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Trap state capture and reemission relaxation in ceramic $La_{1-x}Ca_xMnO_3$ with Ca-content $x=0.51$

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ABSTRACT

An unusual relaxation type of transport phenomenon occurs in La_{049} $Ca_{0.51}$ MnO_3 which is connected with electron or hole trap state capture and reemission out of a 65 meV potential well. The phenomenon is observed in ceramic samples only if (1) charge order domains occur with a lateral distance between 3 and 30 nm and if (2) *E*- and *H*-field sensitive near boundary metastable states exist.

1. Introduction

Manganite ceramic increasingly comes into the focus of the applied physics community because of its unusual defect properties. Specifically, several relaxation types of transport as well as several kinds of metastable electronic–magnetic states have been discovered. They include Warburg diffusion [1], charged boundary transport [2], electroresistive effects [3], relaxor ferroelectrics [4] as well as a new type of storage device (EPIR-effect) [5].

All these phenomena seem to be related to the carrier emission out of shallow trap states and recapture at other locations. Such a carrier relocation changes the space charge potentials at external and internal boundaries in current direction and sometimes also alter the electronic–magnetic state near the boundary. The shallow trap states themselves are usually connected which the oxygen non-stoichiometry which is predominantly found at the surfaces and at the grain boundaries of the manganite ceramic.

Specifically, in $La_{1-x}Ca_xMnO_3$-ceramics a large variety of unusual transport phenomena is observed depending not only on the application of external *H*- (magnetoresistance, MR) and *E*-fields (electroresistance, ER), but also very much on the individual preparation conditions. In this work, we report on an unusual new relaxation type of transport which apparently is connected with electron/hole trap state capture and reemission, and which occurs under specific conditions which are fulfilled only close to $x=0.5$.

2. Experimental details

$La_{1-x}Ca_xMnO_3$ ceramics with a perovskite structure were prepared using the conventional solid state reaction method. Oxides La_2O_3, MnO_2, and carbonate $CaCO_3$ with a high purity were weighed at stoichiometric composition and ground thoroughly in an agate mortar with ethyl alcohol. Before weighing, La_2O_3 and $CaCO_3$ were pre-heated in air at 900 and 300 °C for 4.5 h, respectively, in order to remove the moisture and CO_2. The mixture was first fired at 900 °C for 4.5 h, then cooled down to room temperature. After pre-heating, the dry mixed powders were pressed into pellets and subsequently sintered in air at 1350 °C for 12 h. Then the as-sintered perovskite powders were pressed into a rectangular shape with 3 mm × 7 mm × 4 mm and were re-sintered in air at 1400 °C for 12 h for the final resistance measurements. The resistance measurements were performed using the four-probe method in the temperature region from 10 K to room temperature. For the impedance measurements we used a model 6420A Wayne-Kerr Precision impedance analyser. The crystal structure of the samples was determined using a X-ray diffractometer (DRON-3,Japan) with CuKα radiation ($\lambda=1.5405$ Å). The sample composition was determined by EDS.

The XRD patterns of all samples show peaks which match those reported for $La_{1-x}Ca_xMnO_3$ by Zhong et al. [6]. This

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indicates that structurally all samples are single phase. The direct comparison yields a cubic symmetry for the x=0.17 sample (a=0.7759 nm) and an orthorhombic one for the x=0.51 sample (a=0.5419 nm, b=0.7641 nm, c=0.5429 nm).

3. Sample magnetic–electronic status

Fig. 1 shows the AC-impedance of x=0.51 versus temperature curves $Z'(T)$ for different frequencies ω in comparison to those of x=0.17. While the impedance of x=0.17 shows the expected insulating behaviour, that of x=0.51 shows relaxation type of peaks which get smaller with increasing frequency. Note, however, that we have a drop of the impedance with frequency in both cases, which is probably due to space charge capacitances (stable charges) which short out the high frequency output amplitudes.

Fig. 2(a) shows the resistivity versus temperature curve $\rho(T)$ of the x=0.17 sample, showing an insulating behaviour, while a Curie temperature T_c=220 K (arrow) is taken from magnetization measurements. According to Schiffer et al. [7], which we take as a reference here, at x=0.17 one should indeed find a fm insulator, but with T_c=180 K. Possibly the sample is somehow metastable.

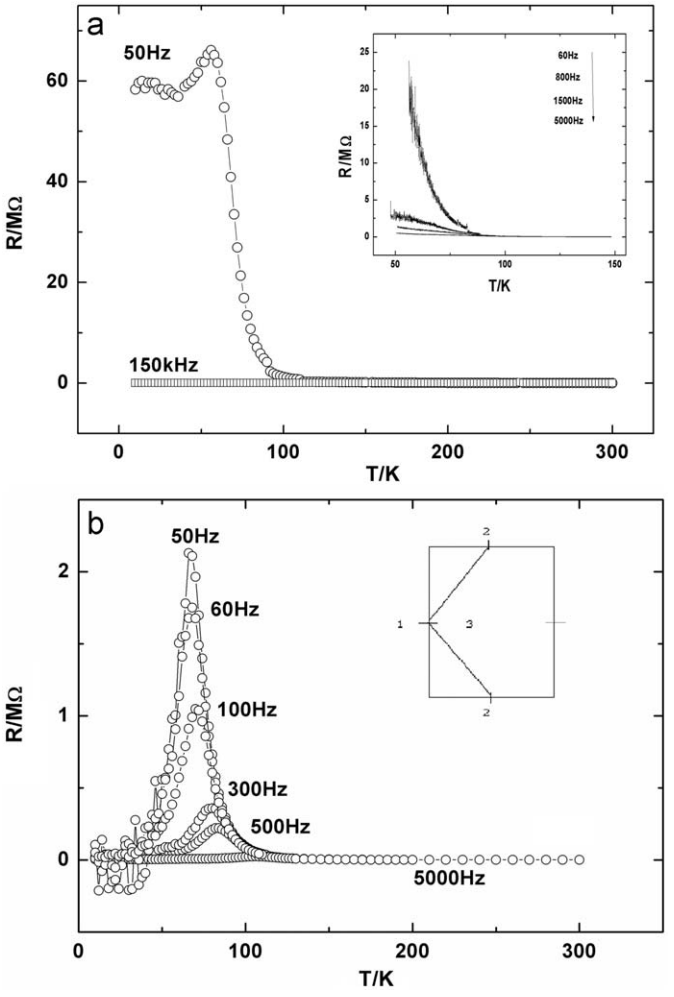

Fig. 1. Real part of the AC-impedance of x=0.51 (b) versus temperature, showing relaxation peaks which shift with the measuring frequency and of x=0.17 (a) showing a more conventional behaviour. The peak to peak AC-voltage is 0.5 V. (a) Inset: additional data for intermediate frequencies. (b) Inset: tetragonal trap state symmetry in a laterally bounded stripe domain. Numbers 1–3: trap sites in different magnetic–electronic environments.

In that case, percolative transport via changing phase volume fractions under E- and H-fields which are proposed to occur in high quality near equilibrium state crystals [8] is unlikely.

On the other hand, it has been argued that metastable situations can be described by deGennes-type magnetic–electronic states [9,10]. That should also hold for the metastable situations which are provoked by the local strain- or space charge electrical fields originating from defects which are concentrated at or near the boundaries. In that case, metastable state scenarios would only differ by the core of the domains being close to an equilibrium state or not.

Fig. 2(b) shows the resistivity versus temperature curve of x=0.51. Here, a similar conflict exists. According to Schiffers phase diagram a Neel point occurs at T_N=187 K. Our sample has indeed a low magnetic moment (20% of that of the x=0.17 sample) but the $\rho(T)$ curve of our sample (measured at 45 μA constant current) drops to almost zero already at 75 K.

Both samples show a strong electroresistive (ER-) effect [11] and both are located in composition close or inside of the (equilibrium) phase separation regions of the phase diagram, i.e. $0.17 < x < 0.19$ (fm metal/fm insulator) and $0.47 < x < 0.49$ (fm metal/charge order (CO) afm) [7]. This suggests that in exactly the compositional regimes where equilibrium phases coexist, also metastable phases exist which are sensitive to E- and possibly H-fields.

If, accordingly the metastable states are the subject of the spin–electron–lattice interaction triangle just as the equilibrium states are, we can assume the same for the individual defect states

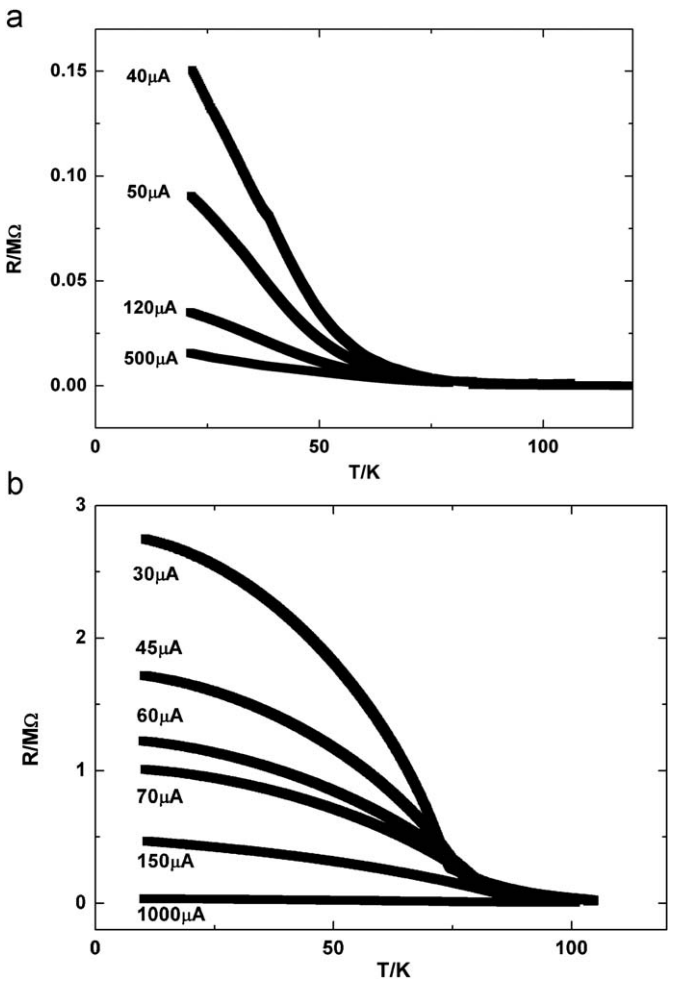

Fig. 2. DC-resistance versus temperature of the sample with x=0.17 (a) under different current loads and that of x=0.51 (b).