~0.3. Our neutron and EXAFS data suggests that La₂Co^{3+(-Δq)}Mn^{3+(+Δq)}O₆ is a more appropriate way to describe La₂CoMnO₆ and not La₂Co³⁺Mn³⁺O₆ where Δq→1. The neutron data indicates that these Co and Mn ions are fully charge ordered at low temperatures and the disordering induces an electrical transition which is also reflected in the infrared spectra. We note that charge ordering can render a material insulating or semiconducting [5].

The origin of the increase in baseline absorption at 1000 cm⁻¹ is likely to be an increase in free carrier mobility, mass or both. As seen in GMRs (gigantic magnetoresistance materials) infrared absorption can be a good indicator of the electrical properties of a material.

5 Conclusions

In the material La₂CoMnO₆, we have found two temperature driven transitions. The first is electrical at 400K and may result from charge ordering. The loss of charge ordering also manifests itself by changes in the infrared spectra. The second is a structural transition at 600K, which does not manifest itself by changes in optical conductivity.

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