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Optical conductivity in $La_{0.8}Sr_{0.2}Mn_{1-x}Ru_xO_3$

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Abstract

The series $La_{0.8}Sr_{0.2}Mn_{1-x}Ru_xO_3$ ($0 \leq x \leq 0.15$) were prepared by an organic gel-assisted citrate process in order to perform infrared measurements. The Curie (T_C) and the metal–insulator (T_{IM}) transition temperatures decrease when the Ru content increases, and it is associated to a more and more insulating behaviour. In the optical conductivity at room temperature, the middle infrared region upshifts by transiting from the metallic to the insulating state according to increased carrier localisation. Ru breaks the long-range magnetic order and softens the double exchange interaction because the optical measurements show us that Ru favours the carrier localisation energy.

Keywords: Sol-gel processes; Optical properties; Perovskites; Manganites

1. Introduction

The study of the structural and magnetic properties of a large number of perovskite related materials with the general formula $Ln_{1-y}A_yMnO_3$ (Ln: trivalent lanthanide, A: divalent cation) has been a major subject of interest since those compounds show a colossal magnetoresistance upon application of magnetic field. While changing both the nature of divalent cation on the A-site and the *y* value, the doped manganites could exhibit a rich diagram. They enable, therefore, a promising understanding of the mechanism of those systems. The double exchange (DE) interaction [1] still governs the physics of the system and is the main mechanism which explains the ferromagnetic metallic state. In this case, both Curie temperature T_C and metal-to-insulating temperature T_{IM} are associated with almost the same value. Many groups doped also the Mn-site and observed systematically a decrease of the temperature transition. When Ru is substituted in an anti-ferromagnetic insulating matrix, it was shown to increase the ferromagnetism and the metallicity, [2–4] but if it is substituted in a ferromagnetic metal phase, it causes opposite effect and decreases the ferromagnetism and the metallicity. [5] Because Ru doping may cause some unexpected changes in magnetic and transport properties, we have carried out infrared measurements on $La_{0.8}Sr_{0.2}Mn_{1-x}Ru_xO_3$ with the expectation to find some correlation between optical properties and transport/magnetic properties. The samples were prepared by an organic gel-assisted citrate method that allows us to obtain high density samples with a very smooth surface after polishing.

2. Experiment

Polycrystalline samples of $La_{0.8}Sr_{0.2}Mn_{1-x}Ru_xO_3$ ($0 \leq x \leq 0.15$) were prepared by an organic gel-assisted citrate process. [6] All the required cations in the appropriate ratios were dissolved into a nitrate solution and chelated by adding triammonium citrate. A polyacrylamide network was formed in situ by the organic monomers consisting of acrylamide and *N*,*N*′-methylene-bis-acrylamide which were co-polymerised by heating at about 100 °C. The gel was calcined at 750 °C for 5 h and the final powders were pressed into pellets under 4000 bar/cm^2 and sintered at 1250 °C during 12 h in air. The pellets were annealed under an oxygen flow at 800 °C during 50 h. The samples were polished using the diamond paste to 0.25 μm in order to obtain samples which are smooth enough for optical reflectivity. The structure and phase purity were checked by X-ray powder diffraction (XRD) by using a Bruker D8 diffractometer with a Cu Kα radiation

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($\lambda = 1.5418$ Å). Structural parameters were refined by the Rietveld method using the FULLPROF program.[7] Compositions were checked by energy dispersive X-ray (EDX). Electron spin resonance (ESR) measurements were performed in the X-band with a Bruker ER 200 EPR spectrometer. The transport measurements were carried out by using the conventional four probe method in the range of temperature from 77 K to 350 K. Reflectivity measurements were performed between 5 meV and 3 eV on a Bruker IFS66v Fourier transform spectrometer at room temperature. Optical conductivity spectra $\sigma(\omega)$ were obtained through Kramers–Kronig transformation (KKT) by extrapolating the reflectivity below 5 meV and over 3 eV by using Lorentz oscillators.

3. Results and discussions

The XRD patterns of powders exhibit a single rhombohedral phase indexing in the space group $R\bar{3}c$ for all the series of $La_{0.8}Sr_{0.2}Mn_{1-x}Ru_xO_3$ ($x = 0$, 0.05, 0.1 and 0.15). Two examples are given in Fig. 1. The lattice parameters that are reported in Table 1 increase slightly with Ru content. EDX measurements showed that the chemical compositions of all of the samples are close to the nominal value. From the ESR data, a paramagnetic-to-ferromagnetic transition upon cooling was observed in all compositions. The Curie temperature (T_C) was determined by the method reported elsewhere[8] (see Table 1). The T_C decreases linearly with the Ru content from

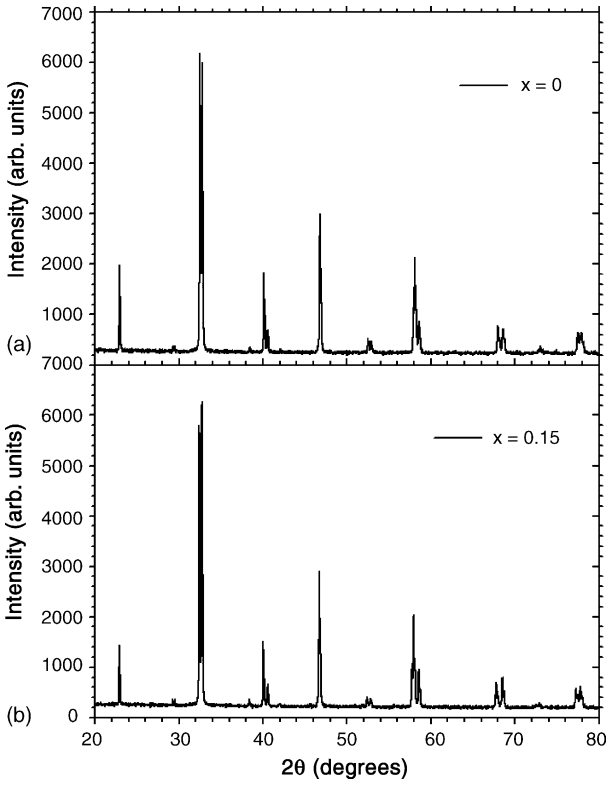

Fig. 1. XRD patterns of $La_{0.8}Sr_{0.2}Mn\,O_3$ for $x = 0$ (a) and for $x = 0.15$ (b).

Table 1
Lattice parameters a and c, the T_C values obtained as Ref.[4]

x	a (Å)	c (Å)	T_C (K)	T_{IM} (K)	ρ (300 K)
0	5.5153 (2)	13.3574 (5)	311	309	0.0213
0.05	5.5215 (2)	13.3550 (4)	276	281	0.0550
0.10	5.5274 (2)	13.3592 (4)	264	251	0.0867
0.15	5.5329 (2)	13.3630 (4)	234		0.1073

T_{IM} estimated from the maximum of the resistivity measurements and resistivity at room temperature vs. Ru content x.

311 K for $x = 0$ to 234 K for $x = 0.15$. We obtained similar results as those obtained by doping with non-magnetic element like Al[9] or Co and Ni,[10] which is, according to the authors, due to a break of the long-range ferromagnetic order. The temperature dependence of resistivity exhibits an insulator-to-metal (IM) transition with a T_{IM} value which remains close to T_C (see Table 1). An insulating behaviour is found in the whole temperature range for $x = 0.15$. Theses results suggest stronger carrier localisation. The emergence of this insulating behaviour is consistent with the gradual breakdown of the DE interaction with Ru doping, and the I–M transition disappears above 10%. The reflectivity and conductivity spectra taken at room temperature are shown in Fig. 2. By bearing in mind that the compound with $x = 0$ is the only one which is a ferromagnetic metal at room temperature

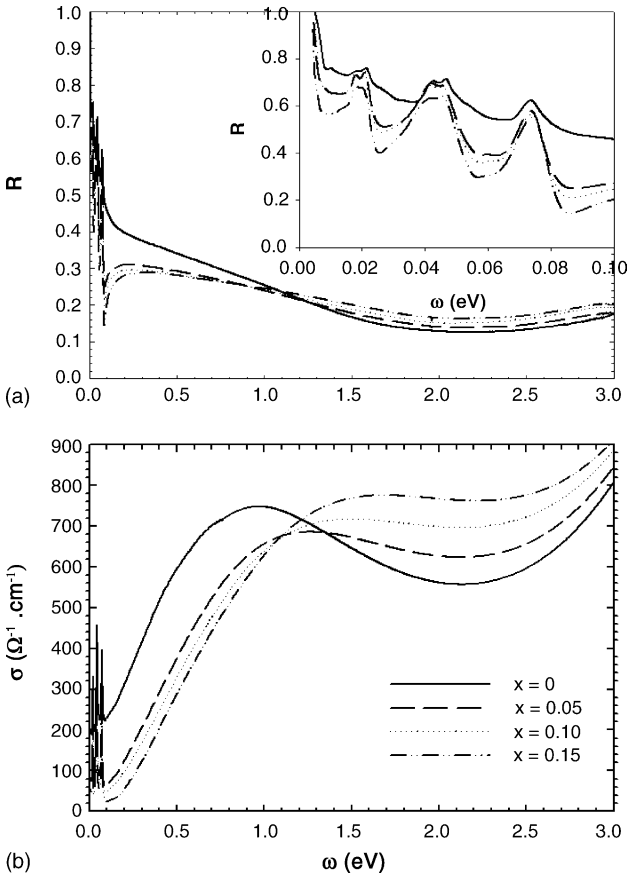

Fig. 2. Reflectivity (a) and conductivity (b) spectra obtained at room temperature of the series of $La_{0.8}Sr_{0.2}Mn_{1-x}Ru_xO_3$ ($0 \le x \le 0.15$).

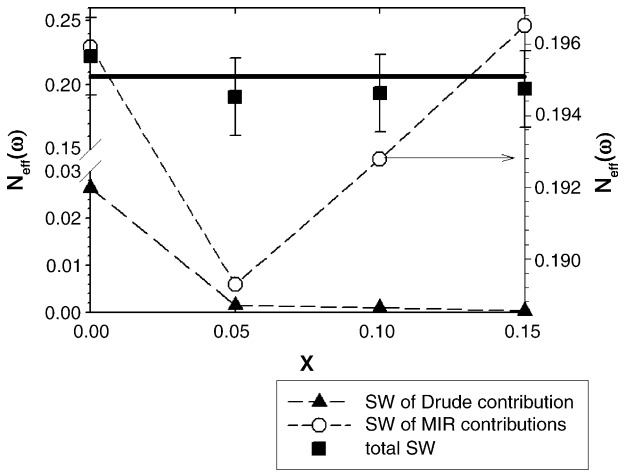

Fig. 3. The effective number of carriers per unit cell $N_{\text{eff}}(\omega)$ vs. Ru content for each contribution: Drude, MIR and total (assuming m^* equal to the electron mass). Lines are only guides for the eyes.

whereas the others are paramagnetic insulators, we can explain the shape of the optical spectra. Actually, for $x = 0$, the compound shows a metallic-like behaviour associated with a screening of the phonons, and for $x = 0.05$ an more insulating behaviour. At low frequencies, we observe the three strong phonon bands expected for cubic perovskites ABO_3 and a free carrier contribution, the so-called Drude contribution that can be attributed to the mobile holes induced by Sr doping. At room temperature, the conductivity at $= 0$ decreases gradually when x increases which is in reasonable agreement with the static resistivity values, about one order of magnitude larger. This agreement is remarkable for measurements carried out on ceramics. Considering the phonon part, the external mode lies at the lowest frequency ≈20 meV which corresponds to the vibration of the La or Sr ions against the MnO_6 octahedron. The bending mode at ≈42 meV represents the internal vibration of both Mn and apical oxygen ions against planar oxygen. The higher energy peak located at ≈72 meV is the stretching mode and corresponds to the motion of the Mn ion against the MnO_6 octahedron. Note that both external and bending modes are split into two bands, due to the non-cubic structure. In order to fit the conductivity spectra, we consider two contributions in the middle-infrared (MIR) region. The undoped $LaMnO_3$ contains only Mn^{3+} species and has only a weak contribution in the MIR region centred at 0.75 eV. Doping with 20% of Sr on the La-site induces 20% of Mn^{4+} species and in this case, a second contribution appears around 1.1 eV at the expense of the first one whose energy decreases down to 0.4 eV. We calculated the effective number of carriers per unit cell $N_{\text{eff}}(\omega)$ by applying Eq. (4.3) from Ref. [11] on the whole spectral weight below 2 eV ($\text{SW} = \int_0^{2\,\text{eV}} \sigma(\omega)\,\text{d}\omega$) for each composition (shown in Fig. 3), assuming that the hole mass is the electron mass. When Ru is substituted for Mn, $N_{\text{eff}}(\omega)$ remains close to 0.2 as shown in Fig. 3. This number is in good agreement with the starting number of Mn^{4+} per unit cell for $x = 0$. According to the resistivity values, the number of carriers of the Drude contribution decreases strongly when x increases. Simultaneously, the $N_{\text{eff}}(\omega)$ of the MIR contributions increases (Fig. 3). This SW transfer from the low energy region representing by free carriers to the high energy region characteristic of more localised carriers shows that carriers are more trapped by the lattice when the Ru content increases. The significant increase of the MIR contribution energy from 1 eV to 1.5 eV is also representative of this carrier localisation.

4. Conclusions

In conclusion, the Ru doping causes a decrease in both the ferromagnetism and the metallicity of $La_{0.8}Sr_{0.2}Mn_{1-x}Ru_xO_3$. In the optical conductivity, the middle infrared region shifts from the low-frequency region to higher frequency. Ru seems to break the long-range magnetic order and softens the DE interactions. The optical results showed that Ru favours the carrier localisation in low-doped compounds.

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