Antisites driven magnetic transition study in $\text{La}_2\text{NiMnO}_6$

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Abstract $\text{La}_2\text{NiMnO}_6$ is a unique compound of multiferroics that exhibits two magnetic transitions of Curie points $T_{C1}$ and $T_{C2}$ below room temperature on a partial conversion of charge carriers, $\text{Ni}^{3+} \rightarrow \text{Ni}^{2+}$ and $\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$, stabilized with O$^2-$ vacancies in distorted octagons in a double perovskite of a spin cluster (glass), wherein the spins freezing at a critical $T_f$ point at lower temperatures. The peak temperature and irreversibility temperature shifted to the lower temperature. The dc magnetization $M$ (T) measurements indicate random ferromagnetic and antiferromagnetic interactions and multiple magnetic transitions. The critical slowing properties signify the spin-glass nature proved by the thermomagnetic relaxation measure.

Keywords magnetic properties, exchange-coupled magnets, magnetic transitions, spin-cluster, spin-glass

1. Introduction

Double perovskites ($\text{A}_2\text{BB'O}_6$) have unique properties that arise from various combinations of B and B'. The ordering between B and B in $\text{A}_2\text{BB'O}_6$ gives important functional properties. Therefore, controlling the structural ordering between B and B' could result in altering their functional properties. $\text{La}_2\text{NiMnO}_6$ (LNMO) is a canonical double perovskite due to its fascinating properties: magnetic, electronic, and structural [1-5]. LNMO exhibits broad scientific and novel technological impact as a material with mutual cross-talk in various aspects [1-5]. LNMO shows different polymorphic phases based on calcination temperature and atmosphere. The captions ordering (Ni - O - Mn) has monoclinic ($P2_1/n$ space group) and rhombohedral ($R3$) crystal structure and cations disorder has orthorhombic (Pnma space group) and rhombohedral ($R3c$ & $R3\alpha$) structure depending on calcination temperature and conditions [6-7].

The ordered LNMO shows superexchange interaction between half-filled d orbital’s of one metal ion ($\text{Ni}^{3+}$) and vacant d-orbital of another metal ion ($\text{Mn}^{4+}$). However, cation disorder is common in these compounds which suppresses the ferromagnetism due to anti-ferromagnetic Ni-O-Ni and Mn-O-Mn interactions. There is a hopping of interactions between effective d orbitals of Ni and Mn [7]. The virtual hopping of parallelly aligned spins is allowed and is favored over antiparallelly aligned spins. Neutron [8] and NMR [9-10] studies establish that ferromagnetic transition (~270 K) occurs due to 180$^\circ$ superexchange interaction between ($\text{Ni}^{3+}$-$\text{O}^2$-$\text{Mn}^{4+}$) and this transition temperature is shifted with the presence of antisites disordering. The admixture of ordered and disordered phases develops another ferromagnetic transition between Ni$^{3+}$-$\text{O}^2$-$\text{Mn}^{4+}$[11-13]. Perovskite oxides can be partially substituted with different cations, $\text{Ln}_{1-x}\text{La}_x\text{Ni}_{1-y}\text{Mn}_y\text{O}_{3+x\delta}$, to enhance the structural stability, cations ordering, and to introduce structural and electronic defects. The biphasic (rhombohedral & monoclinic) samples also show two ferromagnetic transitions, one for each phase. These ferromagnetic transitions shift with particle size, the fraction of disorder, and distortion in the unit cell (changes in Ni$^{3+}$-$\text{O}^2$-$\text{Mn}^{4+}$ bond angle).

According to Goodenough-Kanamori, the synthesis route and conditions play a crucial role in influencing the phase (crystal structure) as well as the ordering and bond angle between Ni & Mn cations. A variety of methods, such as solid-state reaction, sol-gel, and coprecipitation have been applied to synthesize perovskite-type oxides[14-21]. The investigations on the solid-state routes at near ambient temperature have made significant progress in recent years. Solid-state reactions are more convenient to use with the benefits of simple processes such as high yield, high selectivity, and controlled particle size and its distribution [14-21]. The present work was carried out to develop an efficient process for synthetic LNMO preparation by solid-state chemical reaction.

In our previous work, we have investigated the structural and morphological properties of LNMO nanocrystallites using X-ray diffraction, scanning electron microscopy (SEM), and transmission electron microscopy (TEM), respectively [22]. The present work focuses on field dependant magnetic transition. A brief analysis of SEM and EDAX suggests the presence of La, Ni, and Mn in our compound. The two-step transition, as reported in our previous work, is also evident and...
becomes even more pronounced if the dc magnetization is measured at a different field of 200, 400, 600, 800, 1000, 1200 Oe respectively. The discussed measurements will also allow us to track down the Ni\(^{2+}\)-O\(^{2-}\)-Mn\(^{4+}\) superexchange interaction and antisite ordering as shown in the M-T curves. The relaxation of thermoremanent dc magnetization (TRM) exhibits non-Debye polydisperse behavior that can be modeled using a stretched exponential function as expected for spin glass state.

2. Experimental Method

LNMO sample was prepared by post-thermal reaction of a refined powder after a solid reaction of La\(_2\)O\(_3\) (99.9% purity), NiO (75% pure Ni) and MnO\(_2\) (80% purity) from Hi-media and Alfa Aesar at 1250 \(^\circ\)C for 60 hours in air. A sintered pellet was crushed into tiny pieces and ball milled (with hard ZrO\(_2\) balls) in ethanol for 10 hours. The particle size and homogeneity affect the rate of diffusion, oxygen vacancy, cations valency and ordering during calcination. The milled powders for different times were calcined at a temperature of 1350 \(^\circ\)C for 24 hours in an air atmosphere. The obtained nanocrystalline powder samples were used for the structural and magnetic properties measurement.

The morphology of the oxide nanocrystallites was investigated by scanning electron microscopy (SEM) and elemental confirmation has been done by EDAX by Zeiss Supra equipment. The magnetic properties were measured using a SQUID magnetometer (MPMS-3, Quantum Design) by recording dc magnetization curves in zero field cool and field cool protocol (ZFC & FC) at different field values from 5-300 K. For ZFC sample was cooled in presence of zero fields to 5 K then data recorded at the different field during warming and again sample was cooled in presence of the applied magnetic field, data recorded during warming. The thermoremanent measurements were also done to determining the relaxation behavior and associated time scale.

3. Results and discussions

Figure 1 (a & b) shows the surface morphology and elemental composition, which are studied utilizing SEM. A typical mixture of spheroid and platelets like particles evident from the micrograph. The grain size found to be 0.5-1.5 \(\mu\)m. The chemical compositions of the samples were estimated through a quantitative analysis of the energy-dispersive x-ray spectroscopy, which gives the average composition within the standard deviation.

![SEM image and EDAX spectrum](image)

Figure 1. (a) SEM image confirming the morphology of LNMO consists of crystallites especially spheroid and platelet type structures, at micron length scale (b) elemental composition by EDAX.

The magnetic moments that directly associated with spin ordering and its transition in LNMO crystallites have been measured by applying an external magnetic field up to 20 kOe. Figure (2) shows the M-H loops of a sample that were acquired at a different temperature, suggesting a strong variation in saturation magnetization \((M_s)\) that arises due to field-induced reordering of the Ni\(^{2+}\) and Mn\(^{3+}/\)Mn\(^{4+}\) spins. It is evident
from the curve, as we decrease the temperature magnetization will go to increased due to very low-
temperature atoms having low kinetic energy so all the spin is only affected via a magnetic field. We attribute
this reduction in $M_s$ due to the degree of surface defects and disorders present in LNMO crystallites. The M-
H loops also suggest that materials show ferromagnetic nature at their Curie temperature (paramagnetic to
ferromagnetic transition).

Now, we focus to examine the presence of magnetic frustration and its variation as a function of applied
magnetic field in LNMO sample. The magnetic property of the LNMO sample was analyzed by M-T
measurements through ZFC-FC protocol. The magnetic results were used to investigate aggregation of
nanoparticle influence or distort the magnetic characteristics (which is directly connected to the magnetic
interaction between the nanoparticles). Figure 3 shows the ZFC/FC curves taken at various applied magnetic
fields (200, 400, 800, 1000, and 1200 Oe). The measurements also reveal that bifurcations induced by
disordered and inhomogeneous magnetization that suppressed continuously as applied magnetic field
increases and trends to a negligible at applied magnetic field 1200 Oe. The splitting point and peak
temperature shifted to the lower temperature side which indicates increment in effective energy barrier due to
enhancing the dipolar interaction. The inset of Figure 3 show the transition ($T_{C1}$) of Ni$^{2+}$-O -Mn$^{4+}$
cations ordering and the Figure 3 show the transition ($T_{C2}$) of Ni$^{3+}$ -O –Mn$^{3+}$ cations ordering. As shown in figure
both transitions are shifted with the magnetic field, which is a sign of field induced transition that useful in
magneto caloric properties. Transition temperature ($T_C$) is extremely sensitive to the volume variations
(lattice distortion) and the strain. The transfer of electron of Ni$^{2+}$ to Mn$^{4+}$ via hooping, changes the antisites
fraction and the interaction between nearest neighbor (NN) to next nearest neighbor (NNN).

The existence of antisites reduces the system's potential to develop a magnetically ordered state, and the
temperature at which the entire system transitions to an ordered state is lower than the optimal temperature
$T_C$. Besides, for an infinite system, some cluster goes into an ordered state for $T<T_C$, while the remainder of
the system remains disordered.
Here we show that the existence of spin glass like magnetic frustration in LNMO using multiple criteria, which is also demonstrated. We examine the relaxation time of glassy state by thermoremanent magnetization. The slow relaxation of thermo-remnant magnetization (TRM) below $T_g$ in spin glass and cluster spin glass systems has been a subject matter of theoretical and experimental investigations by several researchers [23-25].

A generalized theory for strongly interacting SG systems, spin clusters, time dependence TRM should exhibit a stretched exponential behaviour: $M(t) = M_o + M_0 \exp[-(t/\tau)^{1-n}]$, where $M_0$ is the intrinsic static

Figure 3. ZFC and FC dc-magnetization of LNMO under various applied magnetic fields. Inset shows the enlarge portion of magnetization across 250 K.

Figure 4: - Magnetic relaxation fitted with stretched exponent
magnetization component, $M_r$ is glassy component, $\tau$ is the characteristic relaxation time, and $n$ the exponent for the stretched exponential function [23-25]. The value of $n$ usually lies between 0 and 1, for different class of SG systems. For $n = 1$ means the system has mono-dispersive Debye like relaxation and for $n = 0$ implies absence of any relaxation. The intermediate values of $n$ in the range $0 < n < 1$ imply a non-Debye behaviour with distribution of relaxation times due to the presence of a large number of degenerate states in the frozen state. Using the stretched exponential function, we explored the slow relaxation of the TRM in the glassy phase of LNMO. The sample was cooled from 300 to 5 K in the presence of a 100 Oe external magnetic field then magnetic field has been removed and measure magnetization decay as a function of time. The results are shown in Figure 4 where the continuous line shows the best fit to the stretched exponential function with $M_0 = 0.453, M_r = .00538, \tau = (4038 \pm 94) \text{ s}$, and $n = 0.442$ for LNMO. The value of the exponent $n = 0.44$ only lies in the typical range for spin glasses and cluster spin glasses but also indicates strongly poly-dispersive non-Debye relaxation, characteristic of the strongly interacting glassy systems in general.

4. Conclusion
In summary, we investigated the low-temperature magnetic behaviour of La$_2$NiMnO$_6$ using macroscopic and microscopic probes. Analysis of dc-magnetization measurements reveals a spin glass phase have short range magnetic ordering and transition temperature $T_c (H)$, splitting temperature and peak temperature $T_f (H)$ of the ZFC $M(T)$, field-dependant transition that suggest a systemic trends. The observation of slow relaxation of thermo-remnant magnetization below the $T_g$ supports glassy phase.

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