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Training effects induced by cycling of magnetic field in ferromagnetic rich phase-separated nanocomposite manganites

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ABSTRACT

We have carried out an experimental investigation of magneto-transport and magnetic properties of charge-ordered $Pr_{0.67}Ca_{0.33}MnO_3$ (PCMO) and ferromagnetic $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) nanoparticles along with a nanocomposite consisting of those two types of nanoparticles. From the magneto-transport measurements, clear irreversibility is observed in the field dependence of resistance due to magnetic field cycling in the case of PCMO nanoparticles. The value of resistance increases during such a field cycling. However such an irreversibility is absent in the case of LSMO nanoparticles as well as nanocomposites. On the other hand, the magnetic measurements indicate the gradual growth of antiferromagnetic phases in all samples leading to a decrease in magnetization. These inconsistencies between magneto-transport and magnetic behaviors are attributed to the magnetic training effects.

1. Introduction

The rare earth based, doped manganites with the general formula $R_{1-x}A_xMnO_3$ (R – rare earth, A – bivalent atom) have stimulated considerable interest from fundamental and technological points of view [1–9]. Based on the existing theoretical developments, the observation of colossal magnetoresistance (CMR) in doped perovskite manganites opened up a broad and fundamental topic of research that continues to be very active till now [7,10,11]. Beside the CMR effect, manganites exhibit several intriguing properties e.g., phase separation, charge ordering and meta-magnetic transition, etc. Their electronic transport/magneto-transport and magnetic properties of the perovskite manganites are correlated with each other. The physical properties of those materials are dependent on their dimensions [6,12]. The charge-ordering, an ordering of the Mn^{4+} and Mn^{3+} ions in crystals, is a generic property of the half doped manganites. It is occasionally followed by an insulating, antiferromagnetic ordering at lower temperatures. This charge-ordered antiferromagnetic insulating phase can be transformed into metallic ferromagnetic phase by applying several external perturbations such as magnetic field, electric field, and x-ray irradiation. Magnetic field-induced melting of the charge ordering leads to the large magnetoresistance. The critical magnetic field (H_C) for complete melting of the charge ordered state generally varies from system to system according to their electronic band-width. It has been found that external magnetic field, lower than H_C, can partially destabilize charge ordered state leading to an electronic phase separation. In such a scenario with multiple phases, the nucleated ferromagnetic domains propagate within the host antiferromagnetic charge ordered matrix. The formation of the connected ferromagnetic metallic percolation path in the phase separated manganites results in the decrease of resistance. The occurrence of magnetic training effect is frequently observed in cases of mixed valent phase-separated manganites [13]. The consequence of the training effect is the growth of the antiferromagnetic phase fraction owing to either temperature or magnetic field cycling. The outcome of this effect (extrinsic or intrinsic) in phase separated manganites is still not well understood.

In our present report we address the transport, magneto-transport and magnetic properties of $La_{0.67}Sr_{0.33}MnO_3$ (LSMO), $Pr_{0.67}Ca_{0.33}MnO_3$ (PCMO) nanoparticles and PCMO–LSMO nanocomposite. The PCMO nanoparticle shows irreversible magneto-transport behavior due to magnetic field cycling. However for LSMO nanoparticles and PCMO–LSMO nanocomposite, such an irreversibility is absent. On the other hand, the magnetic behavior as a function of external magnetic field shows significant irreversibility for all those compounds. We analyzed these anomalous behaviors by taking into consideration of magnetic training effect.

2. Sample preparation

We have prepared nanocrystalline LSMO, PCMO and PCMO–LSMO nanocomposite *via.* sol–gel route. For the preparation of

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nanocrystalline LSMO and PCMO, the starting elements were preheated in highly pure (purity 99.9%) La_2O_3, Pr_6O_{11}, $CaCO_3$ and MnO_2. The appropriate amounts of oxides have been converted to their nitrate forms by using nitric acid. A suitable amount of citric acid was added to the clear water solution of the nitrates. Subsequently the mixture was slowly heated at 80–90 °C by using the water bath until the gel was formed. The decomposed gel was heat treated for 4 h at 950 °C and 900 °C to get nanocrystalline LSMO and PCMO respectively. For preparation of the PCMO–LSMO nanocomposite, first we have prepared PCMO nanoparticles; it was mixed with the suitable amount of the gel of LSMO at the last stage of the gel formation. Then the gel was decomposed at higher temperature to get the black porous powder. Nanocomposite compound is formed due to the heat treatment at 900 °C for 4 h.

3. Results and discussion

Room temperature x-ray diffraction (XRD) study was done for all prepared samples by using Rigaku diffractometer. It confirmed the single phase nature of the LSMO and PCMO nanostructures. No additional phase was found in the nanocomposite except its parent compounds. Average particle sizes of the samples, estimated from the XRD data using Scherrer's formula (after correction for the instrumental broadening), are ~ 28 nm and ~ 47 nm for LSMO and PCMO respectively. Transmission electron microscopy (TEM) has been carried out to confirm the formation of nanocomposite as well as to estimate the grain size. Our TEM measurement suggests that the PCMO–LSMO nanocomposite was formed and the average grain size was found to be ~ 60 nm. The detailed characterization part of the nanocomposite was given in Ref. [14]

Transport and magneto-transport properties of the pelletized samples have been carried out by the conventional four probe method. The temperature dependence of resistivity in the presence and in the absence of external magnetic field for the samples is shown in Fig. 1. LSMO and PCMO–LSMO nanocomposite shows the usual metal insulator transition around $T \sim 220$ K, whereas with lowering of the temperature PCMO shows charge ordering at $T \sim 220$ K (shown in inset of Fig. 1B). The temperature dependence of resistivity for nanocomposite is qualitatively similar to that for LSMO indicating the existence of the metallic percolating transport path even in nanocomposite.

In order to understand the effects of the magnetic field on the electronic transport properties of the nanostructures under consideration, we have recorded the resistance isotherms at $T=120$ K (Fig. 2). The resistance as a function of external magnetic field [$R(H)$] is measured in the magnetic field cycle of $0 \rightarrow 90 \rightarrow 0 \rightarrow 5 \rightarrow -5 \rightarrow 5$ kOe. The first part of the magneto-transport measurement ($0 \rightarrow 90 \rightarrow 0$ kOe) for LSMO and PCMO–LSMO nanocomposite is shown in left insets of Fig. 2A and B respectively. In the case of metallic LSMO and PCMO–LSMO nanocomposite, almost reversible behavior (during 1st and 5th quadrant measurements, indicated by "1" and "5") was observed due to the presence of ferromagnetic metallic percolating transport path. However, for charge-ordered antiferromagnetic PCMO nanoparticles, the irreversible behavior was observed during increasing and decreasing external magnetic field. Another anomalous behavior was also present at the low magnetic field region especially below $H=30$ kOe. With increasing magnetic field, the charge ordered antiferromagnetic state of PCMO is melted (at $H > 60$ kOe) and it goes to the metallic state for further increase of magnetic field. This low resistive metallic state was preserved down to $H \sim 45$ kOe during the decreasing magnetic field which is clearly shown in the inset of Fig. 2C. For further decrease in magnetic field, particularly for $H < 30$ kOe, the resistance of the compound goes higher compared to its value during increase in magnetic

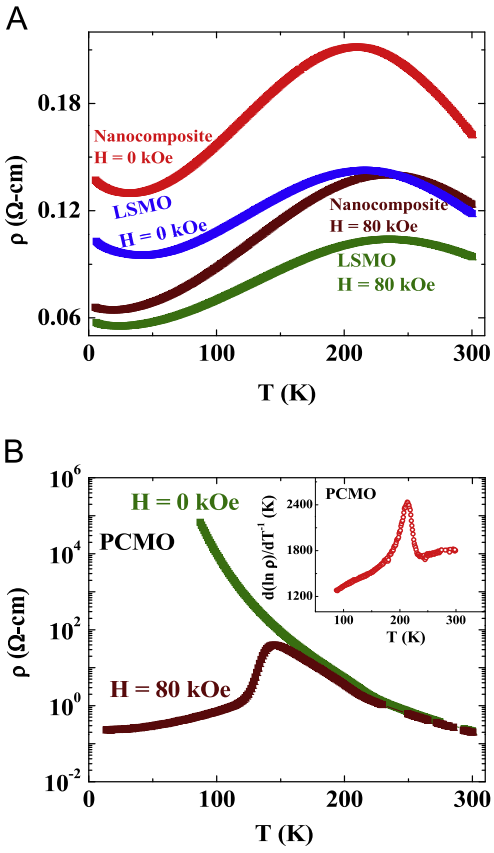

Fig. 1. (A) Resistivity as a function of temperature in the absence and in the presence of external magnetic field ($H=80$ kOe) for LSMO nanoparticles and PCMO–LSMO nanocomposite. (B) Temperature-dependence of resistivity of PCMO nanoparticles in the absence and in the presence of $H=80$ kOe external magnetic field. Inset of (B) shows the signature of charge ordering (*i.e* a peak) for PCMO nanoparticles ($T \sim 220$ K).

field. This increasing nature of the resistance from forward sweeping of magnetic field persisted even at $H=0$ kOe magnetic field.

After the completion of the first part ($0 \rightarrow 90 \rightarrow 0$ kOe) of the magneto-transport measurement, we have studied the effect of the field cycling (5-quadrant), particularly at low field region ($0 \rightarrow 5 \rightarrow -5 \rightarrow 5$ kOe). The variation of the resistance for the samples is shown in main panels of Fig. 2. In the case of LSMO and PCMO–LSMO nanocomposite, the variation of resistance with magnetic field in the 1st quadrant (represented by '1' in enlarged view of a particular portion in inset of Fig. 2A and B) exactly matches with the 5th quadrant (represented by '5') resistance measurements. However, for antiferromagnetic charge ordered PCMO nanoparticles, the irreversibility was found between 1st and 5th quadrant $R(H)$ measurements for the magnetic field cycling (Fig. 2C). The increasing nature of the resistance owing to the external magnetic field cycling was previously observed by the Mavani et al. for the 'Eu' and 'Dy' doped $Pr_{0.5}Ca_{0.5}MnO_3$ compounds [15]. The authors concluded from the magnetic and magneto-transport properties that the anomalous behavior observed in the above-mentioned manganite compounds originates from the magnetic training effect due to the field cycling. On the other hand, Pi et al. reported that the training effect is a common phenomenon of phase separated compounds [13]. Since our nanocomposite compound is phase separated, a signature of the training effect is expected to be present. However as such a change in a bulk sample is rather small. Mavani et al. also pointed out that a small change in bulk magnetic data due to the training effect may be difficult to probe [15]. On the contrary, change in the