Structural, magnetic and electrical properties of a new double-perovskite LaNaMnMoO$_6$ material

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Structural, magnetic, magnetocaloric, electrical and magnetoresistance properties of an LaNaMnMoO$_6$ powder sample have been investigated by X-ray diffraction (XRD), magnetic and electrical measurements. Our sample has been synthesized using the ceramic method. Rietveld refinements of the XRD patterns show that our sample is single phase and it crystallizes in the orthorhombic structure with Pnma space group. Magnetization versus temperature in a magnetic applied field of 0.05 T shows that our sample exhibits a paramagnetic–ferromagnetic transition with decreasing temperature. The Curie temperature $T_C$ is found to be 320 K. Arrott plots show that all our double-perovskite oxides exhibit a second-order magnetic phase transition. From the measured magnetization data of an LaNaMnMoO$_6$ sample as a function of the magnetic applied field, the associated magnetic entropy change $|\Delta S_M|$ and the relative cooling power (RCP) have been determined. In the vicinity of $T_C$, $|\Delta S_M|$ reached, in a magnetic applied field of 8 T, a maximum value of $\sim 4 \text{ J kg}^{-1} \text{ K}^{-1}$. Our sample undergoes a large magnetocaloric effect at near-room temperature. Resistivity measurements reveal the presence of an insulating-metal transition at $T_\rho = 180 \text{ K}$. A magnetoresistance of 30% has been observed at room temperature for 6 T, significantly larger than that reported for the A$_2$FeMoO$_6$ (A = Sr, Ba) double-perovskite system.

1. Introduction

Perovskite and double-perovskites oxides with general formula ABO$_3$ and A$_2$B$'$B$''$O$_6$ respectively (A is an alkaline-earth or
rare-earth metal ion; B and (B′/B″) are transition metals) are of significant interest because of the diverse properties exhibited by them. Their properties include colossal magnetoresistance [1–7], large magnetocaloric effects (MCEs) [8–12], multiferroicity [13], magnetodielectric behaviour [14,15] and large magneto-optic responses [16]. In double perovskites, rock-salt ordering of B′ and B″ ions can be achieved for large size and valence difference between B′ and B″ cations [17].

Recently, Kobayashi et al. [18] reported large, low-field, tunnelling-type magnetoresistance even at room temperature in ordered double perovskites A₂B′B″O₆. The most ordered double perovskite studied to date is Sr₂FeMoO₆ [19–23]. It is known that FeO₆ and MoO₆ octahedra are alternately ordered in a rock-salt lattice and the angle of the Fe–O–Mo chain is nearly 180°. This oxide is a half metal and shows a ferrimagnetic ordering behaviour at low temperature with a high ordering temperature \( T_C \sim 420 \text{ K} \), in which spins at the Fe\(^{3+}\)(3\(d^5\)) and Mo\(^{5+}\)(4\(d^1\)) ions is nearly aligned in the opposite direction. However, this homologous manganese double-perovskite Sr₂MnMoO₆ with Mn\(^{2+}\)(3\(d^5\)) and Mo\(^{6+}\)(4\(d^0\)) ions has been known to be either a paramagnetic (PM) or antiferromagnetic insulator [24]. Hence, the Fe- and Mn-compounds show opposite magnetic behaviours in Sr₂(Fe/Mn)MoO₆. The same result has been observed recently in an NaLaB′B″O₆ (B′ = Mn, Fe, B″ = Nb, Ta) double-perovskite system [25]. The magnetic interactions inside Mn-compounds are ferromagnetic (FM) in nature, but antiferromagnetic for Fe-compounds. The magnetism of A₂B′B″O₆ (A = Ca, Sr; B′ = Mn, Fe; B″ = Ta, Nb) would be a good reference to those NaLaB′B″O₆ compounds, and indeed, in other words, the short-range order of Na and La in A site has no/slight effect on the magnetism, in comparison to the perovskites with Ca and Sr in the A site.

The availability of four distinct cation sites in A′A″B′B″O₆ opens the door to the design of magnetic materials with novel topologies. Furthermore, compounds with this ordered double-perovskite-type show the potential for multiferroic behaviour. However, few of the compounds reported in the literature have not been thoroughly examined, and it was partially the purpose of this work to find a novel compound with useful properties.

In the present work, we have prepared, to our knowledge for the first time, and characterized a new member of the Mn-based materials A′A″MnMoO₆ family, the LaNaMnMoO₆ double-perovskite oxide. Then we report a giant magnetoresistance and moderate MCE over a broad temperature range.

2. Experimental

Powder samples of LaNaMnMoO₆ were prepared using the standard ceramic processing technique by mixing La₂O₃, Na₂CO₃, MnO₂ and MoO₃ up to 99.9% purity in the desired proportion according to the following reaction:

\[
0.5\text{La}_2\text{O}_3 + 0.5\text{Na}_2\text{CO}_3 + \text{MnO}_2 + \text{MoO}_3 \rightarrow \text{LaNaMnMoO}_6 + \delta\text{CO}_2.
\]

The starting materials were intimately mixed in an agate mortar and then heated in air at about 950°C for 72 h with intermediate regrinding. A systematic annealing at high temperature is necessary to ensure a complete reaction. In fact, the powder sample is pressed into pellets (of about 1 mm thickness) and sintered at 1100°C in air for 48 h with intermediate regrinding and repelling. Finally, these pellets were rapidly quenched at room temperature in air.

Phase purity, homogeneity and cell dimensions were determined by powder X-ray diffraction (XRD; X-ray powder SIEMENS diffractometer) at room temperature using Fe radiation. The structure refinement was carried out using the Rietveld technique [26]. The energy-dispersive X-ray analysis was performed using a scanning electron microscope (SEM) (Philips FEI QUANTA 200). DC magnetization of the sample was recorded in the Faraday balance in the temperature range 50–350 K. Magnetization at various fields was measured using a vibrating sample magnetometer in fields up to 8 T. Resistivity measurements as a function of the temperature and the applied magnetic field were carried out on dense ceramic pellets by the standard four-probe technique.

3. Results and discussion

3.1. Crystal structure

Powder XRD patterns indicate that our synthesized LaNaMnMoO₆ sample is single phase. No impurity has been detected. Structure refinements using the Rietveld method have been achieved with the FULLPROF program [27]. Figure 1a shows the XRD patterns (measured, calculated and Bragg reflection
Figure 1. Typical powder X-ray diffraction (XRD) profile (a), the fit between the observed and the calculated profiles (b), the schematic view of the orthorhombic crystal structure (c), and the SEM images (d) of the LaNaMnMoO$_6$ sample. Dots and solid line represent the observed and calculated profiles, respectively. The difference plot is drawn below the profile, and vertical bars represent the allowed reflections.

Table 1. Structural parameters obtained from the Rietveld refinement of the XRD pattern at room temperature and atomic position of the LaNaMnMoO$_6$ with Pnma space group.

| atom | Wyckoff | x    | y    | z    | Occ  | Ueq |
|------|---------|------|------|------|------|-----|
| Na   | 4c      | 0.0135 | 0.25 | −0.0041 | 0.73 | 0.15 |
| La   | 4c      | 0.0135 | 0.25 | −0.0041 | 0.27 | 0.15 |
| Mn   | 4b      | 0.00  | 0.00 | 0.5  | 0.26 | 0.0061 |
| Mo   | 4b      | 0.00  | 0.00 | 0.5  | 0.72 | 0.061 |
| O1   | 4c      | 0.4937 | 0.25 | 0.0697 | 1  | 0.0043 |
| O2   | 8d      | 0.2710 | 0.4710 | 0.7257 | 1  | 0.009 |

positions) at room temperature for LaNaMnMoO$_6$. A good fit between the observed and the calculated profiles was obtained (as indicated in figure 1b). All the peaks are indexed in the orthorhombic system with Pnma space group. The structural parameters obtained from the Rietveld refinement of the XRD pattern at room temperature and the selected bond distances with angles of the LaNaMnMoO$_6$ sample are listed in tables 1 and 2, respectively. The cell lattice sets are $\sim \sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$, where $a_p$ is the unit cell parameter of the parent perovskite aristotype. The same symmetry and the same order of magnitude for the volume of the elementary cell were obtained for its homologous oxides LaNaB'B'O$_6$. 
Table 2. Selected bond distances (Å) and angles (°) in LaNaMnMoO₆.

| NaLaMnMoO₆          |                        |                        |                        |                        |
|---------------------|------------------------|------------------------|------------------------|------------------------|
| Na/La-O (Å)         | −01/2.44660            | −01/2.27352            | −02/2.9878*2           | −02/2.63919*2          |
|                     | −02/2.80315*2          |                       |                        |                        |
| (Na/La-O) (Å)       | 2.6925                 |                       |                        |                        |
| Mn/Mo-O (Å)         | −01/1.56077*2          | −02/2.32082*2          | −02/2.10585*2          |                        |
| (Mn/Mo-O) (Å)       | 1.9958                 |                       |                        |                        |
| Mn/Mo-01-Mn/Mo (°)  | 134.4974               |                       |                        |                        |
| Mn/Mo-02-Mn/Mo (°)  | 169.2965               |                       |                        |                        |

(B′ = Mn, Fe, B'' = Nb, Ta) by Dachraoui et al. [25]. Moreover, our samples present a ratio c/a < √2 (table 1) characteristic of a cooperative Jahn–Teller deformation. The strong orthorhombic distortion of the LaNaMnMoO₆ structure is because of the cooperative coupling of the MnO₆ and MoO₆ Jahn–Teller distorted octahedral B sites.

Figure 1c shows the orthorhombic structure of LaNaMnMoO₆ projected along the (101) direction, where the (Mn/Mo)O₆ octahedra are apparent. A typical feature of the crystal structure of these double-perovskite oxides is the presence of a superlattice owing to the ordered arrangement of the cations in the oxygen octahedral nodes (B sites). The superlattice formation owing to displacement of the anions from their ideal sites may be also considered as another cause.

The SEM image of the LaNaMnMoO₆ ceramic is presented in figure 1d. A larger grain (≈3.5 µm) with well-defined boundaries, which coexist with smaller ones, was noted for the LaNaMnMoO₆ ceramic. The average crystallite size can be evaluated from the width of diffraction peaks using Scherrer formula [28]:

$$C_{XRD} = \frac{K\lambda}{\beta \cos \theta},$$

(3.1)

where $K$ is the grain shape factor, $\lambda$ is the X-ray wave length, and $\theta$ and $\beta$ are the Bragg angle and the width at half maximum of the XRD peak, respectively. The $C_{XRD}$ of LaNaMnMoO₆ powder is found to be 41.57 nm. Obviously, the grain sizes observed by SEM are several times larger than those calculated by XRD, which indicates that each grain observed by SEM is composed of several crystallites.

The ideal structure of the double perovskites is based on the adapted tolerance factor $t$ of the single perovskite [29]. In general, for double perovskites $A_2B'B''O_6$, the tolerance factor can be written as [30] follows:

$$t = \frac{(r_A) + (r_B)}{\sqrt{2} (r_O)},$$

(3.2)

where $r_A$, $r_B$ and $r_O$ are the average ionic radii of the A site, B site and oxygen, respectively. The closer to $t = 1$, the more the structure corresponds to ideal cubic. Therefore, except in rare cases, one can consider the following rule for the double-perovskite family: for $1.05 > t > 1.00$, a cubic structure is adopted within the space group; for $1.00 > t > 0.97$, the most likely structure corresponds to the I 4/m tetragonal space group and if $t < 0.97$, the compound becomes either monoclinic (P21/n) or orthorhombic [31]. Table 3 shows the evolution of the tolerance factor of our sample LaNaMnMoO₆ and of its homologous double-perovskite oxide LaNa'B'B''O₆/A₂MnMoO₆ with different symmetry. These values are in good agreement with those mentioned below. Our crystallographic data were used to also calculate this tolerance factor for LaNaMnMoO₆ such as

$$t = \frac{(A - O)}{\sqrt{2} (B - O)},$$

(3.3)

where A–O and B–O are the bond length (Na/La–O) and (Mn/Mo–O), respectively. This factor is 0.956 which is close to the Goldschmidt one (equation (3.2)).
3.2. Magnetic properties

A previous study shows that LaKMnMoO₆ compound exhibits an FM behaviour at low temperature. The Curie temperature $T_C$ is 180 K [34]. Magnetization versus temperature for the LaNaMnMoO₆ sample are plotted in figure 2. Our synthesized sample LaNaMnMoO₆ exhibits a PM to FM transition at $T_C = 320$ K with decreasing temperature. $T_C$ has been determined from the peak position of the $dM/dT$ curve, as shown in figure 2. Changing potassium content to sodium does not destroy the FM behaviour observed in LaKMnMoO₆ compound at low temperature; however, it induces an increase in the Curie temperature $T_C$ from 180 K for LaKMnMoO₆ to 320 K for LaNaMnMoO₆. This result can be explained by the decrease of the average ionic radius $\langle r_A \rangle$ of the A cation site of $A' A'' B' B'' O_6$ double-perovskite samples and/or the distortion of the octahedral MnO₆ and MoO₆ as observed in the Pr₀.7Ba₀.3−xMnO₃ perovskite sample [36]. The FM behaviour increases with decreasing the average ionic radius $\langle r_A \rangle$ from 1.500 Å with $T_C = 180$ K for the LaKMnMoO₆ double-perovskite sample to 1.375 Å with $T_C = 320$ K for LaNaMnMoO₆.

Our oxide is FM at low temperature. Such FM behaviour has not been observed in this homologous Sr₂MnMoO₆ sample [24].

FM–PM transition of LaNaMnMoO₆ was modelled using a phenomenological model given by Hamad [37]. The dependence of magnetization on the variation of temperature is written by

$$M = \frac{(M_i - M_f)}{2} \tanh(A^*T_C - T)) + B^*T + C,$$

(3.4)
Figure 3. Magnetization versus temperature for the LaNaMnMoO$_6$ sample at 50 mT magnetic field. The solid line represents modeled result and the symbol represents experimental data.

Table 4. Model parameters for the LaNaMnMoO$_6$ sample in 500 Oe applied magnetic field of $M(T)$ curve.

| $\mu_0H(T)$ | $(M_i - M_f)/2$ (emu g$^{-1}$) | $T_C$ (K) | $S_C$ (emu g$^{-1}$ K$^{-1}$) | $B$ (emu g$^{-1}$ K$^{-1}$) |
|-------------|--------------------------------|----------|----------------------------|---------------------------|
| 0.050       | 4.5980                         | 319.54   | -0.6                       | -0.00231                  |

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- $M_i/M_f$ is an initial/final value of magnetization at an FM–PM transition;
- $B$ is the magnetization sensitivity $dM/dt$ at FM state before transition;
- $A = 2*(B - S_C)/(M_i - M_f)$;
- $S_C$ is the magnetization sensitivity $dM/dT$ at Curie temperature $T_C$; and
- $C = (M_i - M_f)/2 - B*T_C$.

Fitting the $M(T)$ measurements of our powder LaNaMnMoO$_6$ by the expression (3.4) based on this phenomenological model shows a good concordance between theoretical and experimental study (figure 3). Model parameters for the LaNaMnMoO$_6$ sample under magnetic field 0.05 T are listed in table 4.

In order to confirm the FM behaviour at low temperatures of our sample, we performed magnetization versus magnetic applied field up to 8 T at several temperatures. We plot in figure 4 the $M(\mu_0H)$ curves for LaNaMnMoO$_6$ compound. The magnetization rises sharply for low magnetic applied field and then saturates for $\mu_0H$ higher than 1 T. The saturation magnetization at 10 K and 5 T, deduced from the $M(\mu_0H)$ curve, is 2.1 $\mu_B$/mole. The LaNaMnMoO$_6$ compound reaches approximately 50% of the theoretical saturation of Mn$^{3+}$ ($4 \mu_B$ for $S = 2$).

The $M(\mu_0H)$ curves can be simulated by the law-approach to saturation (figure 5) in the term [38]:

$$M = M_s* \left( 1 - \frac{a}{(\mu_0H)^n} \right),$$

(3.5)

where $0 \leq n \leq 1$, $M_s$ is the saturation of magnetization, $(a/\mu_0H^n)$ indicates the deviation of magnetization from saturation and the factor $n$ changes with respect to the origin of deviation. The $a$-factor correlates with the FM correlation length. The values of $a$, $n$ and $M_s$ are given in table 5. The large $n$ factor and the small $a$ factor for the compound should be associated with the long-range spin order of magnetic moment.

We report in figure 6, the Arrott curves $M^2$ versus $\mu_0H/M$ for the LaNaMnMoO$_6$ sample. All the $M^2$ versus $\mu_0H/M$ curves clearly show a positive slope for the complete temperature range, which means that a second-order FM to PM phase transition occurs (according to the criterion proposed by Banerjee [39]). The $T_C$ values deduced from the Arrott curves are very close to those obtained from the $M(T)$ curve ($T_C = 320$ K).
Figure 4. Magnetization $M$ versus magnetic applied field $\mu_0 H$ up to 8 T at several temperatures for LaNaMnMoO$_6$ powder.

Figure 5. The simulated curve $M(\mu_0 H)$ at 10 K for the LaNaMnMoO$_6$ sample.

Table 5. Simulated parameters of $M(\mu_0 H)$ at 10 K for the LaNaMnMoO$_6$ sample.

| LaNaMnMoO$_6$ | $M^m$s (emu g$^{-1}$) | a | n |
|---------------|------------------------|---|---|
|               | 29.743(0)              | 0.031(0) | 1.176(7) |

Table 6. Parameters fit of spontaneous magnetization and the inverse of susceptibility versus temperature.

| Bloch’s Law: $M_0 = M_s (1 - (T/T_C))^\beta$ | Curie Weiss Law: $1/\chi = -(T/T_C)+(1/C)T$ |
|-----------------------------------------------|-----------------------------------------------|
| $M_0$ (emu g$^{-1}$) | $T_C$ (K) | $\beta$ | $-(T/T_C)$ (T g emu$^{-1}$) | $1/C$ (T g emu$^{-1}$ K$^{-1}$) |
| 27.769(1) | 319.986(0) | 0.243(6) | 6.176(1) | 0.019(3) |

Figure 7a shows the temperature dependence of the spontaneous magnetization and the inverse of the magnetic susceptibility evolution versus temperature for LaNaMnMoO$_6$ compound.

We have simulated our experimental measurements of spontaneous magnetization and the inverse of susceptibility versus temperature by theoretical expression based on Bloch’s Law and Curie Weiss Law,
Figure 6. Arrott curves ($M^2$ versus $\mu_0 H/M$ isotherms) for LaNaMnMoO$_6$.

Figure 7. (a) Spontaneous magnetization and inverse of susceptibility versus $T$ for LaNaMnMoO$_6$ compound with simulation (red straight line). (b) The Ln–Ln plot used to determine the critical exponent $\beta$. (c) The Ln–Ln plot used to determine the critical exponent $\gamma$.

respectively. We have obtained a best fit between experimental and theoretical study. Parameters fit are listed in table 6.

The effective magnetic moment ($\mu_{\text{eff}}^{\text{exp}}$) can be estimated using simple Curie Weiss formula:

$$\chi = \frac{C}{T - T_C},$$

(3.6)

where $C = (\mu_{\text{eff}}^{\text{exp}})^2/8$ [40].
From the determined (C) parameter, we have deduced the experimental effective moment: \( \mu_{\text{eff}}^{\text{exp}} = 5.547 \mu_B \). Compared to the theoretical value calculated considering all the magnetic species inside the structure, both the Mn\(^{3+}\) (3d\(^4\)) and Mo\(^{5+}\) (4d\(^1\)) ions contribute to the PM behaviour and the effective magnetic moment of the compounds, \( \mu_{\text{eff}}^{\text{th}} \) is given by the following equation: \( \mu_{\text{eff}}^{\text{th}} = \sqrt{\mu_{\text{eff}}^{\text{th}}(\text{Mn}^{3+}) + \mu_{\text{eff}}^{\text{th}}(\text{Mo}^{5+})} = 5.196 \mu_B \). The observed discrepancy between both values indicates that in the PM state, the spins do not exist as individuals; they are rather assembling in small groups revealing the presence of the FM correlations in the PM phase.

The calculated value of the critical exponent \( \beta \) is obtained from fitting \( \ln(M) \) versus \( \ln(T - T_C) \) plot to a be straight line (figure 7b). Similarly, \( \ln(1/\chi) \) versus \( \ln(T - T_C) \) plot allows the determination of \( \Upsilon \) (figure 7c). The \( \beta \) and \( \Upsilon \) values are 0.237(2) and 0.850(2), respectively. Using these critical exponents, we have represented the modified Arrott plots for LaNaMnMoO\(_6\) compound, as shown in figure 8a. These values are close to those expected for the tricritical mean-field theory model (\( \beta = 0.25, \Upsilon = 1 \)) [41]. Moreover, \( \delta \) exponent can be determined by fitting the Ln–Ln plot of \( M(\mu_0H) \) curve at \( T_C \) (figure 8b,c). The determined value of \( \delta = 3.61 \) for the LaNaMnMoO\(_6\) sample is smaller than is calculated from the Widom relation [38]: \( \delta = 1 + (\Upsilon / \beta) = 4.586 \); this difference is related to the existence of the magnetic inhomogeneity (Griffiths Clusters) in the vicinity of the transition temperature.

Table 7. Parameters fit for the LaNaMnMoO\(_6\) sample in 1 T, 2 T and 3 T applied magnetic field of \( (-\Delta S_M(T)) \) curves.

| \( \mu_0H(T) \) | \( A \) (emu g\(^{-1}\) K\(^{-1}\)) | \( (M_i - M_f)/2 \) (emu g\(^{-1}\)) | \( T_C \) (K) | \( B \) (emu g\(^{-1}\) K\(^{-1}\)) |
|-----------------|-----------------|-----------------|----------|-----------------|
| 1               | 0.427(1)        | 0.200(3)        | 320.270(0) | -0.028(1)       |
| 2               | 0.420(9)        | 0.331(9)        | 320.340(0) | -0.049(5)       |
| 3               | 0.393(6)        | 0.520(8)        | 320.510(0) | -0.076(8)       |
Figure 9. (a) Magnetic entropy change versus temperature under various magnetic applied field changes. (b) The plot fit (red line) of magnetic entropy change versus temperature for 1 T, 2 T and 3 T according to the percolation model (via equation (3.8)).

3.3. Magnetocaloric characterizations

A giant field-induced entropy change is one of the important criteria for magnetocaloric materials. In fact, the isothermal measurements of magnetization allow us to determine the magnetic entropy change of the sample under an applied magnetic field, according to the classical thermodynamic theory based on Maxwell’s relations using the following equation:

$$\Delta S_M(T, H) = \sum_i \frac{M_{i+1}(T_{i+1}, H) - M_i(T_i, H)}{T_{i+1} - T_i}. \quad (3.7)$$

$M_i$ and $M_{i+1}$ are the experimental values of the magnetization measured at temperatures $T_i$ and $T_{i+1}$, respectively, under an applied magnetic field $H$. The magnetic entropy change can be measured through either the adiabatic change of temperature by the application of a magnetic field, or through the measurements of classical $M(H)$ isotherms at different temperatures [42]. In our work, we have used the second method based on magnetization measurements versus magnetic field. Figure 9a shows the behaviour of the magnetic entropy change as a function of temperature under several values of external magnetic field for our double-perovskite sample.

According to the phenomenological model [43], the magnetic entropy change of a magnetic system under adiabatic magnetic field variation from 0 to final value $H_{\text{max}}$ is available by

$$\Delta S_M = \left[-A \left(\frac{M_i - M_f}{2}\right) \text{sech}^2(A(T_C - T)) + B\right] H_{\text{max}}. \quad (3.8)$$
Using the above equation, we numerically calculated the variation of the magnetic entropy ($\Delta S_M$) depending on the temperature of our sample (figure 9b). The theoretical and experimental results are illustrated in table 7 under a magnetic field of 1 T, 2 T and 3 T. A good concordance is observed.

Under an applied magnetic field of 2 T, the absolute value of $\Delta S_M$ of the LaNaMnMoO$_6$ sample is 1.5 J kg$^{-1}$ K$^{-1}$ around $T_C$, and it reaches 3.99 J kg$^{-1}$ K$^{-1}$ under a magnetic field change of 8 T. Although the $\Delta S$ values in our compound are smaller than that observed in Gd ($\Delta S_M = 4.2$ J kg$^{-1}$ K$^{-1}$) for $\Delta H = 2$ T [41] considered as the best magnetic refrigerant, the LaNaMnMoO$_6$ sample can be considered as a potential candidate for magnetic refrigeration.

In order to confirm the important MCE of our specimens, it is interesting to consider the relative cooling power (RCP) which can be determined from the following relation:

$$RCP = -\Delta S(T, H) \times \delta_{\text{FWHM}}.$$  \hspace{1cm} (3.9)

$\delta_{\text{FWHM}}$ is full width at half maximum of $\Delta S(T)$ curve [45]. The RCP value is 41.99 J kg$^{-1}$ under an applied magnetic field of 8 T. These results are interesting, compared with those of materials considered as good for applications in magnetic refrigerators. Our sample undergoes a large MCE above room temperature.

The magnetic field dependence of the magnetic entropy change of materials with a second-order phase transition can be expressed as [46]:

$$\Delta S_M^{\text{Max}} \approx (\mu_0 H)^n,$$  \hspace{1cm} (3.10)

where $n$ depends on the magnetic state of the sample and it is obtained from the fit plot of $\Delta S_M^{\text{Max}}$ versus $\mu_0 H$ via equation (3.8) (figure 10). The value of $n$ deduced from the fitting is equal to 0.66(5) (inset of figure 10). This value is different from the calculated using the relation;

$$n = 1 + \frac{\beta - 1}{\beta + \gamma},$$  \hspace{1cm} (3.11)

[47] ($n = 0.29(8)$). This difference shows the signature of magnetic inhomogeneities in our sample.
Figure 11. (a) Temperature dependence of $\Delta C_p$ under different field variations for the LaNaMnMoO$_6$ sample. (b) Temperature dependence of calculated $\Delta C_p$ for 1, 2 and 3 T applied magnetic fields via the percolation model (equation (3.11)).

Figure 11a shows the temperature dependence of heat capacity $\Delta C_p$ under different field variations in our sample calculated from the $\Delta S_M$ data using the following relation:

$$\Delta C_p = T \frac{\partial \Delta S_M}{\partial T}. \quad (3.12)$$

$\Delta C_p$ presents positive values above $T_C$ and negative ones below $T_C$. The maximum/minimum values of $\Delta C_p$, observed at 323/317 K are 52.261/−68.839 J kg$^{-1}$ K$^{-1}$ and 78.630/−150.178 J kg$^{-1}$ K$^{-1}$ under 1 T and 2 T, respectively.

Figure 11b shows the calculated $\Delta C_p$ as a function of temperature at 1 T and 2 T, using equation (3.11) below:

$$\Delta C_p = [-TA^2(M_i - M_f)\text{sech}^2(A(T_C - T))\tanh(A(T_C - T))]H_{max}, \quad (3.13)$$

together with the corresponding experimental data for comparison. The predicted values of temperature dependence of $\Delta C_p$ under 1, 2 and 3 T magnetic field variations in the LaNaMnMoO$_6$ sample are shown in table 8.

Based on figure 11b, a good agreement is observed between experiment and calculation, showing the ability of the phenomenological model in the ordered double-perovskite single-crystal LaNaMnMoO$_6$, particularly for low magnetic fields.
Figure 12. The temperature dependence of resistivity for LaNaMnMoO$_6$ under various magnetic fields 0, 3, and 6 T. Symbols are the experimental data and red solid lines are the resistivity calculated using equation (3.14) corresponding to the parameters indicated in Table 9.

Table 9. Obtained parameters corresponding to the best fit to the equation (3.12) of the experimental data of LaNaMnMoO$_6$ at 0, 3, and 6 T.

| $\mu_0 H$ (T) | 0   | 3   | 6   |
|--------------|-----|-----|-----|
| $\rho_0$ (Ω cm) | 1120.7 | 677.48(3) | 543.36(6) |
| $\rho_2$ (Ω cm K$^2$) | 0.017(5) | 0.020(9) | 0.018(2) |
| $\rho_{45} (10^{-8} \Omega$ cm$^{45}$) | 1.052(6) | 1.009(6) | 0.942(5) |
| $U_0/K_B$ (K) | 869.97 | 873.46 | 863.52 |
| $T_C$ (K) | 321.04 | 320.08 | 323.19 |
| $\rho_3 (10^{-5} \Omega$ cm) | 0.1066(7) | 0.077(6) | 0.079(7) |
| $E_a/K_B$ (K) | 955.23 | 955.34 | 934.33 |

3.4. Electrical properties

The temperature dependence of the resistivity $\rho(T)$ without and for an applied magnetic field of 3 T and 6 T are plotted in Figure 12. The electrical resistivity of LaNaMnMoO$_6$ powder attains 1533 Ω cm at 70 K. Then it passes a maximum at $T_{\rho} = 180$ K and drops down to 1018.93 Ω cm at room temperature. The magnitude of resistivity is markedly higher than found for Ba$_2$YIrO$_6$ single crystal ($\rho(300$ K) = 40 mΩ cm) [48].

For comparison, our compound shows that it is metallic at low temperatures ($T < T_{\rho}$), whereas his homologous Sr$_2$MnMoO$_6$ sample is an insulator [24].

It should be noted here that there is a large difference between the electric ($T_{\rho} = 180$ K) and magnetic ($T_C = 320$ K) transition temperature values. The significant difference between $T_{\rho}$ and $T_C$ values may be owing to several factors: (i) smaller crystallite size of sample than that measured using XRD, (ii) influence of extrinsic contributions such as a large number of grain boundaries, and (iii) spin-polarized tunnelling between FM grains through an insulating grain boundary layer, and so on. The discrepancy of the grain size may be that the size measured using SEM is for grains consisting of more than one crystallite [49].

To understand the transport mechanism in the whole temperature range, we used the phenomenological percolation model [50,51], which is based on the phase segregation of FM and PM semiconductor regions.

Following this model, we carried out a quantitative analysis of the resistivity temperature dependence data for our sample. According to Li [51], the resistivity for the entire temperature range may then be
expressed as follows:

\[ \rho(T) = (\rho_0 + \rho_2 T^2 + \rho_4.5 T^{4.5}) \left( \frac{1}{1 + \exp(-U_0(1 - T/T_C^{\text{mod}})/k_B T)} \right) + \rho_a T \exp \left( \frac{E_a}{k_B T} \right) \left( 1 - \frac{1}{1 + \exp(-U_0(1 - T/T_C^{\text{mod}})/k_B T)} \right). \]  

(3.14)

Based on the phase segregation mechanism (percolation model), the total resistance of the system could be visualized as the sum of the resistivity of the phase separated FM–metallic and PM-insulator: \( \rho = \rho_{\text{FM}} f + \rho_{\text{PM}} (1 - f); f = (1/(1 + \exp(-U_0(1 - T/T_C^{\text{mod}})/k_B T))) \) is the volume concentration of the FM phase, and \( (1 - f) \) is the volume concentration of the PM phase.

In order to see the correlation between the magnetic and electrical properties in our sample \( \text{LaNaMnMoO}_6 \), we have fitted the experimental resistivity data (figure 12) using the above equation. It can be seen that the results calculated from equation (3.14) agree with the experimental data. Then, we found that the percolation model describes well enough the resistivity behaviour in a wide temperature range including the region of phase transition, whatever the external magnetic field. The best-fit parameters are given in table 9. The temperature dependence on the volume concentration of the FM phase \( f \) is shown in figure 13. It is clear that \( f(T) \) remains equal to 1 below the metal–semiconductor transition temperature, which confirms the strong dominance of the FM fraction in this range.
The coexistence of ferromagnetism and metallic conductivity at low temperatures provides evidence of the existence of magnetoresistance MR. Defining the MR at a given temperature as $MR = \Delta \rho / \rho = ((\rho(0) - \rho(H))/\rho(0)) \times 100$; where $\rho(H)$ and $\rho(0)$ are the resistivity in a magnetic applied field H and in a zero field, respectively. The magnetoresistance evolution versus temperature at the applied magnetic field (6 T) is illustrated in figure 14. The MR increases with decreasing temperature for the LaNaMnMoO$_6$ double-perovskite sample. It is found to be approximately 30% at room temperature and approximately 50% at 70 K at 6 T for our synthesized sample. We thus obtain a large magnetoresistance in the LaNaMnMoO$_6$ sample as that observed in the Sr$_2$FeMoO$_6$ compound by Yuan et al. [19]. This result (large MR at room temperature and at low magnetic field) is explained by the effect of grain boundaries. This phenomenon was observed in the Sr$_2$FeMoO$_6$ compound by Kobayashi et al. [18].

4. Conclusion

We have investigated structural, magnetic, magnetocaloric, electrical and magnetoresistance properties of an LaNaMnMoO$_6$ double-perovskite sample. Structure analysis reveals that our sample crystallizes according to the orthorhombic structure with Pnma space group. Magnetic measurements show a PM–FM transition with decreasing temperature. This new double perovskite exhibits an MCE and a large magnetoresistance near room temperature. A combination of both MCE and large MR in LaNaMnMoO$_6$ material makes the appropriate substance for magnetic refrigeration applications at room temperature.

Data accessibility. This article has no supporting data.

Authors’ contributions. S.M.B. carried out the experiments and designed the study, analysed the data and wrote the manuscript. W.C.-R.K. and M.M. helped to analyse the data and helped draft the manuscript. All authors gave their final approval for publication.

Competing interests. We declare we have no competing interests.

Funding. The authors acknowledge the support of the Tunisian Ministry of Higher Education and Scientific Research.

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