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Influence of electron beam irradiation on electrical, structural, magnetic and thermal properties of $Pr_{0.8}Sr_{0.2}MnO_3$ manganites

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ABSTRACT

In this communication, the effect of electron beam (*EB*) irradiation on the structural, electrical transport and thermal properties of $Pr_{0.8}Sr_{0.2}MnO_3$ manganites has been investigated. Rietveld refinement of XRD data reveals that all samples are single phased with orthorhombic distorted structure (*Pbnm*). It is observed that the orthorhombic deformation increases with *EB* dosage. The Mn–O–Mn bond angle is found to increase with increase in *EB* dosage, presumably due to strain induced by these irradiations. Analysis on the measured electrical resistivity data indicates that the small polaron hopping model is operative in the high temperature region for pristine as well as *EB* irradiated samples. The electrical resistivity in the entire temperature region has been successfully fitted with the phenomenological percolation model which is based on phase segregation of ferromagnetic metallic clusters and paramagnetic insulating regions. The Seebeck coefficient (*S*) of the pristine as well as the irradiated samples exhibit positive values, indicating that holes is the dominant charge carriers. The analysis of Seebeck coefficient data confirms that the small polaron hopping mechanism governs the thermoelectric transport in the high temperature region. In addition, Seebeck coefficient data also is well fitted with the phenomenological percolation model. The behavior in thermal conductivity at the transition is ascribed to the local anharmonic distortions associated with small polarons. Specific heat measurement indicates that electron beam irradiation enhances the magnetic inhomogeneity of the system.

1. Introduction

Manganese oxides with perovskite structure provide a gateway to study the interplay of various properties such as structural, electrical, and magnetic phases of matter in a strongly correlated system. The perovskite manganites with general formula $RE_{1-x}AE_xMnO_3$ (where *RE* and *AE* are rare-earth and alkaline-earth ions, respectively) have been extensively investigated for more than two decades due to a wide variety of physical properties exhibited in these materials such as superconductivity, colossal magnetoresistance (*CMR*), ionic conduction, magnetism and dielectric behavior [1–4]. Generally manganites are known to show strong electron correlation. In such systems, spin, charge, orbital, and lattice degrees of freedom are strongly coupled, thereby resulting in various ground states such as ferromagnetic and charge/orbital ordering states. These ground states have comparable energies so that an external disturbance can easily drive the system from one state to another. This leads to the coexistence of phases with different magnetic and electronic properties. The understanding of the fundamental origin of these ordered phases and their dynamic interplay are still an important scientific challenge. The basic physical principle of manganites is mainly due to the competition between the delocalization effects of the electronic kinetic energy and the localization effects of the Coulombic force of repulsion. When the kinetic energy is dominant, one finds a metallic ground state with ferromagnetic alignment. On the other hand, when the localization effects are dominant, insulating behavior with anti-ferromagnetic ground state is observed. There are few models that can explain the transport mechanism in manganite systems. However, most of them can be only applied to either the ferromagnetic (*FM*) or the anti-ferromagnetic (*AFM*) region. In the semiconducting region, the transport mechanism can be explained by Mott's variable range hopping (*VRH*) model, small polaron hopping (*SPH*) model, and the adiabatic small polaron

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hopping (*ASPH*) model [5]. In the metallic region, the transport mechanism is generally governed by the scattering mechanisms such as single magnon, electron-magnon, electron-electron and electron-phonon processes [6,7]. Recently a theoretical percolation model based on phase segregation between metallic and semiconductor regimes has been proposed [8,9]. It is established that such a model could satisfactorily describe various transport properties of manganites in the entire temperature range. Further, the Kondo like upturn observed in resistivity at low temperatures can be addressed using modified percolation model proposed by Dhahri et al. [10]. The theoretical percolation model has also been used to explain the behavior of Seebeck coefficient as a function of temperature [11–14]. However, in the case of Seebeck coefficient, the observed upturn (Kondo like) behavior has not been properly explained using percolation model. Hence, a theoretical attempt on this issue is in order.

Among the rare earth based compounds, praseodymium (Pr)-based *CMR* materials are of great interest. The parent compound $PrMnO_3$ exhibits only anti-ferromagnetic insulator behavior whereas $Pr_{1-x}AE_xMnO_3$ (AE=Sr, Ca, Na) exhibits an *AFM* to *FM* phase transition. In addition to this, they also show numerous remarkable properties like metal-insulator transition (*MI*), charge ordering (*CO*), and phase separation (*PS*) [6,14–18]. Pr-based manganites are potential candidates for various applications such as resistance random access memories (*RRAM*) in the next generation of non-volatile memories which has led to dramatic improvements in the data density and reading speed of magnetic recording systems. This is mainly attributed to the bipolar resistive switching (*RS*) behavior observed in these compounds [19–21]. Various physical characteristics such as electronic, and magnetic properties can be tailored by applying external perturbations like magnetic field, pressure and irradiation [22–29]. The most common method used to crystallize any system is by thermal annealing, but the size of the grains increases during this process and it is perhaps difficult to have control over the grain size of the crystal. Irradiation with energetic particles such as electrons, ions, and neutrons has been one of the better and efficient methods to achieve structural control as a good alternative to thermal annealing [27–29]. Radiation-induced disorder in manganites has been investigated and it is demonstrated that irradiations with electron beam/ion beam change the Mn–O bond lengths and Mn–O–Mn bond angles which can shift the magnetic phase transition temperatures [22–26].

To the best of our knowledge, no studies have been done on the effect of electron beam irradiation on electrical, magnetic and thermal properties of $Pr_{1-x}Sr_xMnO_3$ compounds. It is well known that $Pr_{1-x}Sr_xMnO_3$ compounds show different resistivity trends which depends on the value of x. Samples with $0 \le x \le 0.15$ are canted anti-ferromagnetic, while a ferromagnetic to anti-ferromagnetic transition is observed for samples with $x \ge 0.2$. Hence $Pr_{0.8}Sr_{0.2}MnO_3$ compound is of great interest and there are some reports on magnetic and electrical studies on such a system in the literature [3,30–34]. However, there is no study on thermal properties such as thermal conductivity, Seebeck coefficient, and specific heat for $Pr_{0.8}Sr_{0.2}MnO_3$. In this work, we report a detailed study regarding the effect of electron beam irradiation on the structural, electrical, magnetic and thermal properties of $Pr_{0.8}Sr_{0.2}MnO_3$ samples. In particular, we demonstrated that the theoretical percolation model can successfully explain the electrical and thermoelectric transport mechanism in the entire temperature range for the $Pr_{0.8}Sr_{0.2}MnO_3$ system.

2. Experimental details

Polycrystalline samples of $Pr_{0.8}Sr_{0.2}MnO_3$ were synthesized using conventional solid state reaction method. For preparation, stoichiometric mixture of Pr_6O_{11}, $SrCO_3$ and MnO_2 powders (99.9% Sigma-Aldrich) was ground and the fine powder was calcined thrice at 1000 °C for 24 h with intermediate grindings. From the same batch of powder, pellets were made with application of identical pressure using a hydraulic press. Then the pellets were sintered at 1300 °C for 36 h and were cooled naturally inside the furnace to room temperature. The electron beam irradiation was carried out in a 10 MeV linac (Linear particle accelerator). The accelerator was operated at beam energy of 7.5 MeV with beam power of 1.5 kW and beam parameters were optimized to deliver uniform surface dose. The irradiation was performed at room temperature for 50 kGy, 100 kGy and 200 kGy. XRD was carried out to analyze the crystal structure and microstructure of crystalline solids using Mini Flex II DESK TOP X-ray Diffractometer which uses Cu-Kα as the source (wavelength, λ=1.541 Å). The electrical resistivity of the samples was measured using a conventional four probe technique. The resistivity measurements were carried out in a closed cycle refrigerator as a function of temperature in the range 10–300 K. The magnetic measurements were carried out using a superconducting quantum interference device (*SQUID*) magnetometer and 9 T *PPMS* based vibrating sample magnetometer (*VSM*) (both Quantum Design) in both zero-field-cooled (*ZFC*) and field-cooled (*FC*) conditions at external magnetic field of 250 Oe. The hysteresis loops (M versus H) of the samples were also recorded at typical temperatures of 5 K and 300 K. Thermal conductivity and Seebeck coefficient measurements were carried out simultaneously in the temperature range 10–300 K using a direct pulse technique. Both the measurements were performed on a warming cycle. For the thermal conductivity measurements, samples were shaped to rectangular bars of dimensions of about $1.5 \times 1.5 \times 5.0$ (mm^3). One end of the sample was attached on a copper block, which functioned as a heat sink. A small calibrated chip resistor was fixed at the other end of the sample which acted like a heat source. The temperature gradient was measured using an E-type differential thermocouple fixed directly on the sample which was electrically insulated from the sample. In order to minimize the heat radiation, the temperature difference was controlled to less than 1 K. The Seebeck voltage was detected using a pair of thin Cu wires electrically connected to the sample with silver paste at the same position as the junctions of thermocouple. The elimination of stray thermal emf was achieved by applying long current pulses to a chip resistor that also serves as a heater where the pulses appear as an off-on-off sequence. Specific heat measurements were performed in the temperature range 80–350 K using an ac calorimeter. The details of these thermal measurements are given elsewhere [6,7].

3. Results and discussion

3.1. X-ray diffraction studies

The X-ray diffraction data were recorded at room temperature for the pristine and as well as electron beam irradiated samples. It is revealed from Rietveld refinement analysis that all the samples were crystalline and single phased (within experimental limits of XRD) with an orthorhombic distorted structure (*Pbnm*). Fig. 1 shows the results of Rietveld refinement of the XRD patterns recorded for pristine and irradiated samples. The calculated pattern is in excellent agreement with the experimental data and the final refinements are satisfactory, in which R-factor and χ^2 (goodness of the fit) are fairly small. Lattice parameters were calculated from the refinement.

As shown in Fig. 2(a), it has been noticed that with increasing dosage of electron beam irradiation, a decrease in cell parameters (a or b or c) is observed for the lower dosage 50 kGy sample while