Designing multi-level resistance states for multi-bit storage using half doped manganites

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Designing nonvolatile multi-level resistive devices is the necessity of time to go beyond traditional one-bit storage systems, thus enhancing the storage density. Here, we explore the electronic phase competition scenario to design multi-level resistance states using a half doped CE-type charge ordered insulating bulk manganite, \( \text{Sm}_0.5\text{Ca}_{0.25}\text{Sr}_{0.25}\text{MnO}_3 \) (SCSMO). By introducing electronic phase coexistence in a controllable manner in SCSMO, we show that the system can be stabilized into several metastable states, against thermal cycling, up to 62 K. As a result the magnetization (and the resistivity) remains unaltered during the thermal cycling. Monte Carlo calculations using two-band double exchange model, including super-exchange, electron-phonon coupling and quenched disorder, show that the system freezes into a phase coexistence metastable state during the thermal cycling due to the chemical disorder in SCSMO. Using the obtained insights we outline a pathway by utilizing four reversible metastable resistance states to design a prototype multi-bit memory device.

Fabrication of non-volatile memory (NVM) devices with high storage density, fast switching speed and low power consumption is of current research interest \([1-5]\). Present day NVM devices mostly use random access memories (RAM), based on resistive switching (RS) phenomenon \([6-10]\). A typical resistive memory device uses two resistive states to store binary digits 0 and 1. Such memory devices based on resistive switching between two states face scaling issues to deal with next generation computing systems \([11]\).

A promising and challenging direction to overcome the scaling issues is to design multi-bit memory devices where the intermediate resistivity states can also be used to store digital data. For example a four-level resistive system can store two-bit data (00 or 01 or 10 or 11) in each chips as compared to one-bit data (0 or 1) in prototype two-level resistive system. The feasibility of multi-level cell has been investigated for phase change memory (PCM) in chalogenides \([12-16]\). In PCM cells the crystallinity is controlled to obtain different resistance states. In spite of having tremendous functionality, the elemental segregation upon repeated cycling remains a major drawback for PCM cells \([17-22]\). In this context, the obvious question arises: can one design multiple resistance states by controlling the electronic phases, commonly seen in phase coexisted transition metal oxides \([23-29]\) to overcome the problem of elemental segregation?

In the present communication, we report a multi-level resistive system by tuning the phase competition in a half doped manganites. The charge-ordered antiferromagnetic insulating (CO-AFM-I) state, in our \( \text{Sm}_0.5\text{Ca}_{0.25}\text{Sr}_{0.25}\text{MnO}_3 \) (SCSMO) sample, melts to a ferromagnetic (FM) metallic state at a moderate magnetic field 70 kOe (one can use any field greater than critical field value \( \sim 45 \text{ kOe} \)) at 10 K and the system converts to a phase coexisted metallic state after the removal of the magnetic field. During the zero field warming, we stop at four representative temperatures (35 K, 45 K, 52 K, 58 K) and perform temperature cycling between each representative temperatures and 10 K. Distinctly different magnetization and resistivity data generated at above four representative temperatures remains more or less unchanged during the temperature cycling. Our Monte Carlo calculations using two-band double-exchange model verifies that the system freezes to a metastable phase during the thermal cycling and attributes it to the chemical disorder. In addition, we show that these metastable states are fully reproducible to use in memory devices. Then, using four such representative metastable states (in principle many more states can be generated) we outline a procedure to design a prototype multi-bit storage device.

Magnetic and magnetotransport measurements.

We prepared high quality polycrystalline \( \text{Sm}_{0.5}\text{Ca}_{0.25}\text{Sr}_{0.25}\text{MnO}_3 \) (SCSMO) sample using well-known sol-gel technique (please see the method section for details). Fig. 1(a) shows the magnetization (\( M \)) vs. temperature (\( T \)), measured in the presence of 100 Oe external magnetic field for SCSMO and \( \text{Sm}_{0.5}\text{Ca}_{0.25}\text{MnO}_3 \) (SCMO) using zero field cooled warming (ZFCW), field cooled cooling (FCC), and field cooled warming (FCW) protocols. FCW curve in both SCSMO and SCMO exactly overlay the FCC curve. The bifurcation between ZFCW and FCW curves in SCSMO as well as peak in ZFCW indicates that small but finite ferromagnetic fractions are induced in SCSMO which is absent in SCMO. This is due to the substitution of larger Sr ions in place of Ca in the parent compound \( \text{Sm}_{0.5}\text{Ca}_{0.25}\text{MnO}_3 \). The dip in the \( dM/dT \) vs. \( T \) curve for SCSMO [see the inset of Fig. 1(a)] also substantiate the presence of ferromagnetic fractions below 62 K. Along with the ferromagnetic transition the inset also depicts an antiferromagnetic transition (\( T_N \))
at 110 K and a charge ordered transition ($T_{CO}$) around 195 K. All these results signifies the presence of phase coexistence at low temperatures.

To further study the phase coexistence in SCSMO, we apply 35 kOe magnetic field and measure $M$ vs. $T$ using three (ZFCW, FCW and FCC) protocols, as shown in Fig. 1(b). Here ZFCW curves also shows a maxima around 60 K similar to ZFCW curve in 100 Oe magnetic field. For SCSMO, 35 kOe magnetic field melts the CO-AFM-I state to FM metallic state although 70 kOe magnetic field had no effect on the parent compound SCMO (see the inset for resistivity comparison). The moderate hysterisis between the FCC and the FCW measurements in 35 kOe indicates the phase coexistence between the FM and The AFM phases over the temperature range 50–100 K, but the phase existence diminishes for 50 kOe magnetic field [see Fig. 1(b)].

In order to explore the evolution of phase coexistence with the temperature, we measure $M$ vs. $T$ and $\rho$ vs. $T$ using different protocols. Initially we cooled the system from 300 K to 10 K. For magnetization measurements a test field (100 Oe) is always applied unless otherwise specified. Magnetization at 10 K remains very small ($< 10^{-2} \mu_B/\text{f.u.}$) and resistivity is found to be insulting in nature [see Fig. 2(a)and (b)]. At this point, we apply and then remove the 70 kOe magnetic field, and record the magnetization (the resistivity) data while increasing the temperature (denoted as ZFW-I) as shown in Fig. 2(a) and (b). We find that the remnant magnetization ($0.33 \mu_B/\text{f.u. at 10 K}$) decreases with increasing temperature. Correspondingly the resistivity increases with increasing the temperature up to 65 K and decreases thereafter. This temperature is very close to the $T_{FM}$ as shown in inset of Fig. 1(a). These result suggest that the phase coexistence developed in the system at 10 K, due to the application and removal of 70 kOe field, persists up to ~65 K.

**Observation of multi-level resistance states**

In the 2nd protocol (ZFW-II) rather than warming the sample continuously from 10 K to 200 K we heat the sample up to 35 K and perform the temperature cycling between 35 and 10 K as shown in Fig. 2(c) (indicated by step-1). After the temperature cycle we further increase the temperature from 35 K up to 45 K and repeat the temperature cycling (indicated by step-2). Similarly we have performed temperature cycling at 52 K and 58 K indicated by step-3 and step-4, respectively. During the temperature cycling, from 35 K, 45 K, 52 K, and 58 K to 10 K, the magnetization remains unchanged and mimics the memory effect. We also performed the resistivity measurements using the same protocol [see Fig. 2(d)] and there is a one-to-one correspondence between the magnetization and the resistivity data. Experimental data for sweep rate dependence, effect of repeated cycling, time dependence, reproducibility of multilevel states (see supplementary Figs.6–10) shows that the generated four resistance states are robust by its design. Not only four but large number of resistance states can be designed using the same protocol.
Physical origin of memory states

During the temperature cycling, say at 35 K [see Fig. 2(c)], it appears that the size of the ferromagnetic regions freezes in a metastable state and as a result the magnetization remains the same. In order to verify the presence of the metastable states we study a standard two-band model Hamiltonian for the manganites in 2D. Due to the octahedral crystal field splitting the Mn $t_{2g}$ levels have lower energy than the $e_g$ levels and the itinerant $e_g$ electrons are coupled with the $t_{2g}$ electrons ($t_{2g}$ form the core Mn spins $S (=3/2)$) via large Hund’s coupling. The $e_g$ electrons are also coupled to the Jahn-Teller phonons with a coupling strength $\lambda$. In addition, antiferromagnetic superexchange interaction $J$ between neighboring core Mn spins is taken in to account. This well investigated Hamiltonian in the double exchange limit \[ H_{\text{HE}} \] reproduces the phase diagram of manganites [32–34]. In SCSMO, $Si^{2+}$ ions (larger in size as compared to $Sm^{3+}$ and $Ca^{2+}$ ions) occupy the A-sites randomly and creates chemical disorder. In order to incorporate this disorder $\sum_i e_i n_i$ is added at each Mn site picked from the distribution $P(e_i) = \frac{1}{\pi} \delta(e_i - \Delta) + \frac{2}{\pi} \delta(e_i + \Delta)$, where $\Delta$ is the disorder potential. In an external magnetic field $h$, a Zeeman coupling term $-\sum_i h \cdot S_i$ is added to the Hamiltonian, where $S_i$ denote classical Mn $t_{2g}$ spin. We use spin-fermion Monte Carlo (MC) technique based on the travelling cluster approximation [35, 36] (TCA) for $24 \times 24$ lattice (see Ref.[39] for details). We ensured that the system is well annealed (using $10^4$ Monte Carlo system sweeps in general) at each temperature.

We measure $\lambda$, $J$, $\Delta$, $h$ and $T$ (temperature) in units of kinetic hopping parameter $t$. The estimated value of $t$ in manganites is $0.2$ eV [31]. We use $J = 0.1$, $\lambda = 1.65$ and $\Delta=0.3$ for SCSMO [39]. Magnetization $|S(q)| = (S(q))^0.5$ at wave vector $q = (0,0)$, where $S(q)$ is magnetic structure factor $= \frac{1}{N} \sum_{\langle ij \rangle} S_i S_j e^{i \mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)}$ is averaged over ten different disorder configurations in addition to the thermal

FIG. 2. Multi-level resistive states in SCSMO: (a) Square symbols (FCC): temperature dependence of the magnetization in 100 Oe magnetic field. Circle symbols (ZFW-I): variation of magnetization with temperature in 100 Oe magnetic field (after applying and removing 70 kOe magnetic field at 10 K). Inset shows the temperature derivative of $M(T)$ data taken for the warming process. (c) Similar to ZFW-I, but temperature cycling is performed while increasing the temperature at four representative temperature points (defined as ZFW-II). Resistivity corresponding to magnetization data in (a) and (c) are plotted (b) and (d) respectively. V-limit is limiting value of our measuring instruments (see method section for details).
averages obtained during the Monte Carlo simulations.

Initially we cooled the system (from $T = 0.1$ to $T = 0.005$) and the corresponding temperature dependence of the magnetization ($M$) for electron density $n = 1-x = 0.5$ is shown in Fig. 3(a) using circle symbols. At $T = 0.005$, we apply and remove the external magnetic field ($h = 0.2$). The magnetization of the system drops to 0.6 from 1 upon removal of the field. The temperature dependence of magnetization after removing the magnetic field at $T = 0.005$ (defined as ZFW-I) is shown by the square symbol in Fig. 3(a). In the second protocol (ZFW-II), similar to our experiment, after removing the field at $T = 0.005$, we increase the temperature only up to 0.01 and perform a temperature cycling below it [i.e. system is cooled to $T = 0.005$ and then heated up to $T = 0.01$] as represented by step-1 in Fig. 3(b). The magnetization remains unchanged during the temperature cycle. Then from $T = 0.01$ we further increase the temperature to 0.0125 and perform a temperature cycling below it. Similarly system is recycled to lower temperature from $T = 0.015$ and $T = 0.0175$. In all cases the magnetization remains unchanged during the temperature cycling. So, our Monte Carlo calculations systematically reproduce the experimental results.

We move now to analyze the phase coexistence of ferromagnetic-metallic and charge-ordered insulating phases using Monte Carlo snap-shots. Fig. 4(a) shows magnetization data using ZFW-II protocol (shown in Fig. 3(b)) indicating four representative points.

Figs. 4(c)–(f) and Figs. 4(g)–(j) show the z components of $t_{2g}$ spins and electron density for each sites for a disorder configuration, respectively. Fig. 4(b) shows $\epsilon_i$ distribution for that disorder configuration. At $T = 0.005$ (after applying and removing $h = 0.2$) the system consists of ferromagnetic metallic and charge-ordered insulating [see Fig. 4(c) and (g)] phases. The electron density is more or less homogeneous ($\sim 0.65$) within the ferromagnetic clusters and charge-ordered (short-range) elsewhere. Comparing with the impurity locations [Fig. 4(b)] it is apparently clear that the ferromagnetic-metallic clusters are within the homogeneously distributed $\epsilon_i$ regions and are pinned to the disorder configuration. This is the reason for which the magnetization remains finite even after removing the magnetic field. The size of the ferromagnetic-metallic clusters decreases in size with temperature as shown in Figs. 4(d) and (h). Interestingly going from $T = 0.005$ to $T = 0.01$ [i.e. from Fig. 4(c) to Fig. 4(d)] the magnetic regions get depleted but remnant ferromagnetic regions at $T = 0.01$ are always part of the bigger ferromagnetic regions seen in $T = 0.005$. During the temperature cycling from $T = 0.01$ to $T = 0.005$ (i.e. step-1) the ferromagnetic regions [compare Figs. 4(d) and (e)] get pinned in a metastable state due to the disorder configuration [shown in Fig. 4(b)] and as a result magnetization remains the same. For $T = 0.0125$ the ferromagnetic regions (see Fig. 4(f) and (j)) further shrink in size and the magnetization decreases further.
FIG. 4. (a) ZFW-II data from fig. 3(b) is reproduced here highlighting four temperature points using four different symbols; (b) disorder distribution [$\epsilon_i$ distribution] for one copy of disorder. Black (yellow) points represent $\epsilon_i = -0.3$ ($\epsilon_i = 0.3$). (c)–(f): The $z$ components of simulated Mn ($t_{2g}$) spins at each sites and (g)–(j): corresponding electron density at each sites on a 24×24 lattice using one of the disorder configuration [shown in (b)]. (g) is the corresponding electron density for (c), (h) is the corresponding electron density for (d) and so on. Color bar [right of (h)] is for (c)–(f) and Color bar [right of (j)] is for (g)–(j).

FIG. 5. Protocols to write, read, and erase multi-bit digital data: (a) Experiment: Dashed line is using ZFW-II data reproduced from Fig. 2(c). From 10 K we go to 52 K (without any temperature cyclings at 35 K and 45 K) and perform temperature cycling (i.e. going to step-3 directly, see ZFW-3). New step-3 data perfectly matches with the step-3 data of ZFW-II. At T=10 K of new step-3 we apply and remove 70 kOe magnetic field (i.e. going from filled circle symbol to filled square symbol, indicated by an arrow) and then increase the temperature to 45 K. After that we perform a temperature cycling below 45 K (see ZFW-3-2). The magnetization data from new step-2 also matches well with the step-2 data of ZFW-II. (b) Theory: Dashed line is using ZFW-II data reproduced from Fig. 3(b). Here the magnetization data of step-3 is directly accessed without going through step-1 and step-2. New step-3 data (see ZFW-3) perfectly matches with the step-3 data of ZFW-II. Then $h=0.2$ is applied and removed at T = 0.005 of ZFW-3 (i.e. going from filled circle symbol to filled square symbol, indicated by an arrow). After that we increase the temperature to 0.0125 and perform a temperature cycling below it. The magnetization of new step-2 data (see ZFW-3-2) also matches well with the step-2 data of ZFW-II. Please see the text for more details.
Design of two-bit memory device

We have purposefully designed four-level states to store a two-bit (00 or 01 or 10 or 11) digital data in each state. Say, we assign 00 to step-1, 01 to step-2, 10 to step-3 and 11 to step-4. Then the question we ask ourselves: can we write and erase the two-bit data repeatedly in any of the four states? For this we go to 10 K [as discussed in Fig. 2(a)] in the original sample. Then we apply and remove 70 kOe external field, and increase the temperature to 52 K directly (i.e. going to step-3 directly) as shown in Fig. 3(a). Magnetization data from the thermal cycling at 52 K follows the same path as shown in Fig. 2(c). This is to write two-bit information (10) which can be read from resistivity measurement even after removing the temperature probe. We have shown the one-to-one correspondence between magnetization resistivity in Fig. 2. To erase the data we again apply and remove 70 kOe magnetic field at 10 K of step-3. Now in order to write another two-bit data, say 01, we increase the temperature up to 45 K (i.e. step-2) and perform a thermal cycling. This step-by-step procedure establishes a concrete way to write, read, and erase the two-bit digital data in our four-level resistive system.

Similar to experiment we also increase the temperature to \( T = 0.015 \) (step-3) directly from \( T = 0.005 \) (temperature at which magnetic field is applied and removed) by passing two intermediate temperature cycles in our Monte Carlo calculations and perform a temperature cycling below \( T = 0.015 \) [see Fig. 5(b)]. The magnetization data during temperature cycling at \( T = 0.015 \) perfectly matches with the step-3 of ZFW-II (dashed line). During the temperature cycling from \( T = 0.015 \) we apply and removed the magnetic field at \( T = 0.005 \) (i.e. going from filled circle symbol to filled square symbol) to erase the data. Then to write a new data by using the step-2 we increase the temperature directly to 0.0125 and perform a temperature cycling below it. Magnetization data from new step-2 also matches well with the step-2 data of ZFW-II. So, our calculations reproduce the qualitative nature of the experimental results.

We have used a direct temperature probe in our experiments. Temperature probe based on the Joule heating, by using voltage pulse, can be used to design the device. The electronic phase separation (and in turn resistive states) can also be controlled by numerous ways like, applying substrate strain, using mode-selective vibrational excitations, using photo-induction and applying pressure etc.

Methods

Sample preparation

High quality polycrystalline \( \text{Sm}_{0.5}(\text{Ca}_{0.5}\text{Sr}_{0.5})_{0.5}\text{Mn}_3\) compound was prepared by the well-known sol-gel technique by taking appropriate amount of \( \text{Sm}_2\text{O}_3, \text{CaCO}_3, \text{Sr(NO}_3)_2 \) and \( \text{Mn}_2\text{O}_4 \) as the starting materials of purity 99.9%. To prepare the bulk polycrystalline sample the decomposed gel was palletized and subsequently heated for 36 h at 1300°C. For more details (also for crystalline structure study) please see Ref. [30].

Magnetic property measurements

Magnetic properties was measured by utilizing Superconducting Quantum Interference Device Magnetometer (SQUID-VSM) of Quantum Design with maximum magnetic field value of 70 kOe in the temperature range 10 K - 300 K.

Electrical and magneto-transport measurement

The electrical transport and magnetotransport measurements were performed by four probe method using the longitudinal geometry of the bar-shaped samples. Zero field and in field resistance measurements in the temperature range 20 K to 300 K was carried out using Keithley source and measure unit 2651A with the measurement limit of \( 10^{14} \) ohm. Below 20 K, the zero field resistance measurement was extended by using Keithley Electrometer 6517A in the capacitor arrangement method and at 10 K it exceeds our measurements limit (10^{13} ohm).

Conclusion

In summary, our combined experimental and theoretical study outline a simple yet effective path to achieve multi-level resistance states that can give new direction to architect multi-bit storage devices for future spintronic applications. Here we devised the phase coexistence in a controllable manner in a half doped manganite below 60 K and showed that a temperature probe can be used to access four distinct metastable phases for designing a two-bit memory device. In principle it can be extended to generate many more distinctly resistive/magnetic states to devise more than two-bit devices. At the end we demonstrate the writing, reading and erasing mechanism in our prototype two-bit device. It is expected that our results will motivate experimenters to explore electronic phase separated materials to engineer future multi-bit memory devices.
REFERENCES

[1] Scott, J. C. Is There an Immortal Memory? Science 304, 62-63 (2004).
[2] Meijer, G. I. Who Wins the Nonvolatile Memory Race? Science 319, 1625-1626 (2008).
[3] Chen, X., Wu, G., and Baoa, D. Resistive switching behavior of Pt/MgO/2ZrO2/Pt devices for nonvolatile memory applications. Appl. Phys. Lett. 93, 093501 (2008).
[4] Pan, F. et al. Nonvolatile resistive switching memories: characteristics, mechanisms and challenges. Prog. Nat. Sci.: Mater. Int. 20, 1 (2010).
[5] Hwang, C. S. Perspective of Semiconductor Memory Devices: from Memory System to Materials. Adv. Electron. Mater. 1, 6 (2015).
[6] Sawa, A. Resistive switching in transition metal oxides. Mater. Today 11, 2836 (2008).
[7] Jeong, D. S. et al. Emerging memories: resistive switching mechanisms and current status. Rep. Prog. Phys. 75, 076502 (2012).
[8] Kim, S. Physical Electrothermal Model of Resistive Switching in Bi-layered Resistance-Change Memory. Sci. Rep. 3, 1680 (2013).
[9] Ielmini, D. Resistive switching memories based on metal oxides: mechanisms, reliability and scaling. Semiconductors Sci. Technol. 31, 063002 (2016).
[10] Russo, P., Xiao, M., Liang, R., and Zhou, N. Y. UV-Induced Multilevel Current Amplification Memory Effect in Zinc Oxide Rods Resistive Switching Devices. Adv. Electron Device Materials, 17, 681-695 (2018).
[11] Wang, M. et al. Investigation of One-Dimensional Thick-
[39] Chai, X., Xing, H., and Jin, K. Evolution of photoinduced effects in phase-separated $Sm_{0.5}Sr_{0.5}Mn_{1-y}Cr_yO_3$ thin films. Scientific Reports 6, 23280 (2016).

[40] Rini, M. et al. Control of the electronic phase of a manganite by mode-selective vibrational excitation. Nature 449, 7274 (2007).

[41] Baldini, M. et al. Pressure induced magnetic phase separation in $La_{0.75}Ca_{0.25}MnO_3$ manganite. J. Phys. Condens. Matter 24, 045601 (2012).

[42] Lee, D. H. and Lim, S. H. Increase of temperature due to Joule heating during current-induced magnetization switching of an MgO-based magnetic tunnel junction. Appl. Phys. Lett. 92, 233502 (2008).

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AUTHOR CONTRIBUTIONS

ID and KP developed the concept of the study. SB and KD prepared the samples. SB performed the most of the experimental work. KD and ID performed partial measurements and KP performed the numerical work. SB and KP wrote the draft of the paper and all authors reviewed the manuscript.

SUPPLEMENTARY INFORMATION

FIG. 6. Sweep rate dependence (supplementary figure): Temperature dependence of magnetization data for the different sweep rates 2 K/min, 5 K/min and 15 K/min for ZFW-II protocol (see the main text). Inset in the figure shows the zoomed portion of one of the step.
FIG. 7. Effect of repeated cycling (supplementary figure): Temperature dependent (a) magnetization [(b) resistivity] data for 5 K/min using protocol ZFW-II where 10 temperature cycling are performed in step-2. Insets show the zoomed portion of step-2 data. Experimental data remains unaffected with repeated cycling.

FIG. 8. Time dependence-I (supplementary figure): (a) M(T) and (b) $\rho$ (T) measured in the ZFW-II protocol. Magnetization [in (a)] and resistivity [in (b)] data are taken for 10 hours at 25 K of step-2 to see the time evolution [see the inset (a) and (b)]. Magnetization and resistivity remains more or less same even after 10 hours.

FIG. 9. Time dependence-II (supplementary figure): (a) M(T) and (b) $\rho$ (T) measured using ZFW-II protocol. In one case magnetization data is taken immediately after removing the magnetic field at 10 K (see main text) while in other magnetization data is taken one hour later after removing the field. Resistivity data are also taken in a similar fashion. This shows that system do not loose its identity with time.
FIG. 10. Reproducibility of multilevel states (supplementary figure): Insets of (a) and (b) show repetition of Fig. 4(a) and (b), but the we stopped at 10 K of step ’3’. Then we apply and remove a 70 kOe magnetic field (shown as dotted arrow). Then the magnetization and resistivity with temperature [using ZFW-II protocol] are measured and plotted in main Figs. (a) and (b), respectively using blue solid lines. Line with red circles in the main plot are from the inset. This show that all the four steps can be obtained repeatedly.