

Cu doping as a tool for understanding CMR

B.Vertruyen¹, R.Cloots¹, A. Rulmont¹, S. Dorbolo²,
P. Vanderbemden² and M. Ausloos³

¹ LCIS, Chemistry Institute B6, University of Liège, B-4000 Liège, Belgium

² MIEL, Montefiore Institute, University of Liège, B-4000 Liège, Belgium

³ SUPRAS, Physics Institute B5, University of Liège, B-4000 Liège, Belgium

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Abstract. Doping at the Mn-site in CMR manganate-based perovskites has been shown to affect strongly the physical properties of those compounds. We study here the effect of copper substitution in the low doping range on the electrical transport properties of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. It turns out that the transition temperature decrease observed in doped samples can be drastically reduced by addition of silicon dioxide SiO_2 . It is shown that copper is trapped in a secondary phase composed of La,Ca,Si,Cu and O. The resultant Mn-site vacancies appear to be less detrimental to the electronic conduction than the likely antiferromagnetic clusters induced by the copper ions in the Mn-O network.

Introduction

A few years ago, the discovery of colossal magnetoresistance (CMR) properties in LnMnO_3 -based perovskites (Ln = lanthanide) revived the interest for the manganate family. Despite a huge amount of experimental and theoretical work, the physical mechanisms at the origin of magnetoresistance are still very badly known. Most of the tentative explanations are based on the double exchange model of Zener [1], where the strong Hund coupling requires a ferromagnetic alignment of the manganese ions to allow for electronic conduction by the e_g electrons. It turns out that the physical properties of manganates are very sensitive to carrier concentration and crystallographic distortions of the perovskite structure. Those parameters have been extensively studied in doped manganate compounds : $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$, where Ln is a lanthanide ion and A generally an alkaline-earth ion. [2] A growing interest has also been devoted to Mn-site-doped manganates ($\text{LnMn}_{1-y}\text{B}_y\text{O}_3$, where B is often a transition metal ion), in order to find out how the Mn-O network governs the physical properties.[3,4] We have chosen to focus on the low-range copper substitution at the manganese site in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. We report here about an interesting feature put into evidence when silicon dioxide SiO_2 is added to the reactant mixture.

Experimental

A series of samples of nominal composition " $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3 + y \text{SiO}_2$ " ($x = 0, 0.04, 0.08$; $y = 0, 0.02, 0.04, 0.08$ – see table 1) were prepared by a standard solid state reaction. Mixtures of lanthanum oxide (La_2O_3), calcium carbonate (CaCO_3), manganese oxalate ($\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), copper oxide (CuO) and silicon dioxide (SiO_2) were thoroughly ground with petroleum ether and heated to 1473 K with intermediate grindings. Pellets were pressed uniaxially and fired to 1573 K for 48 h.

The samples were characterized by X-ray diffraction, scanning electron microscopy and Energy-Dispersive X-ray analysis (EDX). The physical properties were measured using a Physical Properties Measurement System (PPMS) from Quantum Design. Resistivity measurements were carried out with the standard four-probe method. Magnetic measurements (not reported here) were also performed.

Results

Figure 1 displays the electrical resistivity vs. temperature curves. The peak temperatures are collected in table 1, together with the label given to each sample. The magnetic transition temperature T_C (not reported here) is always within 5 K of T_{p1} , the temperature of the first electrical transition. Under application of a magnetic field, the resistivity decreases (not shown here). As expected, magnetoresistance is mainly observed around the peak temperature and at low temperature (grain-boundary-related magnetoresistance). The chemical homogeneity of the different samples was checked by EDX analysis and X-ray diffraction. Only the Si-free sample (C4S0) is found to be homogeneous. In each Si-containing sample there is a secondary phase mainly composed of Si, La, Ca, O - and Cu when Cu is present. In such samples, the copper levels detected in the main manganate phase are comparable to the experimental error. Finally, it should be mentioned that it was put in evidence by scanning electron microscopy that the C4S0 sample is more porous and has noticeably smaller grains than the other samples.

Table 1 : Labels, compositions and resistance peak temperatures

Label	Composition ^a	T_{p1} [K]	T_{p2} [K]
C0S8	$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + 8\% \text{SiO}_2$	256	
C4S0	$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.96}\text{Cu}_{0.04}\text{O}_3 + 0\% \text{SiO}_2$	187	168.5
C4S2	$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.96}\text{Cu}_{0.04}\text{O}_3 + 2\% \text{SiO}_2$	241.5	177
C4S4	$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.96}\text{Cu}_{0.04}\text{O}_3 + 4\% \text{SiO}_2$	245	
C4S8	$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.96}\text{Cu}_{0.04}\text{O}_3 + 8\% \text{SiO}_2$	246	
C8S4	$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.92}\text{Cu}_{0.08}\text{O}_3 + 4\% \text{SiO}_2$	229	146

^a SiO_2 contents are given in molar percentage for 1 mol of manganate.

Figure 1 : Resistance vs. temperature curves under zero magnetic field

Discussion

Those experimental results allow us to study the influence of copper doping in presence or absence of SiO_2 . The sample C0S8 illustrates the effect of a SiO_2 addition on a copper-free sample. In the series of samples C4S0, C4S2, C4S4 and C4S8, the SiO_2 content is progressively increased while keeping a constant copper level. A sample with a higher copper content (C8S4) was prepared for comparison.

SiO_2 addition to a copper-free sample $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ does not drastically alter the electrical transport properties. The transition temperature is lowered by about 10 K when compared to the best pure $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ samples [2]. A transition temperature similar to that of the C0S8 sample is often observed for pure $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ samples, due for example to oxygen non-stoichiometry.[5] In the case of the C0S8 sample, the formation of the secondary phase mainly composed of La, Ca, Si and O leaves A-site-vacancies in the manganate compound. It is well known that vacancies alter the crystallographic structure and strongly affect the electrical conduction.[6] The transition temperature decrease in the sample C0S8 is thus not an intrinsic effect of SiO_2 addition but is the consequence of the vacancies induced by the presence of SiO_2 .

The decrease in transition temperature observed for the Cu-doped sample C4S0 was expected. Indeed, previous works [3,7] on Mn-site doping have shown that substitutions in the Mn-O network lower the transition temperature. In our case, a 4%Cu-doping lowers the transition by about 80 K. We attribute the unusual resistivity peak structure (broad peak with two maxima) to a microstructural effect. The microscopic characterisation has indeed revealed high porosity and noticeably small grains in this sample. Such features are generally thought to induce peak broadening.[8]

The effect of a SiO_2 addition to the reactant mixture is studied in the samples C4S2, C4S4 and C4S8, for a fixed level of copper. The C4S4 and C4S8 samples display single-peak resistivity curves, with identical transition temperatures. EDX analysis has shown that copper concentrates in the secondary phase. In those samples, it seems that all (or almost all) copper ions are trapped in the secondary phase. Beyond a critical SiO_2 concentration, the manganate phase becomes copper-free, and the transition temperature remains constant. The C4S2 sample displays an intermediate behaviour : the resistivity curve shows two well-resolved peaks. The high-temperature peak almost coincides with the peak of the C4S4 and C4S8 samples, whereas the second peak is at a much lower temperature. From those results, it appears that the critical SiO_2 concentration must correspond to similar molar amounts of copper and silicon. This is confirmed by the C8S4 sample, that also displays a double peak in its resistivity curve.

At this stage, two issues have still to be addressed : (i) the temperature of the transition in the C4S4 and C4S8 samples, (ii) the origin of the double peak behaviour.

Although the peak temperature in the C4S4 and C4S8 samples remain lower than that of Cu-free samples, it is much higher than that of the SiO_2 -free sample (C4S0). When the copper ions are trapped in the secondary phase, they leave vacancies on Mn sites. Since the Mn-O network is fundamental for the electrical conduction, it is to be expected that such vacancies will lower the transition temperature. Besides, vacancies on the Mn-site are more detrimental to the conduction than vacancies on the A-site. It is indeed observed that the transition temperature is less depressed in the sample C0S8, which contains only A-site vacancies. The higher decrease in transition temperature for the SiO_2 -free Cu-doped sample (C4S0) indicates that a copper ion on a Mn site alters the Mn-O network much more than a simple vacancy. In some previous studies [7,9] on higher Cu-doping range, it was suggested that Cu ions induce antiferromagnetic coupling of

neighbouring Mn ions, leading to antiferromagnetic clusters formation. Since the electrical conduction is hindered in such clusters, this explains the decrease in transition temperature.

The origin of the double peak behaviour is difficult to establish unambiguously. Such double peak features are often attributed to inhomogeneities, either compositional, structural or electronic. [10,11] Since the double peak appears in samples with intermediate SiO₂ levels, it is likely that some copper remains in the manganate phase. There could be a compositional inhomogeneity, with Cu-free zones in the neighbourhood of the secondary phase grains. Another possibility is a phase separation of antiferromagnetic clusters from the ferromagnetic background, leading to a double peak feature via a percolation mechanism.

Conclusion

Doping at the Mn-site in CMR manganate-based perovskites has been shown to affect strongly the physical properties of those compounds. We have studied the effect of copper substitution in the low doping range on the electrical transport properties of La_{0.7}Ca_{0.3}MnO₃. It turns out that the transition temperature decrease observed in doped samples can be drastically reduced by addition of silicon dioxide SiO₂. It was shown that copper is trapped in a secondary phase composed of La,Ca,Si,Cu and O. The resultant Mn-site vacancies appear to be less detrimental to the electronic conduction than the likely antiferromagnetic clusters induced by the copper ions in the Mn-O network.

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