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De-stabilization of charge-order state through in-homogeneity in random ionic distribution in the particles of polycrystalline $Eu_{0.2}La_{0.3}Sr_{0.2}Ca_{0.3}MnO_3$ sample

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Abstract. In this study the perovskite manganite $Eu_{0.2}La_{0.3}Sr_{0.2}Ca_{0.3}MnO_3$ batch integrated sample is studied, with special modification done to introduce localized structural strain without micro-level (grains) modification. This consequence successfully generates opposite nature of high orthorhombic strain along *b*-axis in these samples, although the general structure is same for both with *Pnma* space group. The sharp magnetic transitions (both Curie temperature and charge-order transition) are reported to be mixed in presence of random ionic distribution in its structure. The diffused insulator-metal behaviour, de-stabilization of magnetic state and phase transitions associated with inherent anisotropic strain is discussed and is explained based on chemical disorder-induced structural strain in the present system.

Keywords. Charge order; in-homogeneity; structural strain.

1. Introduction

The correlation between the structural and magnetic degrees of freedom in doped manganite perovskites generating different fascinating electronic and magnetic state is the subject of interest from the last two decades. The charge-ordered (CO) state of manganites is associated with a real space ordering of Mn^{3+}/Mn^{4+} species in a 1:1 pattern. The modification/de-stabilization of CO state in half-doped manganites becomes the subject of interest due to varieties of controlling parameters like magnetic field, doping, bi-axial strain, pressure, electric field, size reduction, etc. [1–10]. The result presented by Sarkar *et al* [8] showed that size reduction can lead to an arrest of the high temperature phase in perovskite materials, which prevents the growth of low temperature phase that needs a specific crystal structure for its stabilization. Later on, Gutiérrez *et al* [11] showed that large compressive strain triggers a change from a ferromagnetic (FM) and metallic ground state to an insulating and anti-FM state, whereas a tensile strain produces an anti-FM but metallic state. However for some other half-doped manganites, anti-FM insulator state remains unaffected irrespective of the strain state [11]. Again, the influence of disorder and corresponding phase separation on half-doped manganites due to the broadening of the first-order phase transition region was reported by Chaddah *et al* [12]. Further, the presence of metastability and field-induced arrest around the first-order insulator-metal transition region in half-doped manganites was also reported in literature [13]. The suppression of charge-ordering transition due to the enhanced surface disorder was also reported [7,14]. The disappearance of anti-FM phase and emergence of FM metallic phase in half-doped nanoparticles was reported by Pramanik and Banerjee [15]. This inter-related effects as well as the large number of contradictory experimental reports and theoretical models relating to the properties of these materials with internal in-homogeneity revealed the complexity of the problem demanding more research in this field [9–19].

In order to put further light on this controversial issue on origin of suppression of CO state of manganites, we have selected polycrystalline $Eu_{0.2}La_{0.3}Sr_{0.2}Ca_{0.3}MnO_3$ batch integrated sample, which is specially modified by different final heat treatment that introduce unlike-strain in its structure due to chemical disorder (Samples A and B in oxygen atmosphere) without modifying it in micro-level (grains). The general orthorhombic structure with *Pnma* space group is influenced by local chemical disorder in such a way that the nature

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of high orthorhombic strain along *b* axis becomes opposite in these two samples. The detailed study on magnetic and transport properties of these samples show that the sharp magnetic transition (both Curie temperature and CO transition) of Sample A is drastically modified in Sample B due to in-homogeneous ionic distribution. The de-stabilization of magnetic state, phase transitions and its behaviour with different chemical disorder for Sample B associated with inherent structural anisotropic strain is discussed. The comparative study of Samples A and B is reported and explained based on chemical disorder-induced structural strain in the present system.

2. Experimental

Polycrystalline $Eu_{0.2}La_{0.3}Sr_{0.2}Ca_{0.3}MnO_3$ was prepared by a chemical process described in our earlier report [20]. The final annealing was performed at 1000°C for 15 h in air followed by furnace cooling to room temperature. One part of the sample was further annealed under closed oxygen atmosphere for 6 h at 1000°C. Henceforth, we will refer the samples by their respective final heat treatment, such as sample annealed at 1000°C in air as Sample A and the remaining sample annealed at 1000°C under closed oxygen atmosphere as Sample B. The single phase of compounds was confirmed by the powder X-ray diffraction (Seifert XRD 3000 P) using CuK_α radiation. The size and morphology of the grains of the samples were observed in a JEOL JSM 35 C scanning electron microscope (SEM). Bulk oxygen homogeneity of both samples was verified through iodometric titration method. The temperature-dependent electrical resistivity (ρ) at different constant applied magnetic fields was recorded using a commercial cryogen-free high-magnetic field system from Cryogenic Ltd, UK. DC magnetic measurements were performed using a Quantum Design SQUID magnetometer (magnetic property measurement system (MPMS) XL 7, Ever-cool model). In case of zero-field-cooled (ZFC) mode, the sample was cooled down to the desired temperature at zero magnetic field, while for the field-cooled (FC) mode the sample was cooled in a static magnetic field.

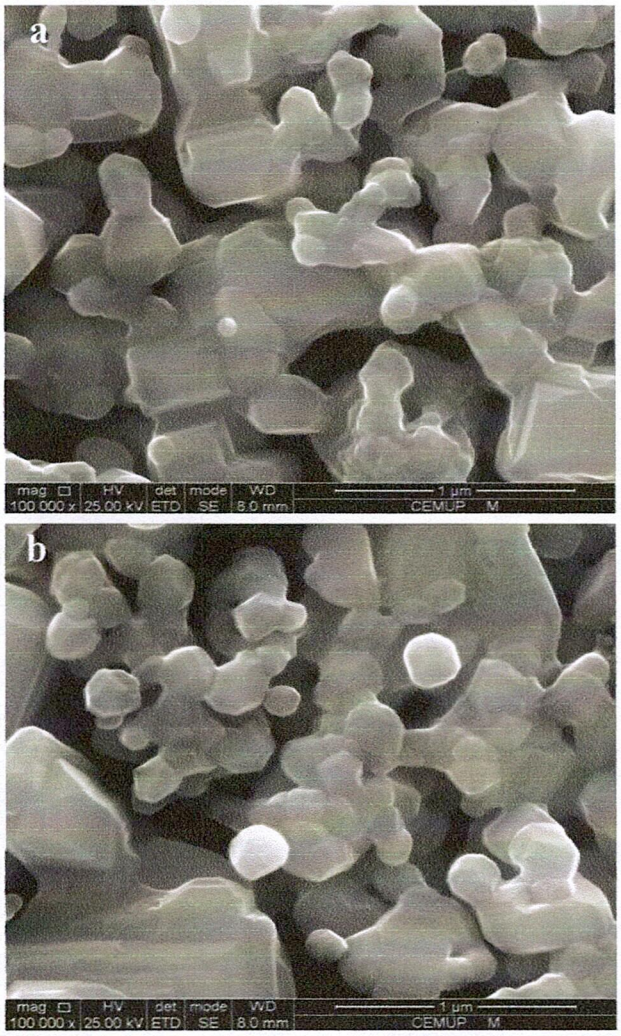

Figure 1. SEM images of (**a**) Sample A and (**b**) Sample B.

3. Experimental Results and discussions

The microscopic characterizations of the presently studied compounds were performed through SEM. The SEM images

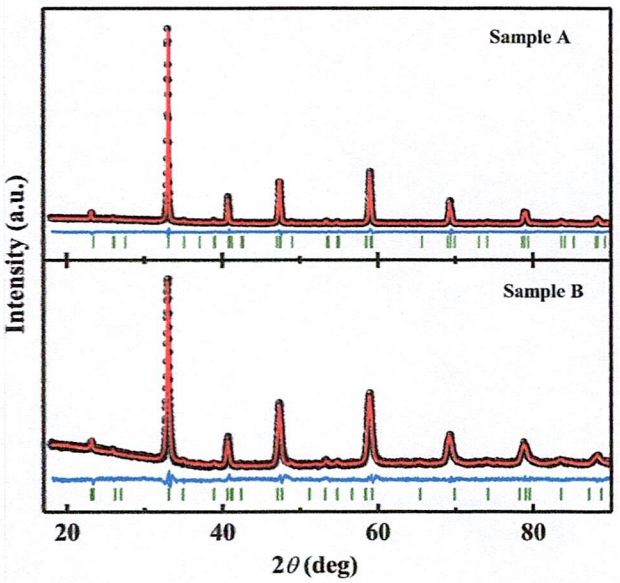

Figure 2. Experimentally observed (dots), Rietveld calculated (continuous line), and their difference (continuous bottom line) profiles for Sample A and Sample B at room temperature obtained after Rietveld analysis of the XRD data using orthorhombic space group *Pnma*. The vertical tick marks between the observed and difference plots show the Bragg peak positions.