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Effect of A-site dopant on the piezoresistive characteristics of $La_{0.8}Sr_{0.2}MnO_3$ ceramics

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Abstract This letter reports the effect of the A-site doping (2, 4, and 6 mol% Bi and Li) on the piezoresistance phenomenon in $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) polycrystalline ceramics. The fractional change in resistivity was found to be nominal for Li-modified samples but samples modified with 4 and 6 mol% Bi_2O_3 exhibited 1.8% and 2.3% fractional change in resistivity $[(\rho_o - \rho_\sigma)/\rho_o]$ at 19.2 MPa which is significantly higher than that for pure LSMO. The enhancement in piezoresistive phenomenon is attributed to distortion of Mn–O bond due to substitution of smaller ion on to La-site. All the samples showed a sudden increase in resistivity with applied stress in the range of 0.5–2 MPa and the behavior was found to saturate as the magnitude of applied stress increases. Magnetic measurements as a function of field and temperature were conducted to confirm the A-site substitution.

Piezoresistive phenomenon corresponds to variation in resistivity proportional to applied stress [1–5]. Recently, we have reported the effect of B-site doping on the piezoresistive properties of lanthanum strontium manganite, $La_{0.8}Sr_{0.2}MnO_3$ (LSMO), ceramics [6]. It was found that LSMO modified with 2 mol% Nb exhibited ~2% change in resistivity at 19.2 MPa pressure as compared to 0.5% for the pure LSMO. A dramatic improvement was obtained for 5 mol% Nb-modified LSMO composition which exhibited a linear change in resistivity with uniaxial stress and the fractional change was of the order of 3% at 19.2 MPa stress. The origin of the enhanced piezoresistance was found to be related to Nb-substitution on the Mn-sites which distorts the Mn–O bond lowering the magnitude of stress required for the manganite lattice transformation. In this manuscript we investigate the effect of A-site substituents on the piezoresistive coefficient. The development of novel piezoresistive materials is crucial for next generation of force and pressure sensors.

The ceramic compositions were synthesized using the conventional mixed-oxide processing route. Reagent grade powders of La_2O_3, $SrCO_3$, MnO_2, Bi_2O_3, and Li_2CO_3 were obtained from Alfa Aesar, Co. MA, USA. After drying the powders were pressed into pellets and calcined at 1,025 °C for 4 h to obtain the perovskite crystal structure. Sieved powders were pressed into plates of size $40 \times 12.7 \times 1.5\ mm^3$ in a hardened steel die using a hydraulic press at a pressure of about 15 MPa. The green body was pressed at 207 MPa in a cold isostatic press. The pressed bars were sintered in a high temperature furnace (Lindberg) in the temperature range of 1,300–1,450 °C for 6 h. The crystal structure was determined from the X-ray diffraction pattern measured using Siemens Krystalloflex 810 D500 X-ray diffractometer. The XRD pattern of the sintered samples with Li doping showed perovskite phase with very small amount of secondary phase as shown in Fig. 1a, while those with the 4% and 6% Bi showed the presence of significant fraction of 2nd phase as shown in Fig. 1b. The indexing of the peaks was done based on the orthorhombic unit cell [7, 8]. The second phase is associated to the presence of Bi-rich liquid phase formed during the high temperature sintering. Samples with 4 mol% Bi exhibited

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large fraction of second phase and as such the measurements conducted on the samples are influenced by the secondary phase.

Microstructural analysis of the polished and thermally etched sintered samples was conducted using the Zeiss Leo Smart SEM. The microstructure of the sintered samples for all the compositions showed the presence of the porosity which decreased with increasing dopant concentration. The grain size was also found to increase with increasing Li and Bi content. The piezoresistive measurements were carried out in a modified 'Instron microtester'. Figure 2a and b show the picture of the measurement system and sample holder used for characterizing the piezoresistivity. The resistance change was measured using HP 34410 digital multimeter. For each measurement, the sample was enclosed in a charge shielding and sandwiched between the insulating alumina plates. A compressive load was applied on the sample at the rate of 240 N/min with uniaxial stresses reaching up to 19.2 MPa at the end of the test. A holding time of 3 min. was allowed after applying 60N of compressive load. Figure 3 shows the piezoresistive behavior of the A-site doped LSMO ceramic compositions. These compositions show a positive change in resistivity with applied uniaxal stress. All the samples showed a sudden increase in resistivity with applied stress in the range of 0.5–2 MPa and behavior was found to saturate as the magnitude of applied stress increases. The fractional change in resistivity is nominal for Li-modified samples but increases significantly for Bi-modified samples.

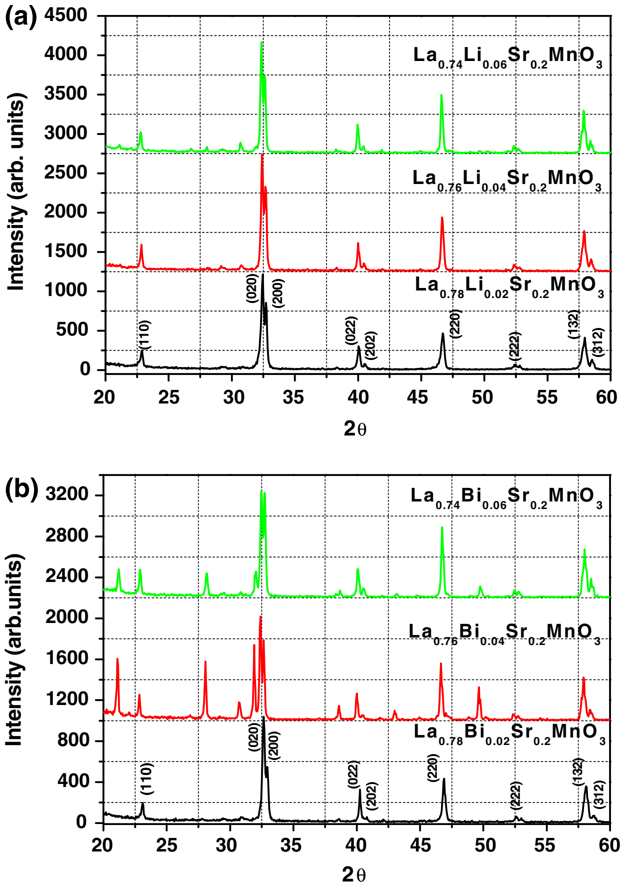


Fig. 1 X-ray diffraction plots for the Li and Bi modified samples (**a**) 2, 4 and 6 mol% Li-modified LSMO, and (**b**) 2, 4 and 6 mol% Bi-modified LSMO

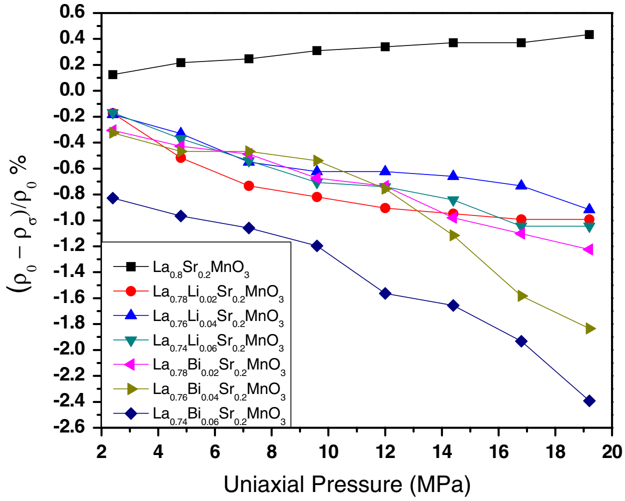
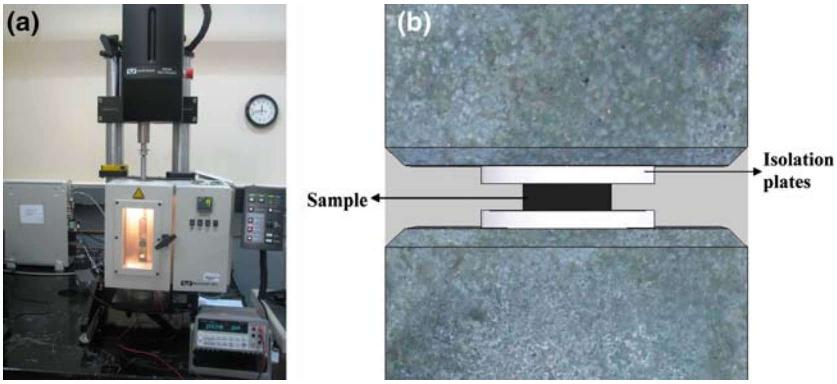


Fig. 3 Change in electrical resistivity with applied uniaxial stress

Fig. 2 (**a**) Picture of the measurement system, and (**b**) Schematic diagram of the sample holder



Samples modified with 4 and 6 mol% Bi_2O_3 exhibited -1.8% and -2.3% fractional change in resistivity $[(\rho_o - \rho_\sigma)/\rho_o]$ at 19.2 MPa. These numbers are significantly higher as compared to pure LSMO which exhibits +0.5% fractional change in resistivity [6]. It is interesting to note that the fractional change in resistivity with uniaxial stress is negative for A-site modified composition while it is positive for B-site modified compositions.

Prior investigations have shown that piezoresistance originates due to the easiness of the manganite lattice transformation with pressure and grain structure playing important role in controlling the magnitude. The ionic radius of Li^{+1} ion (0.76 Å) and Bi^{+3} (1.03 Å) is smaller than that of La^{+3} (1.032 Å) or Sr^{+2} (1.18 Å) and thus incorporation of these ions on to A-site will impact the Mn–O bond length [9]. Thus, the results of Fig. 3 can be explained if the substitution takes place on the A-site. In order to confirm this hypothesis, magnetic measurements were performed to investigate the change in magnetization and Curie temperature.

The magnetic properties of all the compositions were measured using a Quantum Design 'SQUID' magnetometer. Figure 4a shows the magnetization loops as a function of the applied magnetic field for LSMO modified with Li or Bi at room temperature. The room temperature hysteresis loops with 4 mol% Li and 6 mol% Li or Bi were found to saturate with 1T applied magnetic field while samples with 2 mol% Li, 2 and 4 mol% Bi can not be saturated at the same applied magnetic field. Generally, the magnitude of magnetization increased with the doping concentration except for the case of 4 mol% Bi which may be attributed to the presence of large fraction of second phase and porous microstructure. Figure 4b shows the temperature dependence of magnetization for Li and Bi modified LSMO ceramics. Pure LSMO has T_c around ~300 K, while the T_c for the samples doped with 6 mol% Li or Bi and 4 mol% Li is ~325 K. As the dopant amount decreases to 2 mol%, the Curie temperature decreases to that of unmodified LSMO ceramics. An increase in the Curie temperature pertains to the fact that the smaller ion substitution takes place at A-site. The size effect of the Li and Bi ions on the Curie temperature is based on the variation in the tolerance factor. The tolerance factor for perovskite structure is given by:

$$t = (r_A + r_X)/\sqrt{2}(r_B + r_X)$$

The smaller size Li and Bi ions when substitute at the La site their is a reduction in average A-site radius, r_A.

Further, evidence of the substitution on A-site can be obtained by measuring the overall resistivity of the sample. The effect of A-site doping on the electrical resistivity is shown in Fig. 5. The substitution on A-site leads to

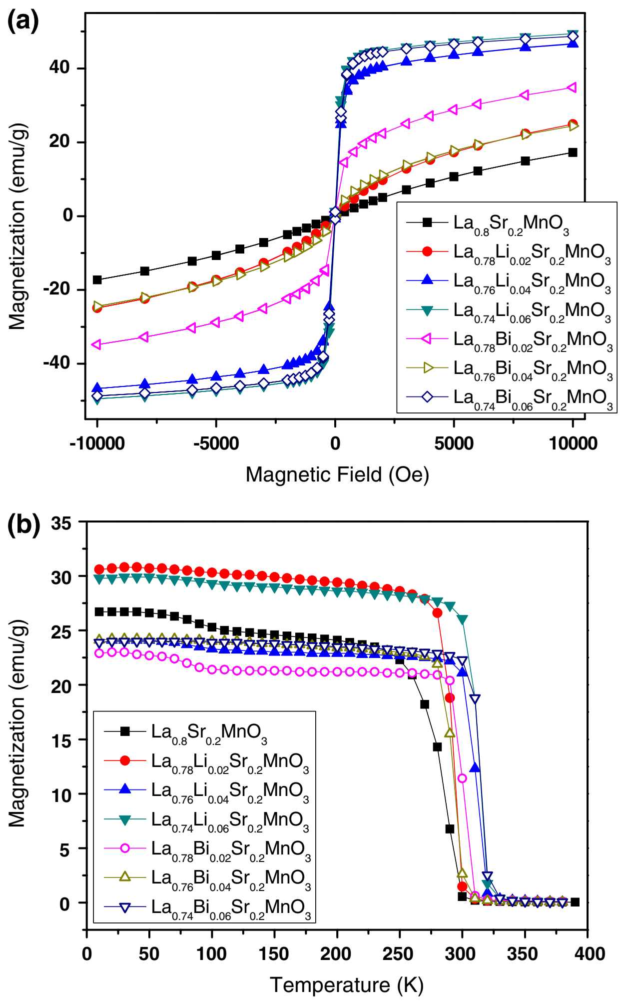


Fig. 4 (**a**) Magnetization as a function of the magnetic field for Li and Bi modified LSMO ceramic compositions, and (**b**) Magnetization as a function of the temperature for Li and Bi modified LSMO ceramic compositions

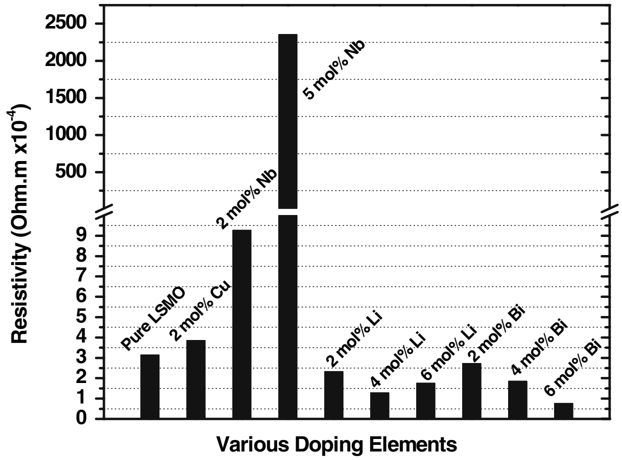


Fig. 5 Room temperature resistivity for A and B site modified LSMO ceramics

decrease in the electrical resistivity of pure LSMO. The samples with 6 mol% Bi exhibited lowest resistivity of the order of 0.767×10^{-4} Ω-m. In comparison, the addition of B-site dopants (CuO and Nb_2O_5) leads to significant increase in the resistivity. This data indicates that the dopants occupy the A-site in LSMO ceramics. The substitution of Li on La-site will increase the oxygen vacancies inherently present in this system leading to decrease in overall sample resistivity. The decrease in resistivity due to Bi substitution may be due to change in the ratio of Mn^{+3}/Mn^{+4} ions. The data in Fig. 5 further clarifies that large piezoresistance in the Bi-modified LSMO is due to distortion of the Mn–O bond.

In conclusion, this letter reports the large piezoresistance at low uniaxial pressures in 6 mol% Bi-modified $La_{0.8}Sr_{0.2}MnO_3$ ceramics. This high magnitude of piezoresistance is attributed to the lattice distortion due to substitution of the Bi-ion on to the La-sites. The results open the possibility of utilizing this material in design of pressure sensors.

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