Research Article

Fabrication and Transport Properties of Manganite-Polyacrylamide-Based Composites

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We present the fabrication and transport properties of a series of composites made of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ and acrylamide-based copolymers. The most important result is the very narrow transition, of only 27 K, displayed by the peak that appears around the metal-insulator transition of the composites made with poly(acrylamide-vinylacetate). Although the amount of polymer is rather low, different copolymers change drastically the electric transport characteristics.

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1. Introduction

Polycrystalline structures based on perovskitic manganites which display colossal magnetoresistance (CMR) have been the subject of intense research during the last decade because of the great expectations for application of their low field magnetoresistance (see [1–4] and therein references). Although the mechanism leading to the colossal magnetoresistance in polycrystals is not completely understood, the key role of grain borders is unanimously accepted in the transport process. Therefore, a wealth of data reports on experiments trying to control and improve the grain border/intergrain area and further to decipher the underlying physics. It is considered that the magnetic disorder at the interface enhances the spin dependent scattering in that area. As the charge and spin transport occur by tunneling and hopping, many attempts to improve the barrier were made by dilution with a second non-CMR material [5–12]. The dilution not only modifies the barrier geometry but also produces a kind of conditioning by changing the magnetic structure and interactions at the grain border.

An interesting way of managing the grain surface is the dressing of the manganite grains with a very thin polymer layer. Consequently, the sintering involves only the polymeric

interface, hence, requires much lower temperatures and sintering time as compared to the use of oxides. The low processing temperatures are also beneficial for the grain cores since they are no more influenced by interdiffusion. In addition, the use of polymers increases the resistance of the interface, hence, of the whole sample, with orders of magnitude. There are few data concerning the use of polymers in conjunction with CMR manganites by our knowledge, only polyparaphenylene [13, 14], poly(methyl methacrylate) [15], and polyphenylene sulfide [16] have been reported in combination with manganites.

In this paper, we present the use of an acrylamide-vinylacetate copolymer to obtain manganite-polymer composite. The reason is that polyacrylamide and its copolymers are amongst the most used polymers in composite materials due to their outstanding capacity of wrapping the grains. In addition, they confer good mechanical properties to the composite samples.

2. Experimental

The manganite $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) was prepared starting from La_2O_3 , SrCO_3 , and MnO_2 mixed together in warm citric acid (80°C) in the appropriate molar ratio (La:Sr:Mn

SCHEME 1

SCHEME 2

= 0.67:0.33:1). A transparent brownish gel was obtained which further was dried for 5 hours at 150°C in the oven, when a glassy solid oxide precursor could be separated. The precursor was further annealed at 1200°C in air for 12 hours. The complexes formed in both cases were characterized by elemental chemical analysis, TGA, IR spectroscopy, and nitrogen absorption (BET).

Acrylamide-vinylacetate copolymer (PAAm-VAc) was prepared by free radical polymerization of the comonomer mixture (feed molar ratio = 1/1). Aqueous medium copolymerization, initiated by the redox system $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_5$, was carried out at 65°C following the reaction illustrated in Scheme 1.

At the end of the reaction, after 120 minutes, the reaction product was precipitated in methanol, filtered off, and washed several times. Subsequently, the polymer was dried to constant weight at 50°C. The polymer yield, gravimetrically determined, was over 50% (54.47%).

Differential scanning calorimetry (DSC) data showed a softening temperature of 157°C.

For the synthesis of poly(acrylamide-co-methyl methacrylate) (PAAm-MMA), was applied the microwave assisted copolymerization. The reaction was carried out in glass vessels without stirring, with 1% AIBN as radical initiator and dimethylsulfoxide solvent for microwave absorption. Microwaves have the advantage of a rapid and uniform heating so that the radical initiator decomposes almost instantaneously. Consequently, the concentration of the primary radicals is very high; hence, an increased efficiency is expected. In addition, the thermal degradation process is very limited. The copolymerization with methyl methacrylate followed the reaction illustrated in Scheme 2. Finally, the copolymer was conditioned in the same way as described for PAAm-VAc. Nevertheless, in this case the polymer yield is rather low 22.7% for five minutes reaction time. DSC data of this copolymer shows a softening temperature of 178°C.

The composites were prepared by dipping the manganite powder within appropriate solutions of copolymer in chloroform. The powder obtained after drying at room temperature was pelletized in bar shape at 20 kgf/cm² and sintered in an oven at 150°C for one hour. We prepared three types of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ -PAAm-VAc composites with 2%, 4%, and 6% copolymer, respectively. For transport measurements, four copper leads were attached to each pellet by ultrasonic soldering with Cerasolzer.

The electrical resistance was measured using the four probes technique with currents between 1 nA and 1 μA . Because of the polymer matrix, the temperature for measurements was limited at 325 K; therefore, it was difficult to reach the full paramagnetic state of the manganites that was reported at high temperatures.

3. Results and Discussion

The temperature T dependence of the resistance R follows a dependence that roughly reminds the general behavior of fined grained manganites. However, the type of polymer has strong influence on the particular characteristics of each sample.

In the case of the composites with PAAm-VAc, as the temperature decreases, the resistance, of order 0.1–0.9 M Ω , starts to increase very fast reaching a narrow peak followed by a steep metal-insulator transition at lower temperatures. For a further decrease of the temperature, the resistance shows a dip followed by an increase toward a temperature-independent resistance. Figure 1 shows the evolution of the resistance normalized to the peak resistance R_{MI} as a function of the temperature normalized to the metal-insulator transition temperature T_{MT} , measured with a current of 100 nA. What is outstanding is the width of the peak which is the narrowest ever reported, by our knowledge, only 27 K at half width. A second special feature is the wide T range, between 10 and 200 K, where the resistance keeps

FIGURE 1: Temperature dependence of the relative resistance R/R_{MI} for a series of composites made from $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ with 2; 4; and 6% poly(acrylamide-co-vinylacetate) (PAAm-VAc).

an almost constant value. In addition, in this representation, all peaks collapse onto one curve. Magnetic measurements have shown that the paramagnetic to ferromagnetic phase transition occurs at temperatures higher than the limitations imposed by the material composition (325 K); hence, the material is in ferromagnetic state in the temperature range $269 \leq T \leq 305$ K where T_{MI} is located. A simple model for the increase of the resistance in the ferromagnetic state was presented by Yuan et al. [17] that consider the distribution of grain separation and an exchange coupling between grains that can change the sign with the distance between grain borders. As a result, the conductance has a spin dependent contribution due to the ferromagnetic coupling that depends on the grain magnetization and a second contribution which is almost constant mirroring the antiferromagnetic coupling. The latter term behaves like an activated transport; specifically the conductance decreases fast with decreasing T while the conductance due to the ferromagnetically coupled grains increases and becomes constant at low temperature where it is dominant. Thus, the interplay of the conductances could explain both the peak and the constant resistance at low temperatures.

The role of the copolymer is not very clear in this model, but experimentally we found it is very important. For the sake of comparison, we have tried a second copolymer, poly(acrylamide-co-methyl methacrylate) (PAAm-MMA) with the same manganite. Although the amount of polymer was only 2% in both cases, the differences between LSMO-PAAm-VAc and LSMO-PAAm-MMA composites are

FIGURE 2: Comparison between temperature dependence of two composites made from $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ and 2% poly(acrylamide-co-vinylacetate) (PAAm-VAc) and the same manganite with 2% poly(acrylamide-co-methyl methacrylate) (PAAm-MMA).

FIGURE 3: SEM micrograph of the composite made of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ and 2% poly(acrylamide-co-vinylacetate).

noticeable (Figure 2). The T_{MI} of the latter shifts to lower temperatures and the metal-insulator transition is broad. Actually, the whole peak is four times broader than for LSMO-PAAm-VAc. In addition, a low temperature peak appears around 100 K which is rather broad but well defined.

The SEM micrograph of the fracture of the LSMO-PAAm-VAc sample shows a uniform covering of each manganite grain (Figure 3). In the case of the LSMO-PAAm-MMA sample, the polymer appears like a network which separates large clusters of grains (Figure 4). Therefore, in the first case, the polymer acts only at the level of the intergrain tunneling barrier. In the the latter case, the presence of the polymer network-like structure, which encloses large clusters of grains, leads to extra barriers. In addition, we

FIGURE 4: SEM micrograph of the composite made of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ and 2% poly(acrylamide-co-methyl methacrylate).

FIGURE 5: History dependence of the resistance of a composite made from $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ with 4% poly(acrylamide-co-vinylacetate) PAAm-Vinylacetate (lin). Inset: time evolution of the resistance at 290 K for a feeding current of 100 nA.

cannot rule out a temperature dependence of the intergrain contacts due to the dramatic change of the elastic properties of the polymer network as well as the difference in the thermal expansion of the two constituents: manganite and polymer.

Finally, we mention the history dependent resistance of the LSMO-PAAm-VAc composite. There is a significant difference between the R - T dependence when the sample is warmed up after the resistance was measured in a cooling down process. As Figure 5 shows, during the warming process after the first cooling down process, the dip vanishes and the peak decreases with almost 40%. Most likely, this is an effect of phase separation which is typical for manganites

[18–22]. The border between the conductive and dielectric phases is moved by the measuring current; hence, the second run finds another phase arrangement with lower resistance at the peak. The inset to Figure 5 shows the time increase of the resistance for a constant current of 100 nA and at constant temperature close to the dip. A delay of several hours at room temperature without any transport current running through the sample reestablishes the initial state and the R - T curve recovers its initial variation.

In summary, we have fabricated composites with $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ - and polyacrylamide-based copolymers: poly(acrylamide-co-vinylacetate) and, for comparison, poly(acrylamide-co-methyl-methacrylate). The samples with PAAm-VAc display a transition from paramagnetic to ferromagnetic phase with a very narrow breadth, of only 27 K at the half resistance peak, which is the narrowest value, yet reported. An attempt of explanation was made based on the model of oscillatory exchange coupling between grains. A history-dependent process and its relaxation were also revealed.

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