Thermomagnetic Correlation in La$_{0.85-x}$Bi$_x$Na$_{0.15}$MnO$_3$ Soft Ferromagnet due to Nonmagnetic Bi$^{3+}$ Substitution

Lozil Denzil Mendonca$^1$ · M. S. Murari$^2$ · Mamatha D. Daivajna$^1$

Received: 9 March 2021 / Accepted: 11 April 2021 / Published online: 9 June 2021
© The Author(s) 2021

Abstract
We report the structural, magnetic, and magnetocaloric properties of Bismuth (Bi)-substituted manganite La$_{0.85-x}$Bi$_x$Na$_{0.15}$MnO$_3$ ($x=0$, $0.1$, $0.2$, $0.25$, and $0.3$). X-ray diffraction data implicates the rhombohedral structure with $R\bar{3}c$ space group. Bi$_2$O$_3$ has helped in ensuring phase pure, densified compounds even at low sintering temperature and hence avoiding the evaporation of volatile sodium. The increase in grain size and decrease in magnetic transition temperature ($T_C$) are due to the Bi chemical activity and electronic structure. The samples have shown indirect magnetic transformation from soft ferromagnet to canted ferromagnet/antiferromagnet with Bi. Griffiths phase-like behavior in the inverse magnetic susceptibility was observed for $x=0.1$; with further increase in Bi, the samples are found to develop the antiferromagnetic competing phase. The phenomenological model was used to model the thermomagnetic behavior of all the samples. The sample with $x=0.1$ shows an increase in magnetic entropy change upon Bi substitution and the maximum of magnetic entropy change is seen at 275K emphasizing its potential in room temperature magnetic refrigeration.

Keywords Manganites · Bismuth · Canted ferromagnetism · Phenomenological model

1 Introduction

Today most of the scientific advancements with a motive of industrial application have sought the help of century old physical phenomena to reduce the green footprints. The modern environmental movement in this regard started in the late 1960s and spread throughout the globe attracting the attention towards responsible technological advancement favoring environmental protection. The physical phenomena discovered century back were revisited and exploited to have working materials which would cater the needs of present households and industries, upholding the green globe policy. Magnetocaloric effects (MCE) is one such physical phenomenon which was discovered a century ago by Weiss and Piccard in transition metal, nickel (1917) [1]. Following the discovery of MCE, the cooling (or heating) of working sample by the adiabatic demagnetization (or by application of magnetic field) was predicted by Debye (1926) [2] and has been practically demonstrated using the paramagnetic salt: gadolinium sulfate octahydrate in 1933 [3]. The scientists were able to achieve a temperature of two-tenths of kelvin which became breakthrough point for low-temperature physics and to uncover the most unexplored state of matter. This phenomenon of change of temperature in a suitable magnetic substance upon exposure to magnetic field becomes a virtue towards magnetic refrigeration (MR) and is in limelight from few decades serving as a working principle of MR. The featuring of reversible thermodynamic cycle in gadolinium with transition temperature of 295K [4], giant MCE in Gd based alloy (Gd$_5$Si$_2$Ge$_2$) [5], and the potential in competing with conventional refrigerants stimulated the substantial research activity in materials with large MCE at room temperature (RT). In fact, this escalating interest in magnetic refrigeration is owed to its efficiency over the conventional cooling and refrigeration systems. The air conditioning and refrigerators account for almost 15% of the energy utilized in household and commercial buildings due to poor efficiency of conventional vapor compressor. In comparison if conventional vapor compressor can reach about the 40% of the Carnot efficiency, the magnetic refrigerants show 60% of the Carnot efficiency. In this regard
along with the prospects of high efficiency, the magnetic refrigeration parallelsly enables miniaturization and offers low environmental impact [6, 7].

In principle, a magnetic material contains two energy reservoirs: the lattice degrees of freedom leading to usual phonon excitations and spin degrees of freedom enabling magnetic excitations. Generally, these two reservoirs are coupled by the spin–lattice coupling which ensures loss-free energy transfer within a small interval of time [8]. For a material to show promising features towards the MR, both said factors uncompromisingly must be at play. Lanthanum-based manganites are one such class of materials which offer a platform to elucidate spin-lattice coupling. Amidst the emphasis of material with respect to (w.r.t) magnetocaloric properties, rare-earth-based oxides, in particular lanthanum-based manganites, have not been versatile compared to the alloys and crystalline compounds containing rare earths. However, a quantitative compilation of materials based on their absolute value of the maximum magnetic entropy change and the transition temperature ($\Delta S^\text{max}_M$) v/s $T_C$ places this class of material in profitable spectral range [9]. The transitions are mostly at and around the vicinity of RT and the system is most chemically stable compared to any other counterparts [10]. These manganites have been extensively reviewed by M-H. Phan et al. [11] nominate them for their superior magnetocaloric properties, cheap processing cost, and chemical stability over the other potential materials. The specimens with sizeable MCE over transition temperature ranging from 100–375K are reviewed not only for various applications but also opened path for tailoring $T_C$ around RT. A specimen for RT MR should respond to a feeble magnetic field and must have transitions around the RT. The thin films and polycrystalline samples of manganites were significantly tailored in this regard over a decade optimizing the divalent content (La 1-xSr xMnO 3), having the half doped systems, doping heavy rare-earths at A-site (Tb, Dy, Gd, Ce in LaSrMnO 3), etc. In this study, A-site rare-earth cation La 3+ is substituted by a post-transition metal ion Bi 3+, as a result the carrier concentration is expected to remain same as that of parent compound (70:30, Mn 3+ to Mn 4+ ratio). Manganites are the class of material whose physical and chemical properties do not depend only on the valence state of the substituent but also on the size of it. In our case, the ionic radius of La 3+ in nine coordination is 1.216 Å and the ionic radius of the bismuth in the same

2 Materials and Methods

The La 0.85-xBixNa0.15MnO 3 ($x = 0, 0.1, 0.2, 0.25, 0.3$ viz. LBi0, LBi10, LBi20, LBi25, and LBi30 henceforth) samples were synthesized using conventional solid-state reaction with La 2O 3, Bi 2O 3, Na 2CO 3, and MnO 2 precursors of 99.9% purity, (Sigma-Aldrich) mixing them in desired portion according to the reaction Equation (1).

\[
(0.425-x)La_2O_3 + \frac{x}{2} Bi_2O_3 + 0.075Na_2CO_3 + \text{MnO}_2 \rightarrow La_{0.85-x}Bi_xNa_{0.15}MnO_3
\]

To have a large surface area for reaction and uniform mixing, isopropyl alcohol was added with precursors and resulting slurry was ground for 3h. The dry mixture was fired at 900°C in the air for 12h repeating the process thrice. The solid solution so obtained was cold-pressed in to pellets by applying pressure of 40 kg.cm -2 and is sintered at 1050°C for 24 h. The structure details were obtained using standard X-Ray Diffraction system (Bruker D8-Advance) furnished with Cu-Kα X-ray source. The data were recorded at room temperature with a scan rate of 2°/min, step size of 0.02°, and in the angle range of 20°–90°. The morphology was studied using Field Emission Scanning Electron microscope (FESEM) on Oxford Zeiss Sigma Microscope. The magnetic measurements were performed using a commercial; Quantum Design made physical property measurement system (PPMS) based Vibrating Sample Magnetometer (VSM) in magnetic fields up to 90kOe and temperature down to 3K.

3 Results and Discussions

In this study, A-site rare-earth cation La 3+ is substituted by a post-transition metal ion Bi 3+, as a result the carrier concentration is expected to remain same as that of parent compound (70:30, Mn 3+ to Mn 4+ ratio). Manganites are the class of material whose physical and chemical properties do not depend only on the valence state of the substituent but also on the size of it. In our case, the ionic radius of La 3+ in nine coordination is 1.216 Å and the ionic radius of the bismuth in the same
coordination is 1.24Å [13]. The difference being just 2% leads to a marginal increase in the average A-site cation radius, \( \langle r_A \rangle \) (about 0.5%), but a large increase in the A-site cationic variance \( \sigma^2 = \sum x(r_i - \langle r_A \rangle)^2 \) is observed (fractional change being 94% for 30% substitution. View table 1), so any change in the structural and physical property can be viewed as a result of distortion when compared to Mn\(^{3+}/Mn^{4+}\) carrier concentration variation and change in \( \langle r_A \rangle \).

### 3.1 Structure and Morphology

The specimens hold homogenous crystalline form evidenced by the sharp diffraction peaks in the XRD patterns (Fig. 1) taken at room temperature. The samples are single phase without any detectable impurity or secondary phase within the sensitivity limits of the instrument. The Rietveld refinement was performed to quantify the structural details of La\(_{0.85-x}\)Bi\(_x\)Na\(_{0.15}\)MnO\(_3\) samples. Refinement was successful under the \( R_3c \) centrosymmetric space group of hexagonal setting indicating the structure being rhombohedral (Fig. 2 with \( x=0 \) as an example). In the rhombohedral structure, La, Bi, and Na cations are situated at 6a (0, 0, ¼), the Mn cation occupies 6b (0, 0, 0), and O is at 18e (\( x, 0, 1/3 \)) special Wyckoff position and the structure is distorted one. The distortion is characterized by MnO\(_6\) octahedron rotating along the three pseudo cubic directions mimicking \( \bar{a} \bar{a} \bar{a} \) antiphase oxygen octahedral tilt system [14]. The details of structural analysis using Rietveld refinement are tabulated in Table 1. The cell parameters \( a=b \) and \( c \) obtained for LBi0 are consistent with earlier reports [15, 16]. The change in cell parameter \( a \) with increase in Bi\(^{3+}\) is marginal but the change in \( c \) and cell volume \( V \) becomes significant at samples with larger content of bismuth. Furthermore, such increase in the volume is reflected in the plot of staking of the most intense peak of the diffraction pattern (Fig. 3) where the peak is found to shift towards the lower angle (by 0.067° for LBi30 w.r.t LBi0) with improvement in the bismuth content. The observed changes are because of \( 6s^2 \) lone pair dominancy of bismuth. Bi\(^{3+}\) has a highly polarizable \( 6s^2 \) lone pair of electrons, and when this \( 6s^2 \) lone pair characteristic is dominant, bismuth has 9-fold symmetry with a corresponding ionic radius of 1.24Å. On the other hand, if the lone pair characteristic is dormant, Bi\(^{3+}\) does not distort the coordination of the system and its ionic radius falls to 1.16 Å. In large bandwidth manganites, the lone pair characteristic of bismuth has its upper hand [17] thus, the LBi\(_{0.85-x}\)Bi\(_x\)Na\(_{0.15}\)MnO\(_3\) being large bandwidth manganite, lone pair dominancy is expected with bismuth substitution. The larger ionic radius of bismuth compared to lanthanum is

| Sample code  | LBi0   | LBi10  | LBi20  | LBi25  | LBi30  |
|--------------|--------|--------|--------|--------|--------|
| \( \langle r_A \rangle \) | 1.22   | 1.22   | 1.22   | 1.24   | 1.25   |
| \( \sigma^2 \times 10^{-4} \) | 0.734  | 1.080  | 1.310  | 1.382  | 1.426  |
| Structure    | Rhombohedral crystal structure |
| Space group  | \( R_3c \) |
| \( a=b \) (in Å) | 5.502  | 5.506  | 5.507  | 5.509  | 5.512  |
| \( c \) (in Å) | 13.333 | 13.339 | 13.349 | 13.355 | 13.370 |
| Oxygen (\( x \)) positions | 0.449  | 0.451  | 0.451  | 0.449  | 0.454  |
| Cell volume \( V \) (in Å\(^3\)) | 349.502 | 350.203 | 350.643 | 350.979 | 351.818 |
| \( <\text{La-O}> \) (in Å) | 2.654  | 2.658  | 2.659  | 2.658  | 2.667  |
| \( <\text{Bi-O}> \) (in Å) | -      | 2.658  | 2.659  | 2.658  | 2.667  |
| \( <\text{Na-O}> \) (in Å) | 2.470  | 2.483  | 2.481  | 2.474  | 2.502  |
| \( <\text{Mn-O}> \) (in Å) | 1.958  | 1.958  | 1.959  | 1.961  | 1.959  |
| Mn-O-Mn (in deg) | 163.504 | 164.146 | 164.031 | 163.579 | 165.091 |
| \( t_{\text{theoretical}} \) | 0.927  | 0.928  | 0.929  | 0.929  | 0.929  |
| \( t_{\text{experimental}} \) | 0.948  | 0.950  | 0.950  | 0.948  | 0.954  |
| \( W \) | 0.094  | 0.094  | 0.094  | 0.094  | 0.094  |
| \( R_{WP} \) | 21.3   | 19.7   | 19.6   | 20.6   | 21.0   |
| \( R_{EXP} \) | 18.48  | 17.32  | 17.41  | 17.96  | 17.54  |
| \( \chi^2 \) | 1.32   | 1.30   | 1.33   | 1.32   | 1.43   |
| Bragg R-factor | 4.87   | 6.18   | 5.48   | 5.10   | 5.26   |
responsible for the increase in cell parameters and unit cell volume. The marginal variation in the cell parameters and cell volume indicates that crystallographic structure is not showing any significant changes with bismuth substitution. The said fact is confirmed by obtaining the value of $q$, which characterizes the rhombohedral distortion from cubic symmetry. The parameter $q$ is defined by $q = \frac{\sqrt{3}a_{\text{hex}}}{2a_{\text{cub}}}$ where $a_{\text{hex}} = \sqrt{2}a_c$ and $c_{\text{hex}} = 2\sqrt{3}a_c$ are lattice parameters in the hexagonal setting and $a_c$ is cell parameter in the cubic setting. Here, the parameter $q$ tends to unity as symmetry approaches to cubic [18]. The estimated value of $q$ is found to change from 0.989 to 0.990 and is technically constant through the substitution. This indicates the rhombohedral distortion is unaffected by Bi$^{3+}$ substitution. Such behavior with a highly polarizable lone pair of bismuth becomes apparent only if distortions are formed around the bismuth and are limited to the site of bismuth [19].

With dominancy of $6s^2$ lone pair of bismuth in large bandwidth manganites, it is generic that they display shortened Bi–O bond compared to La–O bond even though size of both cations is approximately same. This is arising rather due to the covalent nature of Bi–O bonds. The smaller electronegativity difference between Bi and O leads to
hybridization between $6s$ orbitals of bismuth and $2p$ orbitals of oxygen. The hybridization in turn causes local distortion, or in other words, the unique lone pair characteristic of this ion would prefer to lower the crystal symmetry. Such distortions will be reflected in Mn–O bond lengths and Mn-O-Mn bond angles. The Mn–O bond length is said to increase whereas the Mn-O-Mn angle is found to decrease with bismuth substitution, but such variation in Bi–O, Mn–O, and Mn-O-Mn is not seen in the presented structural details. Basically, the magnitude of distortion is characterized by tolerance factor $t = \frac{r_A + r_O}{\sqrt{2}(r_A + r_O)} = \frac{<A-O>-}{\sqrt{2}(<B-O>)}$, where $r_A$ and $r_B$ are average ionic radii of A-site and B-site respectively and $r_O$ is the ionic radius of oxygen. $<A-O>$ is the average bond length with respect to A-site and $<B-O>$ is the average bond length with respect to B-site of the ABO$_3$ structure. For an ideal cubic perovskite, $t$ is equal to unity. Another parameter which emphasizes the distortion is bandwidth $W$, which is defined as $W = \frac{\cos(\sigma)}{\sin(\sigma)}$ where $\omega = \frac{<Mn-O>MnO}{2}$, $d_{Mn-O}$ is $<Mn-O>$ average bond length and $<Mn-O-Mn>$ is average bond angle. As can be seen from Table 1, $t$ is found to improve, tending towards unity, whereas $W$ is found to remain the same. Contrarily, $\sigma^2$ is found to enhance with increase in $x$ contradicting the reduction in distortion suggested by increasing $t$. These ambiguous variations can be asserted by arguing that local lattice distortions happen along the line connecting Mn and O against other O ions in a plane perpendicular to their direction without causing large changes in Mn-O-Mn bond angles. These distortions can transfer from one atomic site to the other without changing the crystal structure, but they can modify the average lattice constant. If the MnO$_6$ octahedron is thought to be rigid, the Mn–O bond length will increase with an increase in lattice constant as a result of bismuth substitution. This kind of local adjustment of bond lengths and bond angles without involving large-scale cationic distortion resulting in increased lattice volume is reported in compounds of La$_{0.5-x}$Bi$_x$Ca$_{0.5}$MnO$_3$ manganites [20].

Nominal bismuth substitution in alkalai metal-based lanthanum manganites (LaAMnO$_3$) is always advantageous to obtained homogenous system with uniform grain distribution at low temperature. The solid-state synthesis of LaAMnO$_3$ must happen at low firing temperature (<1000°C) to maintain the stoichiometry as alkalai metals are volatile at high temperatures. The low temperature synthesis leads to loosely bound porous particle distribution in the compacted system. However, Bi$_2$O$_3$ is regarded as sintering aid due to its low melting point. Low melting point gives rise to large diffusivity to Bi$^{3+}$ compared to La$^{3+}$ at A-site, which is slower moving species in the solid-state solution during the firing process [21]. Bi$_2$O$_3$ thus improves the overall diffusivity of A-site and ensures the well-defined homogenous grain growth which interns contributes to the conductivity by reduced scattering at the grain boundaries. To verify the grain growth, we obtained the FE-SEM images of specific samples and are shown in Fig. 4. The micrographs provide clear evidence of grain growth where the particle distribution has evolved from porous consistency to well packed densified system. The particles are few micrometers in size and have shown size growth with increase in bismuth content. The visible porosity of the parent compound perhaps due to the low firing temperature which is inevitable as sodium carbonate is volatile at high temperature where lanthanum-based manganites usually form densified system.

### 3.2 Magnetism

The temperature-dependent magnetic susceptibility ($\chi$) of La$_{0.85}$Bi$_{0.15}$MnO$_3$ ($x=0, 0.1, 0.2, 0.25$, and $0.3$) in zero field cooled and field cooled protocol under the applied field of 1000e is shown in Fig. 5 and Fig. 6. All samples display single ferromagnetic (FM) to paramagnetic (PM) transition at a characteristic temperature called Curie temperature ($T_C$). The Curie temperatures were estimated using the discontinuity in susceptibility signified by the inflection point in $d\chi/dT$ verses $T$ curves. The drop in $T_C$ is the most remarkable change observed in magnetic property of specimen upon bismuth substitution. The parent sample possesses $T_C$ above RT which is approximately equal to 323K and is found to reduce to 113K for 30% bismuth substitution. The decrease in $T_C$ is a clear indication of weakened magnetic interaction between the magnetic spins perhaps due to hindered double exchange (DE) mechanism. In manganites, ferromagnetic behavior is appreciated by DE interaction between the magnetic spins, where hopping of an outermost $e_g$ electron of Mn-3d orbital to another via oxygen is initiated by the similar spin state in two interacting ions. Any changes in composition and/or structure leading to variation of Mn$^{3+}$-O$^2-$Mn$^{4+}$ bond angle and/or Mn$^{3+}$/Mn$^{4+}$ ionic ratio would reflect in the magnetism of the specimen. Variation of $T_C$ as a consequence of size (average cationic radius) and change in Mn ionic ratio is discussed by many researchers, but in our case, neither of the entities is changing because of similar ionic radius and ionic state of bismuth and lanthanum. As the samples are phase pure and synthesized at similar preparatory condition, only rational reasoning for observed magnetic changes can be from the electronic structure of Bi$^{3+}$ substituting the La$^{3+}$ in our samples. The electronic structure of Bi$^{3+}$ is such that its outermost orbital (6$s$) consists of a lone pair. In manganites, the oxygen 2$p_e$ electrons are shared simultaneously by manganese $3d$ and $t_{2g}$ orbitals through a bond. However, due to the large electronegativity of bismuth, its 6$s$ orbital hybridizes with O-2$p$ orbital. This hybridization through polar covalent bond would hamper the movement of $e_g$ electron from one Mn site to the other resulting in electron localization around
The formation of localizations state will reflect as distortions in bismuth-substituted samples. The parent compound is FM at low temperature due to optimal ionic density of Mn$^{4+}$ (30%) which favors the ZDE [16], but with an increase in bismuth content, the growth and rotation of FM domains become difficult due to the presence of distortion states. As a result, the magnetization process will become hard and is evident through wide transition region in $x=0.2$ (Fig. 5). Furthermore, as the samples become Bi rich ($x>0.2$), the AFM superexchange interaction enhances and sample exhibits typical canted ferromagnetic (CFM) signature (Fig. 6). The CFM is evident in samples LBi25 and LBi30 where the shape of ZFC curve is quite different compared to the pristine sample. In pristine sample, moments remain finitely constant at low temperature whereas beyond $x>0.2$, the moments are found to decrease with decrease in temperature in ZFC protocol [24, 25].

Curie-Weiss law (CW) always offers a qualitative insight on ferromagnets. As the samples display typical FM or/and CFM/AFM behavior, CW law is used to estimate the Weiss constant $\theta_p$ which signifies the onset temperature of magnetic ordering and effective paramagnetic moment $\mu_{\text{eff}}$. In Fig. 5 and Fig. 6, the left vertical axis w.r.t to temperature shows temperature dependence of inverse susceptibility ($\chi^{-1}$) for LBi0, LBi10, LBi20, LBi25, and LBi30. The $\chi^{-1}$ verses $T$
can be fitted to CW law to get $\theta_p$ and $\mu_{\text{eff}}$. According to CW law, the susceptibility ($\chi$) of ferromagnet in the paramagnetic region is inversely proportional to the excess of its temperature above Curie point. Below this point, the system ceases to be a paramagnet, which means $\chi = \frac{C}{\theta - \theta_p}$ and here, $C$ is Curie constant and $\theta_p$ is Weiss constant which is equal to Curie point $T_C$ for homogenous ferromagnet. Performing the linear fit to the $\chi^{-1}$ verses $T$ (Figs. 5 and 6) above Curie point, $\theta_p$ and $C$ were estimated and are tabulated in Table 2. Mathematically, Curie constant $C$ is defined as $C = \frac{\mu_0 e^2 J(J+1)\mu_B^2}{3k_B}$, where $\mu_0 = 10^{-7}$ $H m^{-1}$ is permeability of free space, $g$ is the Lande factor, $J = L + S$ is the total moment, $\mu_B = 9.27 \times 10^{-24}$ $J T^{-1}$ is the Bohr magneton, $k_B = 1.38 \times 10^{-23}J K^{-1}$ is Boltzmann constant, and $\mu_{\text{eff}}$ is effective paramagnetic moment [12]. The Curie constant obtained from linear fit to inverse susceptibility would give the $\mu_{\text{exp}}$, which is approximately $\sqrt{8 \times C \mu_B}$. The theoretical value of $\mu_{\text{eff}}$ ($\mu_{\text{th}}$) is obtained using the expression $\mu_{\text{th}} = \sqrt{\left(0.7 \times \mu_{\text{eff}}^3 M_{\text{Mn}^{3+}} + 0.3 \times \mu_{\text{eff}}^2 M_{\text{Mn}^{4+}}\right)}$. Here, $\mu_{\text{eff}}(M_{\text{Mn}^{3+}})=4.9 \mu_B$ and $\mu_{\text{eff}}(M_{\text{Mn}^{4+}})=3.87 \mu_B$, both $\mu_{\text{th}}$ and $\mu_{\text{exp}}$ are summarized in Table 2.

As can be seen from Table 2, the Weiss constant has presented a positive value confirming the FM interaction between the spins in all the samples. The $\mu_{\text{th}}$ is expected to be constant with increase in Bi content as bismuth is nonmagnetic ion. However, $\mu_{\text{exp}}$ is greater than $\mu_{\text{th}}$, which means the FM spin clusters are visible in the paramagnetic state of the samples. Further $\theta_p$ is found to be larger than the Curie point and the difference between the two keeps on improving indicating the development of short-range FM/AFM ordering in the PM regime. The most remarkable observation from linear fit to inverse susceptibility under the governance of CW law is the deviation from linear fit beyond LBi0. This characteristic hints the transformation of homogenous paramagnet into inhomogeneous paramagnet upon bismuth substitution. In initial concentrations viz. LBi10 the $\chi^{-1}$ deviates downwards from linear fit and then shows upturn. This deviation below certain temperature signals the onset of short-range FM/AFM correlation above $T_C$. The downturn is considered to be a typical signature of Griffiths Phase singularity. The onset temperature where the discontinuity in linear behavior appears is Griffith’s temperature, below which the FM clusters emerge in PM matrix. Furthermore, upturn deviation from linearity in inverse susceptibility fit indicates the existence of a short-range AFM state. The sample LBi20 shows the presence of both the characteristics which indicates the emergence of competing FM-DE and AFM-SE with bismuth substitution. Such competition can be thought as the basis for reduction in $T_C$. In short, though bismuth is nonmagnetic ion, its substitution in La$_{0.85}$Na$_{0.15}$MnO$_3$ ferromagnet leads to an indirect magnetic transformation.

### Table 2 Summary of Curie-Weiss analysis which gives Curie temperature, Weiss constant, Curie constant, and effective paramagnetic moment

| Sample code | $T_C$ (K) | $\theta_p$ (K) | $C$ (emu.mol$^{-1}$Oe$^{-1}$K) | $\mu_{\text{th}}$ ($\mu_B$) | $\mu_{\text{exp}}$ ($\mu_B$) |
|-------------|-----------|----------------|-----------------------------|----------------------------|-----------------------------|
| LBi0        | 323.01    | 324.35         | 4.68                        | 4.62                       | 5.85                        |
| LBi10       | 274.52    | 278.67         | 4.89                        | 4.62                       | 6.07                        |
| LBi20       | 172.30    | 248.44         | 4.27                        | 4.62                       | 5.76                        |
| LBi25       | 133.57    | 202.84         | 5.29                        | 4.62                       | 6.46                        |
| LBi30       | 113.03    | 182.31         | 5.14                        | 4.62                       | 6.43                        |

3.3 Thermomagnetic Property

In manganites, the magnetic entropy change ($\Delta S_M$) associated with magneto caloric effect (MCE) can be evaluated using magnetization measurements or heat capacity measurements. In the present investigation, we rather adopt simulation using phenomenological model to obtain the thermomagnetic parameters of prepared samples. This attempt is because the magnetization and heat capacity measurement look unreasonable as samples exhibit transitions at low temperature upon bismuth doping except, LBi0 and LBi10. The shortcomings of the model have been brought out by R. Zouari et al. [26] where the author concludes lack of rigorous estimate of MCE in ferromagnetic material by the model. However, many researchers have successfully exploited the model and validated the agreement between the experimental results and simulation performed under the governance of the model. The model was proposed by M.A. Hamad [27], according to which magnetization of a ferromagnetic material varies with temperature in accordance with Equation 2.

$$M(T) = \left\{ \left( \frac{M_i - M_f}{2} \right) \times \tanh(A \times (T - T_C)) \right\} + BT + C \quad (2)$$

Here, $M_i$ is the value of magnetization in the FM state, $M_f$ is the magnetization in post-transition PM state, $T_C$ is the Curie temperature, and $A$, $B$, $C$ are constants for a given material. The relationship between the constants, the magnetic sensitivities ($dM/dT$), and magnetization ($M$) in governance with the magnetic transition is given by $A = \frac{2 \times (B - S_C)}{(M_i - M_f)}$ and $C = \frac{(M_i + M_f)}{2} - BT_C$; here, $B$ is the magnetization sensitivity ($\frac{dM}{dT}$) prior transition, and $S_C$ is the magnetization sensitivity at $T_C$.

The model assumes complete alignment of electronic spins at low temperature. As the temperature is raised, the magnetization starts to fall slowly after certain temperature and the fall becomes abrupt at a critically defined temperature viz. $T_C$. 
Above \( T_C \), the specimen compromises with its FM state because of the increased thermal agitation and the FM state is no longer a stable state with respect to thermodynamic considerations. These assumptions uniquely define \( T_C \) as point of discontinuity in \( M-T \) variation. Hence, differentiating (2)

\[
\frac{dM}{dT} = \left[-A \times \left( \frac{M_r - M_f}{2} \right) \times \text{sech}^2(A \times (T_c-T)) \right] + B \tag{3}
\]

A suitable ferromagnet when exposed to external magnetic field exhibits temperature changes in it. This magneto-thermodynamic relationship is established through entropy change in the specimen. According to thermodynamics, the change in magnetic entropy caused by the varying external magnetic field (varying from 0 to some \( H_M \)) is given by Equation 4.

\[
\Delta S_M = \int_{H_M}^{H} \left( \frac{\partial S}{\partial H} \right)_T \ dH \tag{4}
\]

According to Maxwell’s thermodynamic relation,

\[
\left( \frac{\partial M}{\partial T} \right)_H = \left( \frac{\partial S}{\partial H} \right)_T \tag{5}
\]

which implies

\[
\Delta S_M = \int_{H_M}^{H} \left( \frac{\partial M}{\partial T} \right)_H \ dH \tag{6}
\]

Substituting Equation (3) in (6) enables one to find the magnetic entropy change, i.e.,

\[
\Delta S_M = \int_{H_M}^{H} \left[ \left\{ -A \times \left( \frac{M_r - M_f}{2} \right) \times \text{sech}^2(A \times (T_c-T)) \right\} + B \right] \ dH
\]

\[
\Delta S_M = \left[ \left\{ -A \times \left( \frac{M_r - M_f}{2} \right) \times \text{sech}^2(A \times (T_c-T)) \right\} + B \right] \times H_M \tag{7}
\]

The magnetic entropy is ideally assumed to be zero when the specimen is in its FM state, it grows and becomes maximum in the PM regime. In the path of such transition, there exists a point in temperature scale where the change in entropy is maximum, and according to Equation (7), it happens when \( T = T_C \). If the maximum of the change in entropy is represented as \( \Delta S_{M}^{\text{max}} \), then

\[
\Delta S_{M}^{\text{max}} = \left\{ -A \times \left( \frac{M_r - M_f}{2} \right) \right\} + B \times H_M = S_{C} \times H_M \tag{8}
\]

So, for a sample to possess large value of magnetic entropy change, it must have a large magnetic moment and rapid change in magnetization at \( T_C \). The extent of the entropy change is a significant attribute of magnetic specimen. A physical quantity which evaluates the spread of entropy change is magnetic cooling efficiency or also called the relative cooling power (RCP). RCP is the product of maximum entropy change and full width at half maximum of its independent variable (\( \delta T_{FWHM} \)). The \( \delta T_{FWHM} \) is nothing but the difference in the temperatures (\( T_2-T_1 \)) at which the distribution of \( \Delta S_M \) is half of its maximum value (\( \Delta S_{M}^{\text{max}}/2 \)). The substitution of temperature as \( T^* \) at which \( \Delta S_M = \Delta S_{M}^{\text{max}}/2 \) in Equation (7) gives \( T^* \)

\[
AT_C \pm \text{cosh}^{-1} \left( \frac{2A (M_r-M_f)}{A (M_r-M_f) + 2B} \right)
\]

\[
T^* = \frac{AT_C + \text{cosh}^{-1} \left( \frac{2A (M_r-M_f)}{A (M_r-M_f) + 2B} \right)}{A} \tag{9}
\]

So the \( \delta T_{FWHM} = T_2-T_1 = \frac{AT_C + \text{cosh}^{-1} \left( \frac{2A (M_r-M_f)}{A (M_r-M_f) + 2B} \right)}{A} - AT_C \pm \text{cosh}^{-1} \left( \frac{2A (M_r-M_f)}{A (M_r-M_f) + 2B} \right) \]

\[
\delta T_{FWHM} = 2 \left[ A \times \text{cosh}^{-1} \left( \frac{2A (M_r-M_f)}{A (M_r-M_f) + 2B} \right) \right] \tag{10}
\]

This clearly indicates the \( \delta T_{FWHM} \) is function of \( A \) and \( (M_r - M_f) \) and decreases with the increasing in former (magnetization sensitivity at \( T_C \)) and decrease the latter.

RCP which is \( -\Delta S_{M}^{\text{max}} \times \delta T_{FWHM} \) is given by

\[
\left\{ \left\{ -A \times \left( \frac{M_r - M_f}{2} \right) \right\} + B \right\} \times H_M \times \frac{2A}{A \times \text{cosh}^{-1} \left( \frac{2A (M_r-M_f)}{A (M_r-M_f) + 2B} \right)}
\]

\[
= RCP = \left( M_r-M_f \times 2 \right) \times \frac{B}{A} \times H_M \times \text{cosh}^{-1} \left( \frac{2A (M_r-M_f)}{A (M_r-M_f) + 2B} \right) \tag{11}
\]

The magnetization-related changes in specific heat are given by \( \Delta C_p(T, H) = T \times \frac{\partial \Delta S_M}{\partial T} \). As \( \Delta S_M \) shows the Gaussian-like distribution, \( \Delta C_P \) changes sharply from negative to positive at \( T_C \), \( \Delta C_p<0 \) for \( T<T_C \) and \( \Delta C_p>0 \) for \( T>T_C \).

Differentiating Equation (7)

\[
\frac{d\Delta S_M}{dT} = -2A^2 \times \left( \frac{M_r-M_f}{2} \right) \times \text{sech}^2\left(A \times (T_c-T)\right) \times \text{tanh}\left(A \times (T_c-T)\right) \times H_M
\]

which implies

\[
\Delta C_P = -2TA^2 \times \left( \frac{M_r-M_f}{2} \right) \times \text{sech}^2\left(A \times (T_c-T)\right) \times \text{tanh}\left(A \times (T_c-T)\right) \times H_M \tag{12}
\]

To obtain the thermomagnetic physical quantities viz. \( \Delta S_M \), \( \delta T_{FWHM} \), RCP, and \( \Delta C_P \), we simulated the variation of magnetization and magnetic sensitivity as a function of temperature using Equation 2 and 3, respectively. The rough
estimates of model parameters $M_i$, $M_f$, $B$, $S_C$, and $T_C$ are obtained from experimental data as indicated in Fig. 7. The results of the simulation are summarized in Table 3. The FC protocol of measurement was used for simulation to mask the demagnetization and domain wall effects. Figure 8 portrays temperature variation of $M$ and $dM/dT$, where open symbols express experimental data, and the solid line indicates theoretical fit. The theoretical line following the variation of experimental data emphasizes good agreement between the two.

Figure 9 shows the modeled magnetic entropy change w.r.t temperature. Clearly, the change is maximum at $T_C$ and falls on either side of $T_C$. The $-\Delta S_M$ is found to be positive in the entire temperature region which implies the release of heat in the process of magnetization and confirms the ferromagnetic nature of the specimens [28, 29]. The magnitude of maximum entropy change presents a remarkable feature upon Bi 3+ substitution. $|\Delta S_{M}^{\text{max}}|$ increases drastically from LBi0 to LBi10 and and falls with further substitution of Bi 3+. The distribution of prominent change of entropy which is characterized by full width at half maximum of $\Delta S_M$ decreases from pristine to LBi10, then exhibits a dramatic increase at LBi20 and then drops with further enrichment of bismuth in the samples. In perovskite manganites with nonmagnetic lanthanum at A-site, the nature of magnetism is basically established by manganese ions at B-site. With increased substitution of lanthanum by alkali metals or alkaline earth metals, there occurs generation of Mn 3+ and Mn 4+ ions leading to different charge species. The exchange interaction between these ions may result in anti-ferromagnetic nature or ferromagnetic nature depending on ions involved in the exchange process. The ions of the same species (Mn 3+-O2--Mn3+ or Mn4+-O2--Mn4+) may couple via intervening oxygen to give AFM and the interspecies exchange (Mn3+-O2--Mn4+) would result in FM nature. Furthermore, many factors influence these exchange interactions, but the prominent ones are, ion concentration signified by Mn 3+/Mn 4+ ratio and structure factors characterized by Mn–O bond length and Mn-O-Mn bond angle [30]. In our study, all cations (La 3+, Bi 3+, Na+) at A-site are nonmagnetic and substitution of ions with same valance state is in force. On the other hand, the ionic radii of La 3+, Na+, and Bi 3+ are nearly identical; as a result, neither the structural changes nor the disturbance to charge balance (Mn 3+/Mn 4+) is expected. With this immutable front of specimens, there has been substantial changes in the magnetic behavior and has been reflected in magnetocaloric response. The question arises on what causes the enrichment in the magnetic entropy change at low concentration of Bi 3+ despite nonmagnetic behavior of bismuth and its close proximities to lanthanum both w.r.t valency and size.

In manganites, the magnetic transition viz. AFM-FM and FM-PM are responsible for the onset of magnetic entropy change and are discussed strongly based on Zener double exchange and superexchange interactions [12]. In addition to spin alignments and mutilation during transitions, the large entropy changes in magnetic systems like manganites can originate from spin-lattice coupling during magnetic ordering process [31]. Seemingly, in our case, we attribute the variation in $|\Delta S_{M}^{\text{max}}|$ to two factors like that of magnetic ordering and spin-lattice coupling during the magnetic ordering. The two factors are (i) an increase in the crystallites size and grain growth and (ii) weakened double exchange magnetic interaction due to enriched Bi 3+ content. The increased crystallinity, grain size, and the consequent reduction in the grain boundaries ensure the easy alignment of the magnetic spins in intra and interdomains leading to sharp FM-PM transitions in

| $X$ | $M_i$ (emu.g$^{-1}$) | $M_f$ (emu.g$^{-1}$) | $B$ (emu.g$^{-1}$K$^{-1}$) | $S_C$ (emu.g$^{-1}$K$^{-1}$) | $T_C$ (K) |
|-----|----------------|----------------|----------------|----------------|---------|
| 0   | 4.865          | 0.122          | $-0.001$       | $-0.504$       | 322.968 |
| 0.1 | 14.19          | 0.352          | $-0.005$       | $-1.629$       | 275.045 |
| 0.2 | 18.40          | 0.610          | $-0.002$       | $-0.406$       | 179.036 |
| 0.25| 9.666          | 0.451          | $-0.003$       | $-0.398$       | 136.596 |
| 0.3 | 5.863          | 0.145          | $-0.0008$      | $-0.329$       | 114.221 |

**Thermomagnetic parameters**

| $X$ | $A$ (K$^{-1}$) | $|\Delta S_{M}^{\text{max}}|$ ($\times10^{-3}$ J.kg$^{-1}$K$^{-1}$) | $\delta T_{\text{FWHM}}$ (K) | RCP ($\times10^{-3}$ J.kg$^{-1}$K$^{-1}$) | $\Delta C_P^{\text{min}}$ (J.kg$^{-1}$K$^{-1}$) | $\Delta C_P^{\text{max}}$ (J.kg$^{-1}$K$^{-1}$) |
|-----|--------------|-------------------------------------|----------------|----------------|----------------|----------------|
| 0   | 0.212        | 5                                   | 8.331          | 42             | $-0.26$        | 0.27           |
| 0.1 | 0.235        | 16                                  | 7.533          | 123            | $-0.79$        | 0.81           |
| 0.2 | 0.045        | 4                                   | 39.02          | 159            | $-0.02$        | 0.03           |
| 0.25| 0.086        | 4                                   | 20.66          | 82             | $-0.03$        | 0.04           |
| 0.3 | 0.115        | 3                                   | 15.39          | 51             | $-0.03$        | 0.03           |
LBi10. As the magnetic entropy change depends majorly on magnetic moment and magnetic sensitivity, though bismuth content tends to reduce the moment, it parallely contributes to the significant increase in magnetic sensitivity ($S_C$ for $x=0.1$, Table 3) making the FM-PM transition rather abrupt than gradual. Moreover, the nominal bismuth content aids in effective spin-lattice coupling during the magnetic ordering process evidenced by slight increase in the bond angle (Table 1). However, such behavior might be reflected in the LBi0 when compared to LBi10, but the smaller crystallite size and the large grain boundary density may hinder the easy magnetization of the system around the transition. On contrary, the enrichment of bismuth beyond $x=0.1$ increases the local distortions weakening the DE interaction between the magnetic ions. This directly affects the net magnetization with continuous reduction in it. The combined effect of grain growth and reduction in magnetization is in force in LBi10 so that it displays improved magnetic entropy change when compared to Bi deficient and Bi rich samples. The $\Delta S_M$ in LBi10 is maximum near to room temperature and is maximum among other all concentrations make it assessable toward the RT magnetic refrigerant.
Figure 10 shows temperature dependence of specific heat under the low field of 1000e for all the samples. The $\Delta C_P$ undergoes an abrupt swing from positive to negative around $T_C$ with positive values above $T_C$ and negative values below $T_C$. The maximum and minimum value of $\Delta C_P$ are observed at 325K and 320 K in LBi0, whereas these temperatures for LBi10, LBi20, LBi25, and LBi30 are 277/272, 193/164, 143/129, and 119/107 respectively. The sum of two parts is the magnetic contribution to the total specific heat which affects the cooling or heating power of a magnetic refrigerator [32]. Another important factor describing the applicability of a particular magnetic system towards the magnetic refrigeration is RCP. Table 3 emphasizes the increase of RCP with bismuth content up to LBi20, and then, it falls off at higher bismuth content. As RCP is the product of $-\Delta S_M$ and $\partial T_{FWHM}$, the broad spread of $\Delta S_M$ caused the large RCP in LBi20 sample. Many researchers report that increase $\partial T_{FWHM}$ with bismuth doping is due to disorder and/or possibly some phase separation at the microstructure level or in other words presence of FM clusters in PM regime.

4 Conclusion

In conclusion, even though the lone pair significant bismuth is substituted to A-site of perovskite structure, unobtrusive changes in crystal parameters and consequently dormant changes in bond angles are observed. This is due to the similar ionic size of bismuth and lanthanum as well as distortions being site-specific to bismuth. Bi$_2$O$_3$ as a precursor has not only facilitated the nonmagnetic bismuth ion but also has improved overall density of the samples. The samples have formed into homogenous composition even at low sintering temperature due to the high diffusivity of bismuth, and in turn, it has affected positively in protecting volatile sodium from evaporation. The nonmagnetic ion has caused visible changes in the magnetic ground state of samples. The Curie temperature has dropped drastically at bismuth rich end because of the local distortion created at the site of bismuth. These distortions localize the electrons and in turn appreciating the canting of spins or anti-ferromagnetism in the system. A nominal concentration of bismuth ($x=0.1$) has helped in improving the magnetocaloric property due to the bismuth assisted grain growth and weakened DE magnetic interaction. This improves the magnetic sensitivity and hence magnetic entropy change, thus making the sample a potential candidate for magnetic refrigeration. The sample with $x=0.2$ has shown large RCP value due to disorder and/or possibly some phase separation at the microstructure level.

Acknowledgements We are thankful to UGC-DAE Consortium for Scientific Research, Mumbai Centre, India for funding the study under the grant: UDCSR/MUM/CD/CRS-M-240/2017/1008. Authors are thankful to Dr. Mukul Gupta (UGC-DAE-CSIR, Indore) for XRD measurements, Dr. P.D Babu (UGC-DAE-CSIR, Mumbai) and Dr. A Sundaressan (JNCSR, Bengaluru) for their extended help in magnetization measurements.

Funding Open access funding provided by Manipal Academy of Higher Education, Manipal.

Declarations

Competing Interests The authors declare no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. Weiss, P., Piccard, A.: C. R. Hebdomadaires des Seances de l’Academie des Sciences. 166, 352–354 (1918)
2. Debye, P.: Ann. Phys. 386,(25), 1154–1160 (1926)
3. Giauque, W.F., MacDougall, D.P.: J. Am. Chem. Soc. 57(7), 1175–1185 (1935)
4. Urbain, G., Weiss, P., Trombe, F.: C. R. 200, 2132–2134 (1935)
5. Pecharsky, V.K., Karl Jr., A., Gschneidner: Phys. Rev. Lett. 78(23), 4494 (1997)
6. Smith, A., Bahl, C.R., Bjerk, R., Engelbrecht, K., Nielsen, K.K., Pryds, N.: Adv. Energy Mater. 2(11), 1288–1318 (2012)
7. Lyubina, J.: J. Phys. D. Appl. Phys. 50(5), 053002 (2017)
8. Brück, E.: J. Phys. D. Appl. Phys. 38(23), R381 (2005)
9. Franco, V., Blázquez, J.S., Ingale, B., Conde, A.: Annu. Rev. Mater. Res. 42 (2012)
10. Franco, V., Blázquez, J.S., Ingale, B., Conde, A.: Appl. Phys. Lett. 89(22), 225121 (2006)
11. Phan, M.-H., Seong-Cho, Y.: J. Magn. Magn. Mater. 308(2), 325–340 (2007)
12. Dhahri, A., Dhahri, E., Hili, E.K.: RSC Adv. 9(10), 5530–5539 (2019)
13. Shannon, Robert, D.: Acta Crystallogr. Sect. A: Cryst. Phys., Differ. Theor. Gen. Crystallogr. 32(5), 751–767 (1976)
14. Glazer, A.M.: Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry. 28(11), 3384–3392 (1972)
15. Dodiya, N., Varshney, D.: J. Alloys Compd. 718, 718–728 (2019)
16. Yadav, K., Singh, H.K., Varma, G.D.: Phys. B Condens. Matter. 407(8), 1244–1249 (2012)
20. Wang, X., Cui, Q., Pan, Y., Zou, G.: J. Alloys Compd. 354(1-2), 91–94 (2003)
21. Chakraborty, A., Maiti, H.S.: Ceram. Int. 25(2), 115–123 (1996)
22. Xia, Z.C., Xiao, L.X., Fang, C.H., Liu, G., Dong, B., Liu, D.W., Cheng, L., Liu, L., Liu, S., Doyananda, D., Tang, C.Q., Yuan, S.L.: J. Magn. Magn. Mater. 297(1), 1–6 (2006)
23. Mendonca, L.D., D’Souza, A., Murari, M.S., Daivajna, M.D.: J. Supercond. Nov. Magn. 33, 1809–1819 (2020)
24. Hiroto, T., Kazuyasu, T., Tamura, R.: J. Phys. Condens. Matter. 26(21), 216004 (2014)
25. Gencer, H., Atalay, S.: Int. J. Mod. Phys. B. 19(27), 4115–4123 (2005)
26. Zouari, R., Chehaidar, A.: Phase Transit. 90(2), 167–174 (2017)
27. Hamad, M.-A.: Phase Transit. 85(1-2), 106–112 (2012)
28. Kharrat, A.B.J., Hlil, E.K., Boujelben, W.: J. Alloys Compd. 739, 101–113 (2018)
29. Choura-Maatar, S., M’nassri, R., Cheikhrouhou-Koubaa, W., Koubaa, M., Cheikhrouhou, A., Hlil, E.K.: RSC Adv. 7(79), 50347–50357 (2017)
30. Gencer, H., Atalay, S., Adiguzel, H.I., Kolat, V.S.: Phys. B Condens. Matter. 357(3-4), 326–333 (2005)
31. Guo, Z.B., Du, Y.W., Zhu, J.S., Huang, H., Ding, W.P., Feng, D.: Phys. Rev. Lett. 78(6), 1142 (1997)
32. Zhang, X.X., Wen, G.H., Wang, F.W., Wang, W.H., Yu, C.H., Wu, G.H.: Appl. Phys. Lett. 77(19), 3072–3074 (2000)

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.