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Investigation on the structural and thermal properties of rare earth $La_{0.8}Na_{0.2}MnO_3$ manganite

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Abstract: *An alkali metal doped rare earth $La_{0.8}Na_{0.2}MnO_3$ manganite has been successfully prepared by solid state reaction route. The sample is highly crystalline and single phased. The structure of the sample has been confirmed by analyzing the X.- ray diffraction spectrum and it was found that the sample exhibits the rhombohedral structure with the assigned space group R3c. The particle size has been calculated using Scherer's formula which is about 21 nm. For further confirmation of the structure and structure related parameters, Retveld refinement has been carried out on the XRD data. Differential Scanning Calorimetery (DSC) specific heat measurement in the temperature range 300 K-350 K was done on the sample. Phase transitions around 340 K is observed which is transition from paramagnetic to ferromagnetic (T_C) and around 350 K which is metal to insulator transition(T_{MI}) both of which are consistent with the temperature dependent dc resistivity results already published for the sample of the same composition.*

Keywords: *Nanoparticles, solid state reaction, X-ray diffraction, Retveld refinement DSC specific heat.*

1. Introduction

Mixed-valence perovskite manganites represented by the formula $Ln_{1-x}A_xMnO_3$ (with Ln = La, Ho, Sm etc., and A = divalent like Ca, Sr, Ba as well as monovalents like Na, K, Ag, etc.) gained keen concentration of scientific community because of their huge negative magnetoresistance generally known as colossal magnetoresistance (CMR) in the vicinity of Curie temperature [1]. Researchers recently have devoted their interest to explore the correlation among structure, magnetism and transport in this perovskite system of manganites. These characteristics were interpreted on the basis of the double-exchange (DE) the mechanism [2] and Jahn–Teller (J–T) effect [3].

Compounds of the formula $Ln_{1-x}A_xMnO_3$ have been studied extensively. Earlier the A-site of these perovskites was substituted by divalent alkaline earth metals and these compounds showed very interesting change in behaviour. Later it was found interesting to substitute alkali-metal ions for La because the large difference in valency introducing higher concentration of holes which may result changes in structure and magnetic properties. Since the host atom La and the doped atom Na have approximately equal ionic radius (R_{La}= 1.36 Å, R_{Na} = 1.39 Å) [4] which motivates us the substitution of Na at La site. Since the valence state of sodium is +1, switching to the monovalent doping (A = Na or K) in place of divalents in $Ln_{1-x}A_xMnO_3$ at trivalent lanthanum ion site, every sodium ion substitution results in the oxidation of two Mn^{3+} to Mn^{4+} and hence the cation valency distribution can be depicted as $La^{3+}_{1-x}Na^{+}_{x}(Mn^{3+}_{1-2x}Mn^{4+}_{2x})O_3$[5].

In the recent past, attention was concentrated on the studies of alkaline earth metal doped manganites [6]. T_P and $T_C \approx 250$ K for $La_{0.7}Ca_{0.3}MnO_3$ are below room temperature (RT) and magnetoresistance (MR) characteristic was observed near around T_P which is inconvenient from the application point of view. For $La_{0.7}Sr_{0.3}MnO_3$, T_C (≈370 K) is the highest amongst all the perovskite structured manganites which is because of its higher e_g electron band width and effective double exchange (DE) interaction. It is worthwhile to mention here that lower MR value is also not suitable when there is the talk of practical applications. In this context, monovalent alkali metal (Na and K) doped manganites have been studied [7,8] which possess relatively high T_p and T_c together with large MR values in the vicinity of room temperature (RT) making them suitable for practical applications [9].

It has been also reported that, Na-doped $LaMnO_3$ manganites are well studied in the form of polycrystalline bulk, nanostructures and thin films [10, 11]. Keeping in mind all the above advantages and limitations of the doped mixed valent manganites, in the present communication monovalent Na^{+1} doped $LaMnO_3$ manganites has been reported for their structural and thermal properties.

2. Experimental Details

The polycrystalline $La_{0.8}Na_{0.2}MnO_3$ manganite sample was prepared using ceramic route [12]. The starting materials were La_2O_3, Na_2CO_3 and MnO_2 from Loba Chemie, 99.9 %. All the chemicals were GR grade and used without any further purification. All the starting materials were weighed, mixed, and grounded thoroughly in an agate mortar for 6 hours using acetone and then heated in air up to 1000 °C for 10 h. The samples were again ground for 5 h to obtain fine powder and again calcined at 1050°C. The powder was then mixed using binder made from poly-vinyl alcohol, ground

and pressed at a pressure of 6 Tons into circular pellet of size 10 mm in diameter and 1.5 mm in thickness and sintered at 1100 °C for 10 h.

The crystal structure and phase type was identified by means of X-ray powder diffraction (XRD) at room temperature, using Bruker D8 Advance X-ray diffractometer with Cu*K*α1 (1.5406 Å) radiation. The data was collected with a scanning speed of 2° per 50 seconds over the angular range 2θ (10° < 2θ < 90°) with a step size of 0.02° generating X-ray by 40 kV and 40 mA power settings. Next we did differential scanning calorimetery (DSC) specific heat measurement to look for phase transition in the expected temperature range.

3. Results and discussions

3.1. Structural analysis

The sample of rare earth manganite doped by alkali metal sodium ($La_{0.8}Na_{0.2}MnO_3$) successfully synthesized via ceramic route i.e. solid state reaction method has been subjected to X-ray powder diffraction (XRD) characterization to confirm the phase formation and hence the structure as well as the purity of the synthesized sample. Room temperature XRD pattern of $Ln_{0.8}Na_{0.2}MnO_3$ is shown in Figure 1. The structure of the sample $La_{0.8}Na_{0.2}MnO_3$ was found to be rhombohedral when XRD pattern was analyzed and the assigned space group was *R*3*c*. The broadness of full width at half maximum reveals nano nature of the material and sharp and intense characteristic peak confirms the crystallinity of the prepared sample.

The average size (*t*) of the nanoparticles of the sample is calculated by Debye-Scherrer's formula [13]:

$t = 0.9\lambda/\beta\cos\theta$

where, λ is the wavelength of $CuK\alpha_1$ radiation used, β is the full width at half maximum (FWHM) of the characteristic peak of diffracting angle 2θ. The calculated particle size was found to be 21 *nm*.

The XRD pattern was refined and analyzed for confirmation of crystal structure and structure related parameters using the FULLPROF program [14]. The rhombohedral structure was confirmed and related parameters were satisfactory. Figure 2 shows Rietveld refinement of room temperature XRD pattern of $La_{0.8}Na_{0.2}MnO_3$ material. Structure structural parameters obtained from Retvield refinement are given in the Table 1. Figure 3(a) shows the 3-D structure and 3(b) shows the top view of the prepared $La_{0.8}Na_{0.2}MnO_3$ sample.

3.2. Differential Scanning Calorimetery (DSC)

DSC is a thermo-analytical technique where the difference in the heat energy required in raising the temperature of a sample and reference is measured as a function of temperature. It is mandatory that the reference sample should have defined heat capacity over the range of temperatures to be scanned. The basis of the technique lies in the fact that when a sample undergoes a physical transformation, less or more heat need to flow to it compared to the reference to maintain both samples at the same temperature.

Specific heat measurement $C_P(T)$ is a direct probe of the occurrence of thermodynamical phase transition. As is clear from the Figure 4, the specific heat capacity smoothly increases but shows the dip in the region corresponding to temperature $T_c \approx 340$ K indicative of a phase transformation and a clear change in specific heat in response to the temperature near about $T_{MI} \approx 350$K reveals transition from metal to insulator (T_{MI}). The transition round the same temperature is reported in the temperature dependent *dc* resistivity measurements [15, 16].

4. Conclusion

The rare earth alkali metal doped manganite $La_{0.8}Na_{0.2}MnO_3$ has been successfully prepared by conventional solid state reaction route. The sample was confirmed to be single phased, highly crystalline and very pure through XRD characterization analysis. The analyzed XRD data confirms the rhombohedral structure with the space group *R*3*c*. DSC specific heat measurement shows the phase transition in the vicinity of the temperature i.e. $T_c \approx 340$ K supported by temperature dependent dc resistivity measurement.

Acknowledgement

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Figure Captions

Figure 1: shows the XRD spectrum of the $Ln_{0.8}Na_{0.2}MnO_3$ sample

Figure 2: Represents the refinement of the $Ln_{0.8}Na_{0.2}MnO_3$ sample

Figure 3: Shows (a) 3-D structure (b) Top view of the sample structure

Figure 4: shows the DSC Specific heat characteristic of the prepared sample

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Figure 1:

r

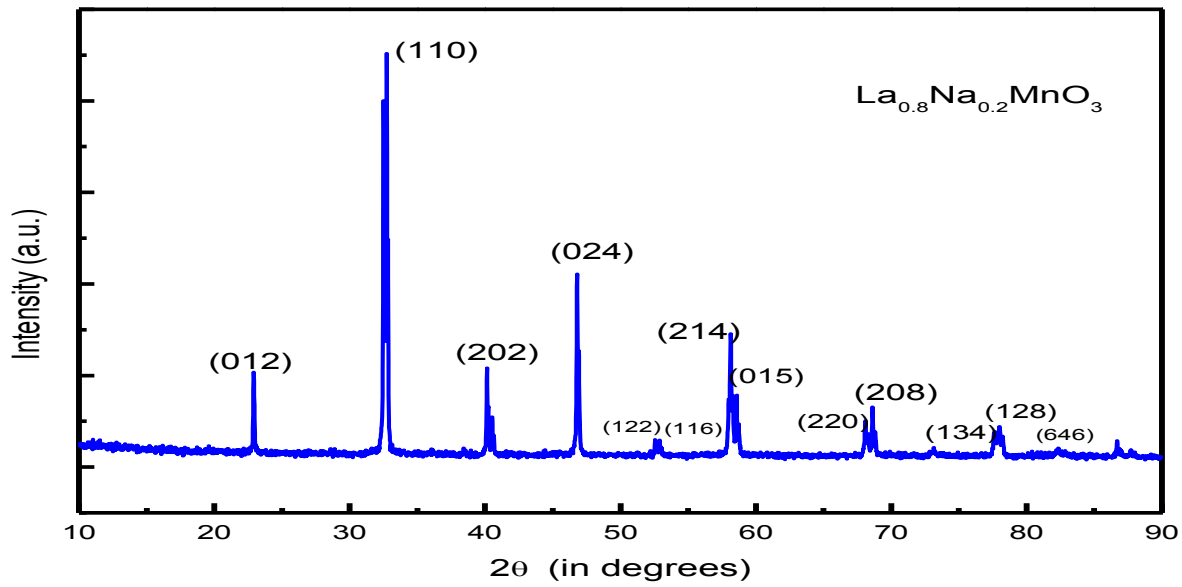

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Figure 2 (colour):

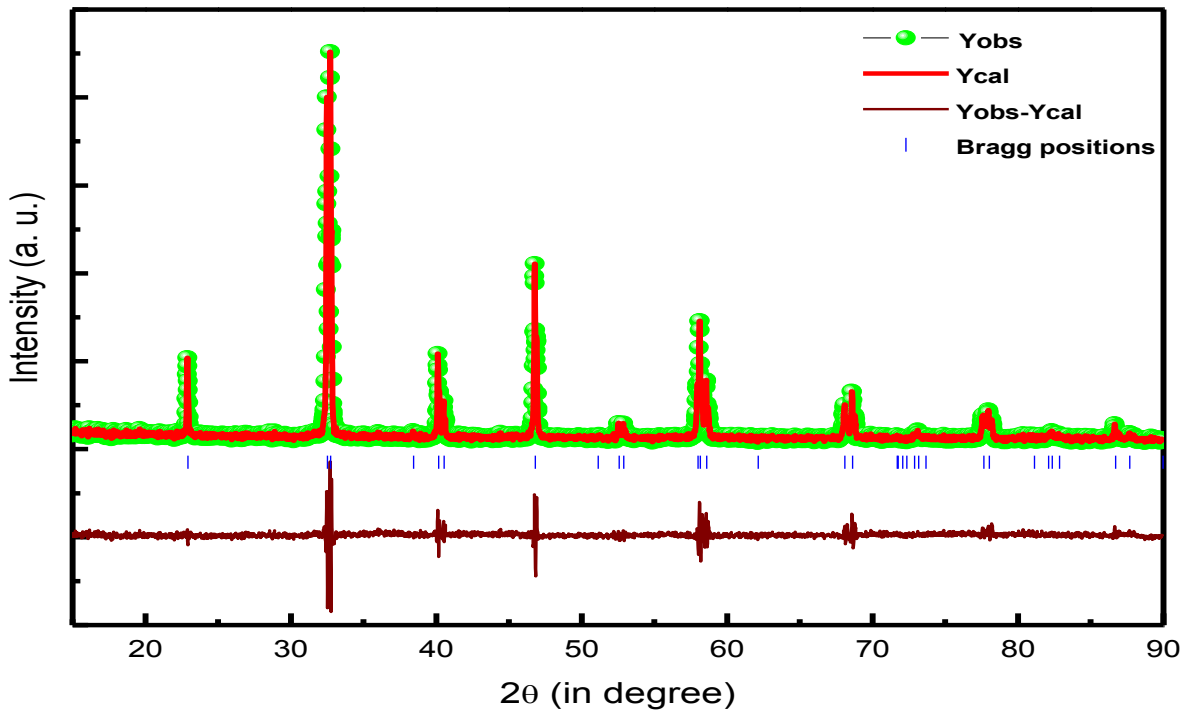

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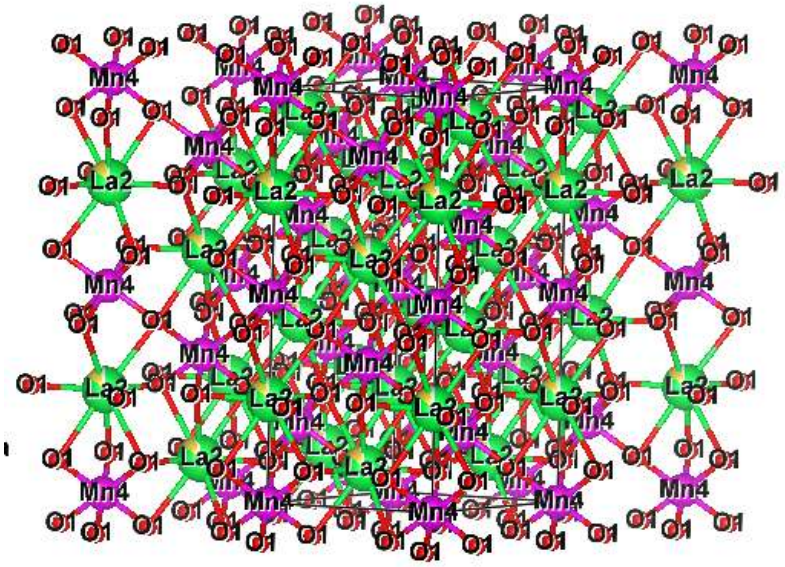
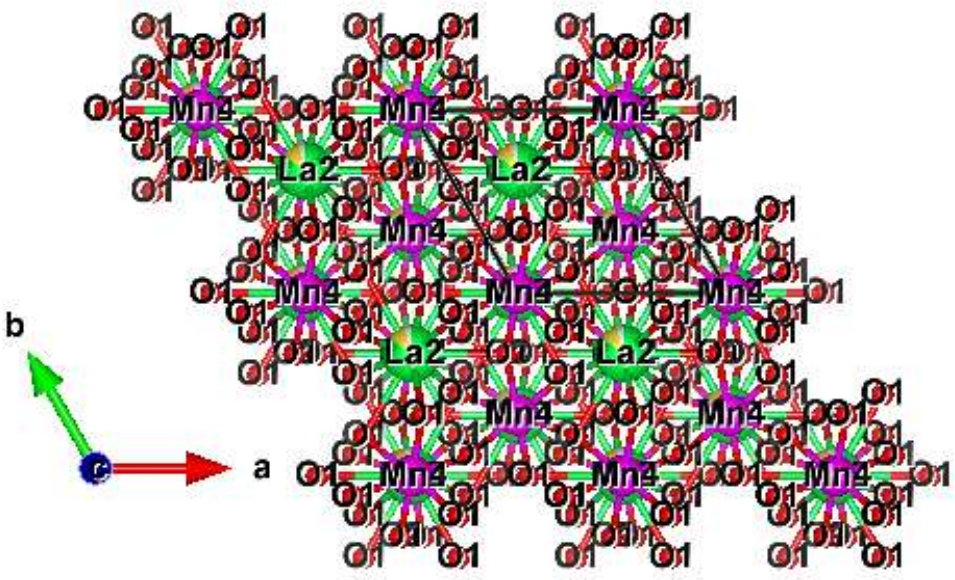
Figure 3



(a) 3-D structure



(b) Top view of the sample structure

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Figure 4:

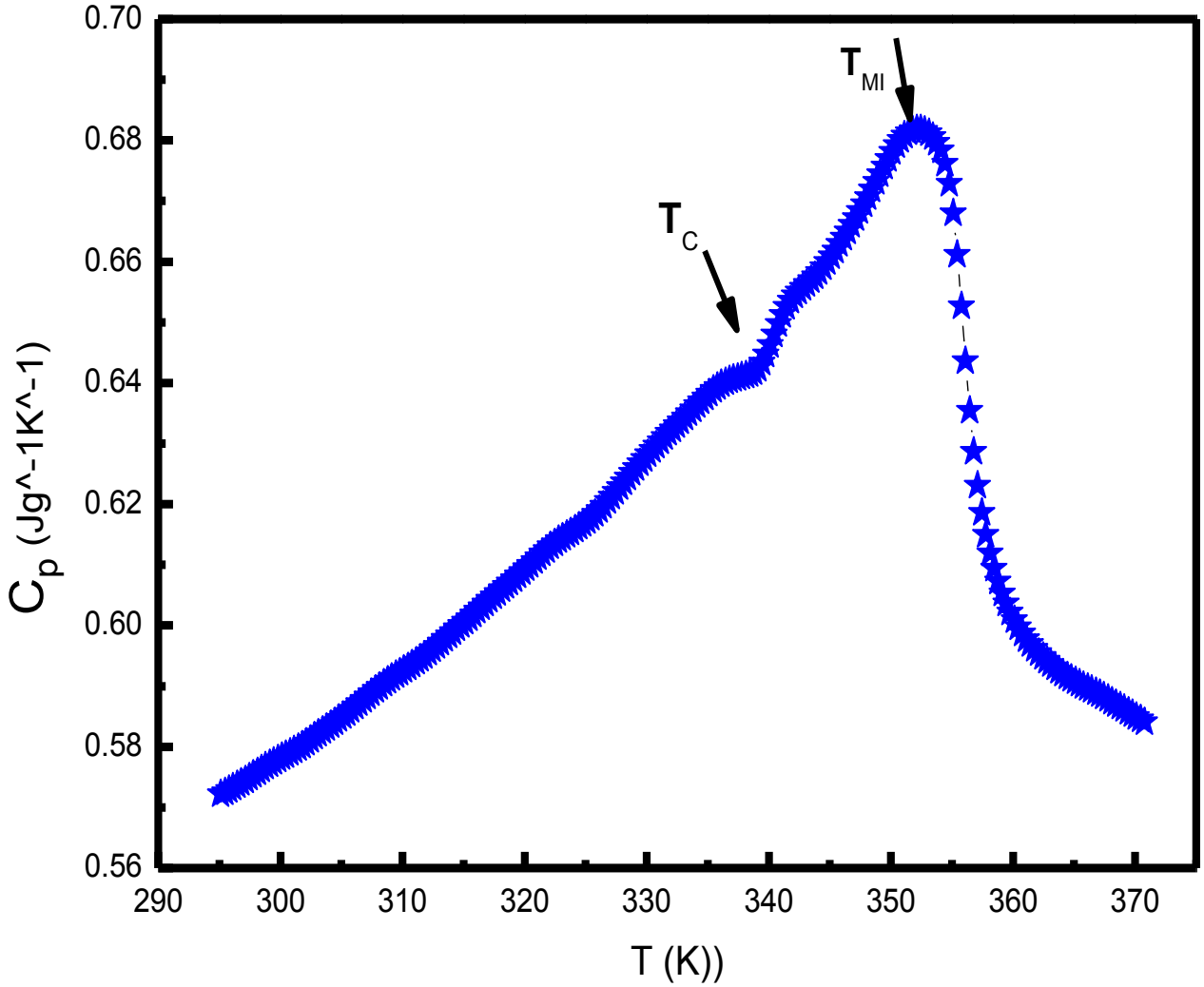

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Table 1:

Table 1: Details of Rietveld refined RT-XRD pattern of the $La_{0.8}Na_{0.2}MnO_3$.

Parameters	**Values obtained**
Space group	*R*3*c*
a (Å)	5.503(3)
c (Å)	13.344(3)
V (Å^3)	349.906
Density (g/cm^3)	6.429
La(*x*, *y*, *z*)	(0.0, 0.0, 0.25)
Sr(*x*, *y*, *z*)	(0.0, 0.0, 0.25)
Mn(*x*, *y*, *z*)	(0.0, 0.0, 0.0)
O(*x*, *y*, *z*)	(0.447(3), 0.0, 0.25)
Bond distance	
La/Na-O	2.749(3) Å
Mn-O	1.96(2) Å
R_F	11.5
R_{Bragg}	12.9
R_{wp}	34.6
R_{exp}	22.6
R_p	43.2
χ^2	2.355
GOF	1.4

