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

Lozil Denzil Mendonca¹ · M. S. Murari² · Mamatha D. Daivajna¹

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Abstract

We report the structural, magnetic, and magnetocaloric properties of Bismuth (Bi)-substituted manganite $\text{La}_{0.85-x}\text{Bi}_x\text{Na}_{0.15}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.25$, and 0.3). X-ray diffraction data implicates the rhombohedral structure with $R\bar{3}c$ space group. Bi_2O_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 ($\text{Gd}_5\text{Si}_2\text{Ge}_2$) [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

✉ Mamatha D. Daivajna
mamata.shet@yahoo.com

¹ Department of Physics, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka 576104, India

² DST PURSE Program, Mangalore University, Mangalagangothri, Mangalore, Karnataka 574199, India

along with the prospects of high efficiency, the magnetic refrigeration parallelly 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 ($\Delta S_M^{\max}$ 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 small and large-scale MR due to 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 ($\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $x=0$ to 0.4), varying the composition of two or more divalent ions in a suitable magnetic system ($\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$, $x=0$ to 0.25), having the half doped systems, doping heavy rare-earths at A-site (Tb, Dy, Gd, Ce in LaCaMnO_3), having mixed valent manganites of post lanthanum elements, doping the Mn-site with other transition metals (Ni, Cu, Cr doping at Mn site in LaSrMnO_3), etc. In any case, there has been a compromise either with room temperature transitions or with magnitude of $\Delta S_M^{\max}$ and cooling efficiency (RCP). Monovalent (Na, K) doped lanthanum manganite system has not been appreciated concerning MR, due to their poor $\Delta S_M^{\max}$ values. However, their transitions are just above the room temperature, and tuning T_C without degrading the properties is achievable. In this regard, the bismuth-substituted system $\text{La}_{0.67-x}\text{Bi}_x\text{Ca}_{0.33}\text{MnO}_3$, $x=0.05$ has motivated showing reduction in the T_C upon bismuth substitution and improvement in the $\Delta S_M^{\max}$ at low field. Recently Dhahri et al. [12] have

exploited such feature of Bi^{3+} substitution in nanostructures of $\text{La}_{0.67-x}\text{Bi}_x\text{Ba}_{0.33}\text{MnO}_3$ with improved $\Delta S_M^{\max}$ near RT.

With this motivation, we synthesized the polycrystalline samples of $\text{La}_{0.85-x}\text{Bi}_x\text{Na}_{0.15}\text{MnO}_3$ with $x = 0, 0.1, 0.2, 0.25$, and 0.3 and report their structural, magnetic, and magnetocaloric properties of the prepared samples.

2 Materials and Methods

The $\text{La}_{0.85-x}\text{Bi}_x\text{Na}_{0.15}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.25, 0.3$ 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).

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-K α 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 1.24 Å [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 $\sigma^2 = \sum x_i r_i^2 - \langle r_A \rangle^2$ 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 $\text{Mn}^{3+}/\text{Mn}^{4+}$ 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 phasic 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 $\text{La}_{0.85-x}\text{Bi}_x\text{Na}_{0.15}\text{MnO}_3$ samples. Refinement was successful under the $R\bar{3}c$ 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, $\frac{1}{4}$), the Mn cation occupies 6b (0, 0, 0), and O is at 18e (x , 0, $\frac{1}{4}$) 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 dominance 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 1.24 Å. 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 $\text{La}_{0.85}\text{Na}_{0.15}\text{MnO}_3$ being large bandwidth manganite, lone pair dominance is expected with bismuth substitution. The larger ionic radius of bismuth compared to lanthanum is

Table 1 Values of average ionic radius ($\langle r_A \rangle$), size mismatch (σ^2) at A-site and Rietveld refined parameters: lattice parameters, cell volume, R-factors, and χ^2 for $\text{La}_{0.85-x}\text{Bi}_x\text{Na}_{0.15}\text{MnO}_3$ ($x = 0, 0.05, 0.10, 0.20, 0.25$, and 0.30) manganites

Sample code	LBi0	LBi10	LBi20	LBi25	LBi30
$\langle r_A \rangle$	1.220	1.222	1.224	1.226	1.227
$\sigma^2 (\times 10^{-4})$	0.734	1.080	1.310	1.382	1.426
Structure	Rhombohedral crystal structure				
Space group	$R\bar{3}c$				
$a=b$ (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
q	0.989	0.989	0.990	0.990	0.990
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
$\langle \text{La-O} \rangle$ (in Å)	2.654	2.658	2.659	2.658	2.667
$\langle \text{Bi-O} \rangle$ (in Å)	-	2.658	2.659	2.658	2.667
$\langle \text{Na-O} \rangle$ (in Å)	2.470	2.483	2.481	2.474	2.502
$\langle \text{Mn-O} \rangle$ (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	20.1	20.6	21.0
R_{EXP}	18.48	17.32	17.41	17.96	17.54
χ^2	1.32	1.30	1.33	1.32	1.43
Bragg R-factor	4.87	6.18	5.48	5.10	5.26

Fig. 1 XRD pattern of $\text{La}_{0.85-x}\text{Bi}_x\text{Na}_{0.15}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.25$, and 0.3)

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

Fig. 2 Rietveld refinement on XRD pattern of LBi0 sample

Fig. 3 Stacking of most intense peak of XRD pattern. The peaks show shift towards the lower angles

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 $q = \frac{\left(\frac{c_{\text{hex}}}{2\sqrt{3}}\right)}{\left(\frac{a_{\text{hex}}}{\sqrt{2}}\right)}$ 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 dominance 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 $t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} = \frac{\langle A-O \rangle}{\sqrt{2}\langle B-O \rangle}$; here, 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. $\langle A-O \rangle$ is the average bond length with respect to A-site and $\langle B-O \rangle$ 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 $W \propto \frac{\cos(w)}{d_{Mn-O}^{3.5}}$ where $w = \frac{\pi - \langle Mn-O-Mn \rangle}{2}$, d_{Mn-O} is $\langle Mn-O \rangle$ average bond length and $\langle Mn-O-Mn \rangle$ 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, σ^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 diffusion resulting in increased lattice volume is reported in compounds of $La_{0.5-x}Bi_xCa_{0.5}MnO_3$ manganites [20].

Nominal bismuth substitution in alkali metal-based lanthanum manganites ($LaMnO_3$) is always advantageous to obtain homogenous system with uniform grain distribution at low temperature. The solid-state synthesis of $LaMnO_3$ must happen at low firing temperature ($<1000^\circ\text{C}$) to maintain the stoichiometry as alkali metals are volatile at high temperatures. The low temperature synthesis leads to loosely bound porous particle distribution in the compacted system. However, Bi_2O_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_2O_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 (χ) of $La_{0.85-x}Bi_xNa_{0.15}MnO_3$ ($x=0, 0.1, 0.2, 0.25$, and 0.3) in zero field cooled and field cooled protocol under the applied field of 100 Oe 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 $d\chi/dT$ versus 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 323 K and is found to reduce to 113 K 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 ($6s$) consists of a lone pair. In manganites, the oxygen $2p_\pi$ electrons are shared simultaneously by manganese $3d t_{2g}$ orbitals through π bond. However, due to the large electronegativity of bismuth, its $6s$ orbital hybridizes with $O-2p$ 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

Fig. 4 SEM images of **a** LBi0, **b** LBi25, and **c** LBi30 at $\times 10,000$ magnification

Bi^{3+} ion [22, 23]. 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 θ_P which signifies the onset temperature of magnetic ordering and effective paramagnetic moment μ_{eff} . In Fig. 5 and Fig. 6, the left vertical axis w.r.t to temperature shows temperature dependence of inverse susceptibility (χ^{-1}) for LBi0, LBi10, LBi20, LBi25, and LBi30. The χ^{-1} versus T

Fig. 5 variation of susceptibility (χ), Inverse susceptibility (χ^{-1}), and linear fit to inverse susceptibility with temperature of LBi0, LBi10, and LBi20

Fig. 6 Variation of susceptibility (χ), inverse susceptibility (χ^{-1}), and linear fit to inverse susceptibility with temperature of LBi25 and LBi30 and first order derivative of χ vs T ($d\chi/dT$)

can be fitted to CW law to get θ_P and μ_{eff} . According to CW law, the susceptibility (χ) 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 $\chi = \frac{C}{T - \theta_P}$, and here, C is Curie constant and θ_P is Weiss constant which is equal to Curie point T_C for homogenous ferromagnet. Performing the linear fit to the χ^{-1} versus T (Figs. 5 and 6) above Curie point, θ_P and C were estimated and are tabulated in Table 2. Mathematically, Curie constant C is defined as $C = \frac{\mu_0 [g^2 J(J+1) \mu_B^2]}{3k_B} = \frac{\mu_0}{3k_B} \mu_{\text{eff}}^2$, where $\mu_0 = 10^{-7} \text{ H m}^{-1}$ is permeability of free space, g is the Lande factor, $J = L + S$ is the total moment, $\mu_B = 9.27 \times 10^{-24} \text{ J T}^{-1}$ is the Bohr magneton, $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is Boltzmann constant, and μ_{eff} is effective paramagnetic moment [12]. The Curie constant obtained from linear fit to inverse susceptibility where χ in the units of $\text{emu.mol}^{-1} \text{ Oe}^{-1}$ would give the $\mu_{\text{eff}}^{\text{exp}}$, which is approximately $\sqrt{8 \times C} \mu_B$. The theoretical value of μ_{eff} ($\mu_{\text{eff}}^{\text{th}}$) is obtained using the expression $\mu_{\text{eff}}^{\text{th}} = \sqrt{(0.7 \times \mu_{\text{eff}}^2)_{\text{Mn}^{3+}} + (0.3 \times \mu_{\text{eff}}^2)_{\text{Mn}^{4+}}}$. Here, $\mu_{\text{eff}}(\text{Mn}^{3+}) = 4.9 \mu_B$ and $\mu_{\text{eff}}(\text{Mn}^{4+}) = 3.87 \mu_B$, both $\mu_{\text{eff}}^{\text{th}}$ and $\mu_{\text{eff}}^{\text{exp}}$ 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 $\mu_{\text{eff}}^{\text{th}}$ is expected to be constant with increase in Bi content as bismuth is nonmagnetic ion. However, $\mu_{\text{eff}}^{\text{exp}}$ is greater than $\mu_{\text{eff}}^{\text{th}}$ which means the FM spin clusters are visible in the paramagnetic state of the samples. Further θ_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 χ^{-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 Griffiths'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 $\text{La}_{0.85}\text{Na}_{0.15}\text{MnO}_3$ ferromagnet leads to an indirect magnetic transformation.

3.3 Thermomagnetic Property

In manganites, the magnetic entropy change (ΔS_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.

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

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 .

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

Sample code	T_C (K)	θ_P (K)	C ($\text{emu.mol}^{-1} \text{Oe}^{-1} \cdot \text{K}$)	$\mu_{\text{eff}}^{\text{th}}$ (μ_B)	$\mu_{\text{eff}}^{\text{exp}}$ (μ_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

Above T_C , the specimen compromises with its FM state because of the increased thermal agitations 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)

$$\frac{dM}{dT} = \left[-A \times \left(\frac{M_i - M_f}{2} \right) \times \text{sech}^2(A \times (T_C - T)) \right] + B \quad (3)$$

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.

$$\Delta S_M = \int_0^{H_M} \left(\frac{\partial S}{\partial H} \right)_T dH \quad (4)$$

According to Maxwell's thermodynamic relation,

$$\left(\frac{\partial M}{\partial T} \right)_H = \left(\frac{\partial S}{\partial H} \right)_T \quad (5)$$

which implies

$$\Delta S_M = \int_0^{H_M} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (6)$$

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

$$\begin{aligned} \Delta S_M &= \int_0^{H_M} \left[\left\{ -A \times \left(\frac{M_i - M_f}{2} \right) \times \text{sech}^2(A \times (T_C - T)) \right\} + B \right] dH \\ \Delta S_M &= \left[\left\{ -A \times \left(\frac{M_i - M_f}{2} \right) \times \text{sech}^2(A \times (T_C - T)) \right\} + B \right] \times H_M \end{aligned} \quad (7)$$

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 $\Delta S_M^{\max}$, then

$$\Delta S_M^{\max} = \left[\left\{ -A \times \left(\frac{M_i - M_f}{2} \right) \right\} + B \right] \times H_M = S_C \times H_M \quad (8)$$

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 (δT_{FWHM}). The δT_{FWHM} is nothing but the difference in the temperatures ($T_2 - T_1$) at which the distribution of ΔS_M is half of its maximum value ($\frac{\Delta S_M^{\max}}{2}$). The substitution of temperature as T^* at which $\Delta S_M = \frac{\Delta S_M^{\max}}{2}$ in Equation (7) gives T^*

$$T^* = \frac{AT_C \pm \cosh^{-1} \left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \right)}{A} \quad (9)$$

$$\begin{aligned} \text{So the } \delta T_{FWHM} &= T_2 - T_1 = \frac{AT_C + \cosh^{-1} \left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \right)}{A} - \\ &\frac{AT_C \pm \cosh^{-1} \left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \right)}{A} \end{aligned} \quad \text{which implies}$$

$$\delta T_{FWHM} = \frac{2}{A} \times \cosh^{-1} \left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \right) \quad (10)$$

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

RCP which is $-\Delta S_M^{\max} \times \delta T_{FWHM}$ is given by

$$\begin{aligned} &\left[\left\{ -A \times \left(\frac{M_i - M_f}{2} \right) \right\} + B \right] \times H_M \times \frac{2}{A} \times \cosh^{-1} \left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \right) \\ \Rightarrow RCP &= \left(M_i - M_f - 2 \times \frac{B}{A} \right) \times H_M \times \cosh^{-1} \left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}} \right) \end{aligned} \quad (11)$$

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 ΔS_M shows the Gaussian-like distribution, ΔC_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)

$$\begin{aligned} \frac{d\Delta S_M}{dT} &= -2A^2 \times \left(\frac{M_i - M_f}{2} \right) \times \text{sech}^2(A \times (T_C - T)) \\ &\times \tanh(A \times (T_C - T)) \times H_M \end{aligned}$$

which implies

$$\begin{aligned} \Delta C_P &= -2TA^2 \times \left(\frac{M_i - M_f}{2} \right) \times \text{sech}^2(A \times (T_C - T)) \\ &\times \tanh(A \times (T_C - T)) \times H_M \end{aligned} \quad (12)$$

To obtain the thermomagnetic physical quantities viz. ΔS_M , δT_{FWHM} , RCP, and ΔC_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. $|\Delta S_M^{\max}|$ increases drastically from LBi0 to LBi10 and reduces with further substitution of Bi^{3+} . The distribution of prominent change of entropy which is characterized by full width at half maximum of ΔS_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 ($\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{3+}$ or $\text{Mn}^{4+}\text{-O}^{2-}\text{-Mn}^{4+}$) may couple via intervening oxygen to give AFM and the interspecies

exchange ($\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{4+}$) would result in FM nature. Furthermore, many factors influence these exchange interactions, but the prominent ones are, ion concentration signified by $\text{Mn}^{3+}/\text{Mn}^{4+}$ 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 ($\text{Mn}^{3+}/\text{Mn}^{4+}$) 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 $|\Delta S_M^{\max}|$ 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

Table 3 Model parameters and estimated thermomagnetic parameters from model simulation for $\text{La}_{0.85-x}\text{Bi}_x\text{Na}_{0.15}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.25, 0.3$)

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^{\max} $ $\times 10^{-3}$ (J.kg ⁻¹ K ⁻¹)	δT_{FWHM} (K)	RCP $\times 10^{-3}$ (J.kg ⁻¹)	$\Delta C_P^{\min}$ (J.kg ⁻¹ K ⁻¹)	$\Delta C_P^{\max}$ (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

Fig. 7 Representative variation of magnetization w.r.t temperature. The inset of the figure indicates magnetization sensitivity (dM/dT) variation w.r.t temperature (T)

LBi10. As the magnetic entropy change depends majorly on magnetic moment and magnetic sensitivity, though bismuth content tends to reduce the moment, it parallelly 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

Fig. 8 Temperature dependence of magnetization and magnetic sensitivity. The open symbols are experimental data and solid line indicates modeled results

Fig. 9 Modeled magnetic entropy change as function of temperature of $\text{La}_{0.85-x}\text{Bi}_x\text{Na}_{0.15}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.25$, and 0.3)

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 ΔS_M in LBi10 is maximum near to room temperature and is maximum among other all concentrations make it assessable toward the RT magnetic refrigerant.

Fig. 10 Modeled specific heat change as function of temperature of $\text{La}_{0.85-x}\text{Bi}_x\text{Na}_{0.15}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.25$, and 0.3)

Figure 10 shows temperature dependence of specific heat under the low field of 1000e for all the samples. The ΔC_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 ΔC_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 $-\Delta S_M^{\max}$ and δT_{FWHM} , the broad spread of ΔS_M caused the large RCP in LBi20 sample. Many researchers report that increase δT_{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_2O_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.

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Declarations

Competing Interests The authors declare no competing interests.

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