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Significant enhancement of magnetically induced Neel transition temperature (T_N) in Ca-substituted $SrMn_{0.5}Ti_{0.5}O_3$ perovskite

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$Sr/CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 25%, 50% and 75%) polycrystalline samples were prepared by conventional solid-state reaction. X-ray diffraction (XRD) was taken to estimate the phase purity of the prepared compounds. Signature of antiferromagnetic ordering (AFM) was observed in the magnetic characterization using PPMS – VSM. Observation of antiferromagnetic (AFM) ordering at temperatures (T_N) ~ 19 K, 25 K and 29.5 K for Ca = 25%, Ca = 50% and for Ca = 75%, respectively. $Sr/CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 75%) exhibit field induced antiferromagnetic to ferromagnetic transition at ~ 30 K with applied magnetic field of 4 T and 5T. The investigated results indicated $Sr/CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 75%) might be a suitable candidate for magnetic refrigerant applications.

1. Introduction

The last couple of decades have seen an immense increase in interest in magnetic materials is partly due to the discovery of a magnetic entropy change in the late 1990s [1-5]. In this context, Gd is the first reference material for magnetic refrigeration, and it is still used to test prototypes. Rare earth-transition intermetallic compounds with ferromagnetic (FM) to paramagnetic (PM) transition (or) antiferromagnetic (AFM) to FM metamagnetic transition possess large MCE [6-13]. Perovskites with formula ABO_3 {A – rare-earth/alkaline-earth, B – transition metal} have been studied in detail due to their interesting switching of magnetic properties with external perturbations [13-19]. On technological demand, the magnetic studies on different kinds of manganites are essential in order to develop a suitable system that will show large magnetocaloric change at a relatively small magnetic field.

Among, the various transition elements, both Mn and Ti are potential candidates to enhance physical properties in perovskite oxides. Mn^{4+} is responsible for double exchange through Mn-O-Mn interactions and Ti-O-Ti interactions helps super exchange mechanism and enhance thermoelectric response in most of the cases. Further, rich variety of phase transitions is known to result when Ca^{2+} is substituted at the Sr^{2+} site. The substitution of the Ca^{2+} for Sr^{2+} is expected to reduce the overall spin state and also introduce lattice randomness. The order of the transition in Sr/Ca based perovskite oxides can be changed by applying either external perturbations like magnetic field (H) and pressure (P) or internal perturbation like doping [18,19]. In this work, we investigated the change in Neel transition with the substitution of Ca^{2+} for Sr^{2+} in the crystallographic A-site.

2. Experiment

Sr/$CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 25%, 50% and 75%) powders were prepared by solid-state reaction from the reactants of $SrCO_3$, $CaCO_3$, MnO_2 and TiO_2. The starting materials were weighed as per stoichiometry and thoroughly mixed. The powders were fired at 1250, 1450 and 1550 K for 11 hours with intermediate grindings. The powders were grounded and pressed into pellets of 10 mm diameter. The pellets were sintered at 1550 K. The phase purity of the prepared sample was examined by Powder X-ray Diffraction (PXRD) using X'pert PRO PANalytical X-ray diffractometer with Cu-K_α radiation of λ = 1.5418 Å from 2θ = 10° to 80° with a step size of 0.025°. The magnetization measurements were carried out using a PPMS-VSM, Quantum Design Inc., in the temperature range from 300 K to 5 K with magnetic field up to 5 Tesla. The temperature dependent magnetization was measured in both zero field-cooled (ZFC) and field-cooled (FC) processes in order to determine the magnetic reversibility and the magnetic transition temperature. With the sample cooled down to 5 K in a zero field, the heating curve from 5 to 300 K was measured in a magnetic field of 0.05 T and the cooling curve from 300 to 5 K was also measured in the same field.

3. Results and Discussion

The Powder X-ray diffraction (PXRD) patterns of the Sr/$CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 25%, 50% and 75%) samples shown in figure 1(a) show the reflection planes (1 1 0), (1 1 1), (2 0 0), (2 1 1) and (2 2 0). The peaks were indexed to the cubic phase and the lattice constant were found to be 3.867, 3.838 and 3.812 Å, respectively, for Ca = 25%, 50% and 75% in Sr/$CaMn_{0.5}Ti_{0.5}O_3$ [11, 20-23]. The decrease in lattice parameter with the increasing Ca in Sr/$CaMn_{0.5}Ti_{0.5}O_3$ is due to the smaller ionic radius of Ca^{2+} compared to Sr^{2+}. PXRD results also indicated the phase purity of the as prepared samples were good.

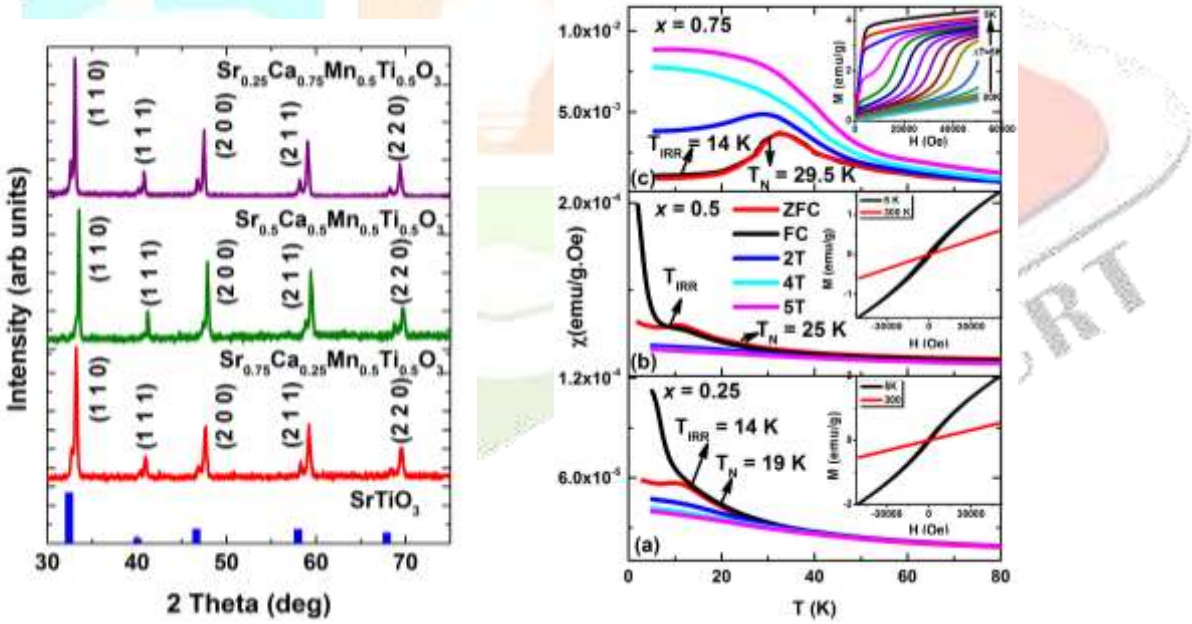

Figure 1 Powder XRD patterns of Sr/$CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 25%, 50% and 75%).

Figure 2 Magnetic susceptibility vs temperature χ(T) of Sr/$CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 25% (a), 50% (b) and 75% (c)) for various magnetic fields from 0.05 Tesla to 5 Tesla. **Inset:** Magnetic hysteresis curves M(H) for various temperatures of Sr/$CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 25%, 50% and 75%).

Fig. 2 (a, b & c) shows the magnetic susceptibility χ(T) of Sr/$CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 25%, 50% and 75%) with magnetic field from 0.05 T to 5 T. The χ(T) curves of samples with Ca = 25% and 50% shows field cooling and zero-field cooling (FC-ZFC) splitting at 14 K (irreversible temperature T_{IRR}). Further, the variation observed in the magnitude of χ(T) approximately at (Neel transition $T_N \approx$) 19 K, 25 K, and 29.5 K for Ca = 25%, 50% and 75%, respectively, revealed the presence of antiferromagnetic ordering. Sr/$CaMn_{0.5}Ti_{0.5}O_3$ with Ca = 25% and 50% exhibit paramagnetic nature with linear increase of magnetic moment from room temperature to low temperature until T_N. The transition T_N shows reasonable shift towards high temperature with the increase of field for Ca = 75% and it does not varies for Ca = 25%

and 50% i.e T_N is almost similar for both H = 0.05 T and H = 5 T for $Sr/CaMn_{0.5}Ti_{0.5}O_3$ with Ca = 25% and 50% (Fig. 2 a and b). Interestingly, contrasting magnetic properties for $Sr/CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 75%) system is observed compared to the other two investigated system as shown in Fig. 2(c). For this system, the T_N is observed at 29.5 K and increasing magnetic field increases the magnetization towards weak ferromagnetic nature. $Sr/CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 75%) exhibit field induced antiferromagnetic to ferromagnetic transition at ~ 30 K with applied magnetic field of 4 T and 5T. For 5 T field, the magnitude of magnetization is increased an order and which is almost equal to ferromagnetic perovskite systems [24]. M(H) curves near the transition temperature are obtained to understand the detailed magnetic nature of the system and it is shown as insets of Fig 2. The magnetization of all investigated systems shows bifurcation between FC and ZFC data defined as the onset of the progressive freezing of spins towards the randomly oriented axes [16]. The bifurcation between FC and ZFC curves is usually happens approximately near the magnetic transitions arises due to the magnetic anisotropy.

It is well known that the substitution of Ti^{4+} (non-magnetic) ion in the Mn^{4+} ion site leads to the suppression of the double exchange interaction and the ferromagnetism [23-25]. As well as from the earlier reports [26-28], it is clear that the FM is totally suppressed with the concentration of $Ti_{0.3}$ in $La_{0.7}Sr_{0.25}Na_{0.05}Mn_{0.7}Ti_{0.3}O_3$ and further increasing of Ti^{4+} ions in the Mn^{4+} site vanished FM totally and induces AFM interactions between Mn-O-Mn. Here we have fixed both Ti^{4+} and Mn^{4+} in equal amount because half-doped systems are more interesting and it is expected that even a small change in the A site and/or external perturbations changes the whole physical properties of the system [29]. We induced disorder in the lattice by both internally (by substitution Ca^{2+} in the Sr^{2+} site (A-site)) as well as externally (by varying magnetic field) lead to the change in the magnetic transition.

To study the complete magnetic nature of the investigated systems, magnetic hysteresis was obtained with 3K temperature intervals. The inset of the figures 2 (a) and (b) shows full M(H) loop measured at 300 K and 5 K. The magnetic isotherm is more enhanced and 5 K loop shows reasonable coercivity for Ca = 25% than Ca = 50%. Therefore, increasing Ca^{2+} content in A-site induces more magnetism in the investigated systems. Further, increase of Ca^{2+} substitution (i.e Ca = 75%) increases the magnitude of the magnetization towards ferromagnetic side, which is almost equal to the magnetization of the ferromagnetic system [24, 30]. The first quadrant M(H) loop for Ca = 75% is shown in the inset figure 2(c). The loop gets saturated like a ferromagnetic material below T_N for magnetic field approximately above 1 Tesla. It concludes that the Ca^{2+} substitution in A-site enhances magnetic matrix from AFM to FM nature. This enhancement also gets reflected in the magnetic entropy change and drives the system suitable for magnetocaloric applications.

4 Conclusion

In conclusion, we have studied the magnetic properties of $Sr/CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 25%, 50% and 75%) polycrystalline samples. The Neel transition temperature is observed at 19, 25, and 29.5 K for Ca = 25%, 50% and 75%, respectively. $Sr/CaMn_{0.5}Ti_{0.5}O_3$ (Ca = 75%) shows magnetocaloric change of 19 J/Kg/K for 5 Tesla, which is higher than the other reported antiferromagnetic perovskite systems and similar to existing conventional ferromagnetic systems and these series of perovskites have easily tunable magnetic properties suggesting that they are excellent candidates for magnetocaloric applications.

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