

INFLUENCE OF P-POLYPHENYLENE IN MANGANITE/POLYMER COMPOSITES

L. K. Gil^{1*}, K. Gross², E. Baca², O. Morán², C. Quinas³ and G. Bolaños³

1 Departamento de Química, Universidad del Valle, Cali, Colombia

2 Departamento de Física, Universidad del Valle, Cali, Colombia

3 Facultad de Ciencias Naturales, Universidad del Cauca, Popayán, Colombia

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RESUMEN

Óxidos de manganeso policristalinos $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) fueron preparados por reacción de estado sólido de los correspondientes precursores. Estas manganitas sirvieron como matriz para la elaboración de dos diferentes variedades de compositas utilizando el polímero conjugado poliparafenileno (PPP) como segunda fase con diferentes fracciones de peso. La síntesis del PPP se llevo a cabo por una polimerización catiónica oxidativa del benceno en presencia de un ácido de Lewis como catalizador, agua como cocatalizados y un agente oxidante, dando lugar a un homopolímero con propiedades pertenecientes al PPP. Las características estructurales del polímero se corroboraron por medio de espectroscopia IR. Las manganitas y el polímero fueron entonces mezclados y posteriormente calcinados a 400 °C para obtener compositas del tipo: $(\text{LSMO})_{1-x}(\text{PPP})_x$. Las propiedades de magneto-transporte de estos materiales fueron estudiadas en campos magnéticos $\leq 2\text{T}$. Un incremento significativo de la magnetorresistencia colosal (CMR) negativa fue observado en un amplio rango de temperaturas. El aumento de la MR es atribuido a un incremento en la corriente de tunelamiento de electrones con espines polarizados como resultado del desorden magnético causado en la manganita por la adición del PPP.

Palabras claves: composites, materials polimericoa

ABSTRACT

Polycrystalline manganese oxides $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) were produced through conventional solid-state reaction of the parent precursors. The so sintetized manganites acted as matrixes for the preparation of two different varieties of composites, in which the conjugated polymer polyparaphenylene (PPP) was used as second phase. The PPP was synthesized using the Kovacic method by cationic polarization of benzene. A Lewis' acid served as a catalyst, water as a co-catalyst and an oxidant agent. This in turn, yielded a homopolymer with similar properties to those of the PPP. The structural characterization of the PPP was carried out by infrared spectra (FTIR) measurements. By mixing the prepared LSMO and PPP powders and subsequent annealing at 400 °C, $(\text{LSMO})_{1-x}(\text{PPP})_x$ composites (x stand for the weigh fraction of PPP) were obtained. The magneto-transport properties of these composites were investigated in applied magnetic fields of up to 2 T. A significant enhancement of the negative colossal magnetoresistance (CMR) was observed on a wide temperature range. The increased MR is mainly attributed to the enhanced spin-polarized tunneling, due to the magnetic disorder in the manganite caused by the addition of PPP.

Keywords: Composites, polymeric materials.

1. Introduction

In general, the phenomena of colossal magnetoresistance (CMR) in the lanthanum manganite perovskite is obtained only in high magnetic fields ($> 1\text{ T}$) within a narrow temperature region

around of the Curie temperature (T_C) [1]. Nevertheless, the most designed magnetoresistance (MR) devices operate under magnetic fields of less than several hundreds of G. Thus, reducing the magnetic field, needed to achieve large MR in manganites, impose a challenge to many research groups. Recently, advances in the thin film deposition technique has allowed to fabricate multilayer magnetic tunnel junctions (MTJ), which displayed large low field MR at low temperatures [2]. On the other hand, low field MR in a wider temperature range has been observed in polycrystalline compounds, presumably due to grain boundary effects. Actually, detailed transport and magnetic studies on polycrystalline manganites have revealed crucial aspects of the physics of these novel oxide materials [3], amongst others that the MR in the polycrystalline samples is dominated by intergrain effects. This finding has leads to the conclusion that transport across grain boundaries, which is extremely sensitive to an applied magnetic field, should be the main mechanism behind the MR effect in the polycrystalline specimens. In this aspect, several results have shown to be most consistent with spin-polarized intergrain tunneling of conduction electrons. One reason that such transport effects should play an important role in the perovskita manganites is the high degree of spin polarization in these materials. Meanwhile, the synthesis of manganite-based two-phase composites has led to promissory advances in the issue of low-field MR [4]. Such combinations displayed considerable improvement in their MR effect over a wide temperature range and/or under low applied fields. The observed enhancement in the MR effect was explained in the frame of the model of spin-polarized intergrain tunneling. So far, it is quite clear, that introduction of a second phase (usually a nonmagnetic or an antiferromagnetic inorganic insulator) plays a decisive role to the MR phenomena, but what kind of embedded compound is suitable for MR enhancement is still missing. Enhanced MR has been reported for some ferromagnet/insulator type two-phase manganite-based composites, like LSMO/CeO₂, LCMO/SrTiO₃, and LSMO/glass, etc, being the second phase an insulating oxide [4]. On the other hand, polymer compounds have been employed for a long time as essential elements in the preparation and modification of properties of inorganic materials [5]. Contrary to the many reports on this theme, reports on polymer combined with manganite oxides for CMR purposes are rather scarce. The distinctive conjugated polymer compound polyparaphenylene (PPP) possess high thermal and chemical stability as well good crystallization grade. Electrically, PPP, being a good insulator, can be used as a transport barrier in a manganite matrix to adjust the intergrain tunneling and hence the MR. Theoretically, it is argued that the addition of PPP to the parent manganite provokes magnetic disorder and hence an enhanced tunneling effect, which in turn heightens the MR. [5] In this work, the polymer PPP was synthesized and introduced in LSMO manganites to form LSMO/PPP composites. Magnetotransport properties of the composites were carefully investigated.

2. Experiment

A solid state reaction was employed to prepare the LSMO compound and the (LSMO)_{1-x}(PPP)_x composites. The polycrystalline LSMO was prepared from chemically pure precursor oxides, which were mixed with acetone in an agate mortar, grounded and finally sintered at 1000 °C in air atmosphere for 64 hours. A Kovacic method through cation polymerization of benzene was used to synthesize the PPP powder. Benzene was found to polymerize smoothly in the system

Lewis acid catalyst-cocatalyst-oxidizing agent to a solid product. The reaction was carried out under temperature 35-37 °C for 35 minutes [6].

Concerning the composites, the parent components LSMO and PPP were first mixed and then finely ground in an agate mortar. The resulting powder was pelletized into discs of 4 mm in diameter, and then annealed rapidly at 400 °C for only 1 h in air atmosphere to get target composites. The pellets were then slowly cooled down to room temperature. Interfacial diffusion between the magnetic oxides and the polymer shouldn't be present due to the low temperature and short time of annealing. Nevertheless, this thermal process allows a well connection between adjacent manganite and PPP particles. After the short thermal treatment at 400 °C, the value of the room temperature resistance strongly decreased (> one order of magnitude) for all composites with $x \leq 0.4$, as determined by direct measurement with an ohmmeter.

3. Results and discussion

The infrared spectrum of PPP (Fig 1) evidences the *para* configuration. In our case the principal absorption band occurred at 804 cm⁻¹, characteristic of *para* substitution, this band is attributable to the C-H out-of-plane. The other bands are 998 and 1476 cm⁻¹, which are attributable to the C-H in-plane vibrations of a *para*-substituted benzene ring and C=C skeletal in-plane vibration, respectively. The wavenumber of the C-H out-of-plane vibration band is tightly related to the degree of polymerization (n). When n increases, the band shifts to a lower wavenumber. Thus the value of n can be estimated according to the wavenumber [7]. For our case, n for PPP is between 10 and 25.

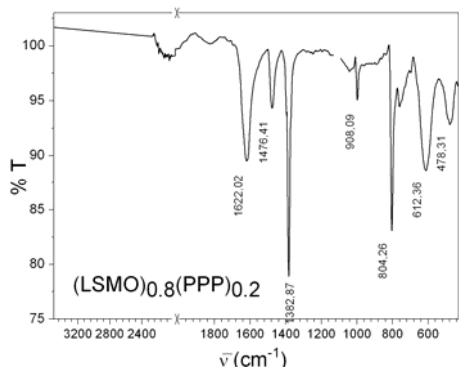


Fig. 1. FTIR spectra of a (LSMO)_{0.7}(PPP)_{0.3} composite.

Figure 2 displays the thermal dependence of the zero-field electrical resistance for composites with $x = 0.3$, $x = 0.4$. A metal-insulator transition of the parent LSMO is determined by the slope change of the respective curves, being ~ 246 K and ~ 236 K for $x = 0.3$ and $x = 0.4$, respectively. Evidently, these temperatures are lower than T_C of the parent LSMO. The lowering of T_C is a characteristic feature caused by grain boundary effects in granular manganites due to the lost connectivity between grains. A further addition of PPP provokes a gradual increase in resistivity till the M-I transition become indistinct and the composite behaves then as an insulator ($x = 0.6$).

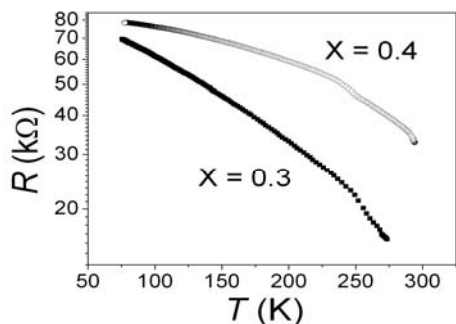


Fig. 2. Temperature dependence of the resistance of $(\text{LSMO})_{1-x}(\text{PPP})_x$ composites for $x = 0.3$ and $x = 0.4$.

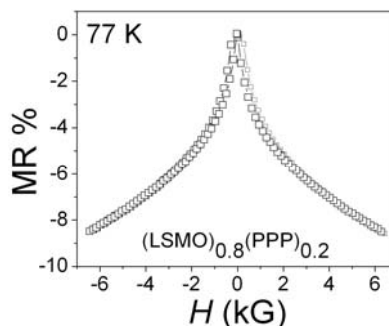


Fig. 3. Field dependence of the MR for a $(\text{LSMO})_{1-x}(\text{PPP})_x$ composites with $x = 0.2$.

The field dependence of the MR for a composite with $x = 0.2$ at 77 K in a magnetic field of ± 0.6 T is shown in Fig. 3. Clearly, this composite displays a remarkable low-field MR even at this temperature. In the low field region ($H < 2$ kG) a sharp increase in the negative MR is observed, whereas the variation of MR features a nearly linear behavior, with a much smaller slope, as the field is further increased. In addition to these properties, the MR shows a cusp like behavior, similar to that observed in manganite thin films. Such behavior has been taken as a sign of the homogeneity of the samples [1]. Contrary to single crystals, in which the negative MR is attributed to the suppression of spin fluctuations, and magnetic domain boundaries do not dominate the scattering process, the MR in the polycrystalline samples should be dominated by intergrain effects. In fact, the improvement in the MR both near room temperature and under a low applied field can be interpreted within a model of spin-polarized intergrain tunneling [8]. Additionally, the magnetic disorder imposed by the addition of PPP could also contribute to the enhanced MR [4].

In conclusion, a remarkable enhancement of the MR at low fields and low temperatures was observed in $(\text{LSMO})_{1-x}(\text{PPP})_x$ composites. This enhancement depends strongly on the PPP content and its origin could be the intergrain spin-polarized tunneling.

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