Magnetic and Magnetocaloric Properties of $\mathbf{La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3}$ ($\boldsymbol{x} = 0, 0.05, 0.1, 0.15, 0.2, 0.25$) Samples

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The effects of Cr doping on structural, magnetic and magnetocaloric properties of $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$) samples were investigated. It has been observed in X-ray analyses that the substitution of Mn by Cr produced no remarkable structural change and only the diffraction peaks for orthorhombic symmetry were obtained for all samples. The decrease in the Curie temperature and saturation magnetization with Cr content could be due to weakening of the ferromagnetism in Cr doped samples. The decrease in magnetic entropy change was attributed to the decrease in saturation magnetization with increasing Cr content.

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1. Introduction

Magnetocaloric effect (MCE) in perovskite manganites has been intensely studied due to the possible technological application in refrigeration technology. Manganites have been widely investigated not only for potential technological applications but also for variety of their magnetic and transport properties [1–6]. In most of recent studies, the aim has been to show the relation between magnetic, transport, and MCE properties of manganites [7–11]. In the literature, many effects have been reported that determine the magnetic and transport properties [12–15]. The magnetic and transport properties of manganites have been mostly explained in terms of the double exchange (DE) interaction which is closely related with the relative concentration of the Mn^{3+} and Mn^{4+} ions and Mn–O bond length and Mn–O–Mn bond angle [16]. It has been reported that A-site substitution indirectly affects the magnetic and transport properties due to the changes in Mn–O bond length and Mn–O–Mn bond angle. On the other side, it has been shown that Mn-site substitution has a more direct effect on magnetic and transport properties of manganites. Therefore, a great number of studies have been conducted on the effect of the replacement of Mn ions by various transition metal ions in different types of manganites [17–23].

Among the various substituting elements for Mn ions in manganites, Cr has a special effect and attracted more attention. Several recent papers on Cr substituted manganites [24–31] have shown that Cr^{3+} substitution for Mn^{3+} generally decreases the Curie temperature (T_C). The change in the Curie temperature can be explained by antiferromagnetic interaction (AFM) Cr^{3+}–O–Mn^{3+}. In addition, Cr substitution is expected to cause a structural effect due to the smaller ionic radius of Cr^{3+} ($= 0.615$ Å) compared with Mn^{3+} ($= 0.645$ Å) and hence these structural deformations could cause an indirect dilution in ferromagnetic DE interaction. Biswas et al. [24] have reported that magnetization and transition temperature increase up to a critical Cr content and then decrease with further Cr content in $Gd_{0.7}Ca_{0.3}Mn_{1-x}Cr_xO_3$ samples. They have explained this on the basis that long-range magnetic order changes to a short range order with Cr content. Kumar et al. [26] have reported that the metal–insulator transition temperature decreases with Cr doping in $La_{0.7}Ca_{0.3}Mn_{1-x}Cr_xO_3$ samples. The decrease in transition temperature was attributed to AFM interaction which originates from super exchange interaction between Cr^{3+}/ Cr^{3+} and Cr^{3+}/Mn^{3+}. Magnetic measurements also corroborated the competition between FM and AFM interactions in Cr doped system. Cabeza et al. [27] found that both the saturation magnetization and the Curie temperature decrease with Cr content in $La_{0.7}Ca_{0.3}Cr_xMn_{1-x}O_3$ compounds. The interpretation was that the decrease in saturation magnetization and the Curie temperature is due to the antiferromagnetic ordering of Cr and Mn ions. Zhang et al. [25] have concluded that $Bi_{0.3}Ca_{0.7}Mn_{0.75}Cr_{0.25}O_3$ compound exhibits a canted antiferromagnetic transition at 120 K. The observed behavior has been suggested to originate from an antiparallel coupling of Cr^{3+} and Mn^{3+} ions. The addition of Cr and Co has been shown to cause insulator–metal transition in isolation antiferromagnetic phase of $Pr_{0.5}Ca_{0.5}Mn_{1-x}M_xO_3$ (M = Cr and Co) [29, 30]. Maignan et al. [31] have reported that the Curie temperature hardly changes when Cr is added to $Sm_{0.56}Sr_{0.44}Mn_{1-x}Cr_xO_3$.

Recent studies have shown that Cr substitution for Mn in manganites is fairly interesting and striking. In this context, Cr doping at Mn sites in Bi based manganites

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is expected to produce more pronounced effect on magnetic and magnetocaloric properties. Therefore, in this study, we investigated in detail the effect of Cr deposition on the magnetic and magnetocaloric properties of $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ (x = 0, 0.05, 0.1, 0.15, 0.2, 0.25) samples.

2. Experimental

Powder chemical compounds with high purity of La_2O_3 (99.9%), Bi_2O_3 (99.9%), Cr_2O_3 (99.9%), and MnO (99.9% pure) purchased from Sigma-Aldrich Co were used to prepare $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ (x = 0, 0.05, 0.1, 0.15, 0.2, 0.25) by solid state reaction method. Details about sample preparation can be found in [25]. First, the powders were mixed in a stoichiometric ratio and grounded. Then, the mixed powders were calcined in air at 1073 K for 12 h. After the samples were grounded and pressed into pellets, they were sintered at 1473 K for 24 h in air.

Structural analysis of the prepared compounds were studied using X-ray powder diffraction (Cu K_α) and scanning electron microscopy (SEM). Magnetic properties of the samples were determined using a Q-3398 (cryogenic) vibrating sample magnetometer (VSM). The magnetic entropy changes of the samples were calculated using isothermal magnetization curves.

3. Results and discussion

Figure 1 shows X-ray spectra at room temperature for all samples prepared with $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ (x = 0, 0.05, 0.1, 0.15, 0.2, 0.25). The results show that the samples are in single phase and have the orthorhombic structure. It is clearly seen in Fig. 1 that the diffraction peak positions are identical for all the samples, indicating no considerable change in structural parameters. The double diffraction line, which is clearly observed just above $2\theta = 30°$ (Fig. 1), has been discussed in detail in our previous studies [32, 33]. The observed double diffraction line was attributed to structural distortion coming from the Jahn-Teller (JT) effect and the polarized $6s^2$ lone-pair character of Bi^{3+} ions [34]. Biswas et al. [24] have concluded that cooperative JT distortion decreases with increase of Cr content due to the non-JT active Cr^{3+} ions replacing the JT active Mn^{3+} ions for $Gd_{0.7}Ca_{0.3}Mn_{1-x}Cr_xO_3$ compounds. Interestingly, for our samples, the observed doublet diffraction lines in X-ray diffraction patterns changed to single line for the further Cr concentration ($x \geq 0.2$). Disappearance of doublet diffraction lines could be due to the weakening of JT distortion with increasing Cr content. The X-ray diffraction patterns results are in good agreement with the literature [24].

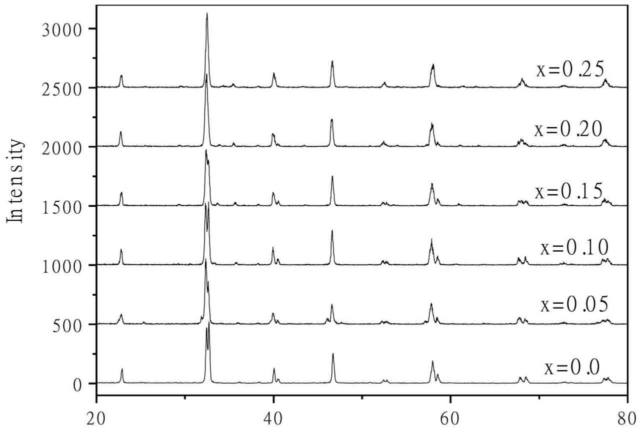

Fig. 1. X-ray diffraction patterns of the $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ (x = 0, 0.05, 0.1, 0.15, 0.2, 0.25) compounds at room temperature.

Figure 2 shows the typical SEM micrographs for $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ (x = 0, 0.05, 0.1, 0.15, 0.2, 0.25) samples with a magnification of 10,000. SEM images of all samples reflect a flat polycrystalline structure with an average gain size of 1 to 7 μm and all samples present an almost equal average grain size.

In order to clarify the magnetic properties, magnetic measurements were carried out on all the samples. For convenience, the magnetic field intensity is expressed in T, i.e. the product of the intensity in A/m by μ_0, is denoted by H everywhere in the text. Temperature dependence of magnetization under an applied field of 0.1 T and field dependence of magnetization at 15 K in the range of -5 T to 5 T applied magnetic field for $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ (x = 0, 0.05, 0.1, 0.15, 0.2, 0.25) samples are shown in Fig. 3a and b. As can be clearly seen in Fig. 3a all compounds demonstrate the ability to shift from ferromagnetism to paramagnetism around the Curie temperature. The Curie temperature (T_C) is defined as the temperature of the maximum value of the variation of the magnetization depending on the temperature. The determined Curie temperatures were given in Table I. It is seen that the Curie temperature decreases from 209 K for $x = 0$ to 127 K for $x = 0.25$. All the magnetization curves (Fig. 3b) show a rapid increase at low fields and then approach saturation at high fields which is a typical ferromagnetic behavior. Table I clearly shows that saturation magnetization (M_s) decreases from 86.13 emu/g for $x = 0$ to 35.69 emu/g for $x = 0.25$. The variation of saturation magnetization (M_s) and the Curie temperature (T_C) depending on Cr concentration is consistent with the literature [24–31].

In recent studies on Cr doped manganites, it has been concluded that the Cr substitution for Mn introduces two additional distinctive antiferromagnetic interactions between Cr^{3+}–O–Mn^{4+} and Cr^{3+}–O–Cr^{3+} [25, 26, 35]. Since our Bi based samples have only Mn^{3+} ions, AFM Cr^{3+}–O–Cr^{3+} interaction could compete with FM interactions and results in spin-glass like or canted antiferromagnetic ground state.

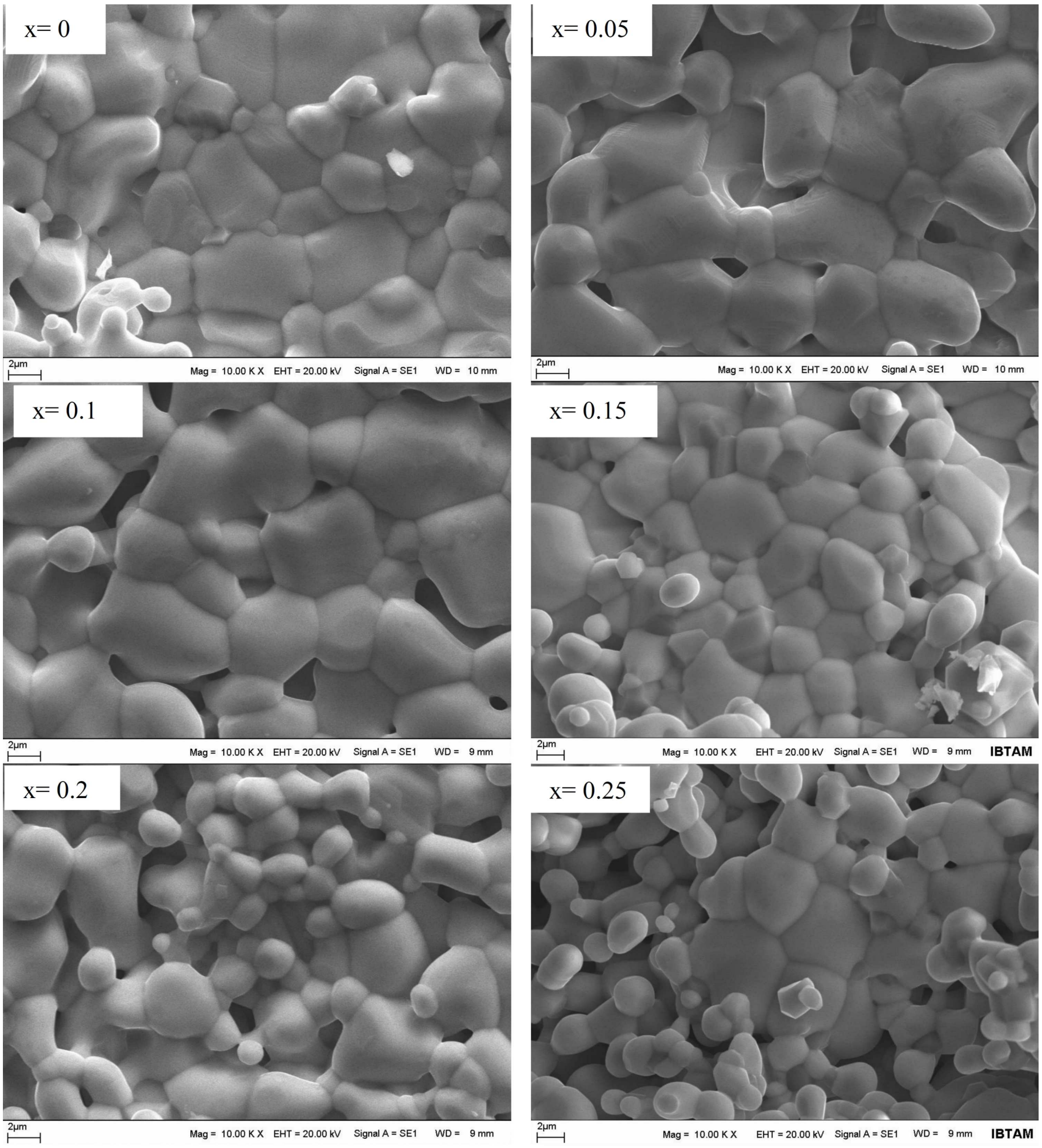

Fig. 2. The SEM photographs of $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ ($x = 0$, 0.05, 0.1, 0.15, 0.2, 0.25) compounds with magnification of 10000.

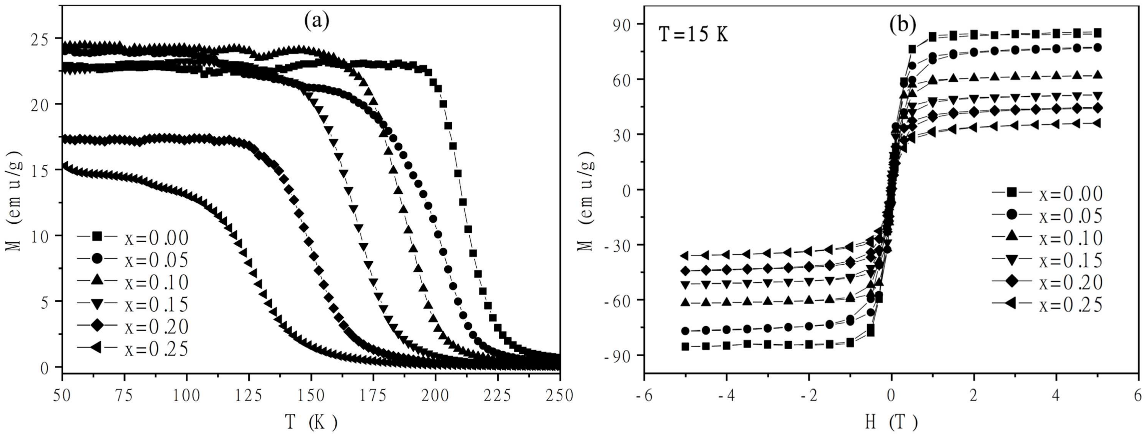

Fig. 3. (a) Temperature dependence of the magnetisation measured at 0.1 T magnetic field, (b) the field dependence of the magnetisation at 15 K in the range of −5 T to 5 T applied magnetic field for $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ ($x = 0$, 0.05, 0.1, 0.15, 0.2, 0.25) compounds.

TABLE I

Curie temperature T_C, saturation magnetization M_S, calculated magnetic moment μ_{th}, magnetic entropy change $|\Delta S_m|$ and refrigeration capacity RC for $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ (x = 0, 0.05, 0.1, 0.15, 0.2, 0.25) compounds.

x	T_C [K]	M_s [emu/g]	μ_{th} [μ_B]	$\lvert\Delta S_m\rvert$ [J/(kg K)]		RC [J/kg]
				ΔH=1 T	ΔH=5 T	ΔH=5 T
0	209	86.13	4.00	1.54	5.51	264.53
0.05	202	78.11	3.65	0.58	2.42	253.15
0.1	185	62.14	3.30	0.64	2.47	202.21
0.15	169	52.25	2.95	0.53	1.99	162.46
0.2	149	44.64	2.60	0.42	1.61	129.86
0.25	127	35.69	2.25	0.31	1.26	100.41

In order to gain a deeper understanding and confirm the weakening of ferromagnetism, we tried to make a rough theoretical calculation of saturated magnetic moment for $La^{3+}_{0.94}Bi^{3+}_{0.06}Mn^{3+}_{1-x}Cr^{3+}_xO^{2-}_3$ according to the formula

$$\mu_{th} = [(1-x)\mu(Mn^{3+}) - x\mu(Cr^{3+})]\mu_B = (4-7x)\mu_B. \tag{1}$$

The magnetic moments of Mn^{3+} and Cr^{3+} ions are 4 μ_B and 3 μ_B, respectively. The theoretically calculated magnetic moments from Eq. (1) were given in Table I. As the Cr doping increases, a reduction in magnetic moments occurs (from 4 μ_B for $x = 0$ to 2.25 μ_B for $x = 0.25$) which is another indication of reduced ferromagnetic properties. In this case, the decrease in the Curie temperature and saturation magnetization with increasing Cr content could be explained by the dilution of ferromagnetic interactions.

In Fig. 4, for samples with $x = 0.15$ and $x = 0.25$, the magnetization is seen as a function of the applied magnetic field at different temperature values of the measured samples. The magnetization isotherm for $x = 0$ sample increases sharply in a very low magnetic field and rapidly saturates as a typical ferromagnetic property. However, the magnetization curves for $x = 0.25$ samples do not show full saturation even at 6 T magnetic field which is another evidence of weakening of ferromagnetism with increase of Cr content.

The magnetic entropy change of the samples can be calculated using the magnetization curves under the magnetic field, as shown in Fig. 4. According to the classical thermodynamic law, the magnetic entropy change obtained from a magnetic field ranging from zero to the maximum value is given by

$$\Delta S_m(T,H) = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \tag{2}$$

By using Eq. (2), the magnetic entropy change was calculated from isothermal magnetization curves (Fig. 4). Figure 5a–c shows the changes in magnetic entropy depending on the temperature at various magnetic field values for the samples x = 0, 0.15, and 0.25. The magnetic entropy curves obtained from the samples have a certain peak value around the Curie temperature T_C. The peak temperatures and peak values of $|\Delta S_m|$ increase with the magnetic field. The magnetic entropy changes of all $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ (x = 0, 0.05, 0,1, 0.15, 0,2, 0.25) samples, for the H = 1 T are shown in Fig. 5d. Under 1 T magnetic field, as the Cr doping increases, the peak value of the magnetic entropy change $|\Delta S_m|$ decreases from 1.54 J/(kg K) for $x = 0$ to 0.31 J/(kg K) for $x = 0.25$. All the peak values at 1 and 5 T magnetic fields were given in Table I.

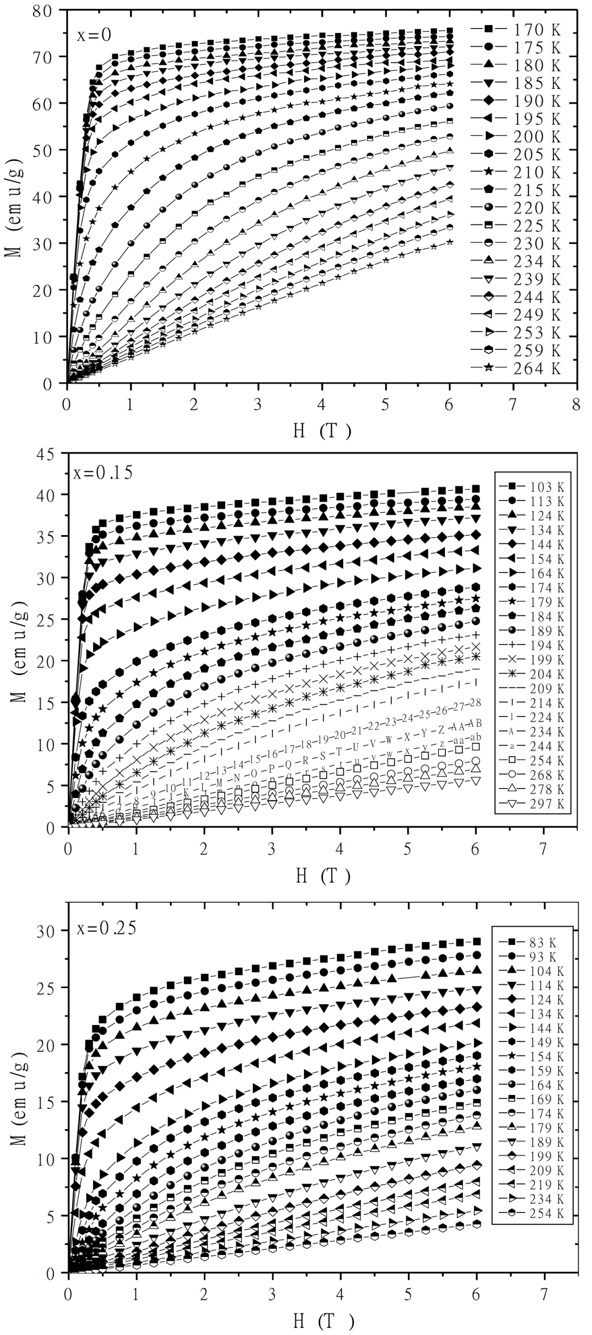

Fig. 4. Isothermal magnetisation curves at various temperatures for x = 0, 0.15, and 0.25 samples.

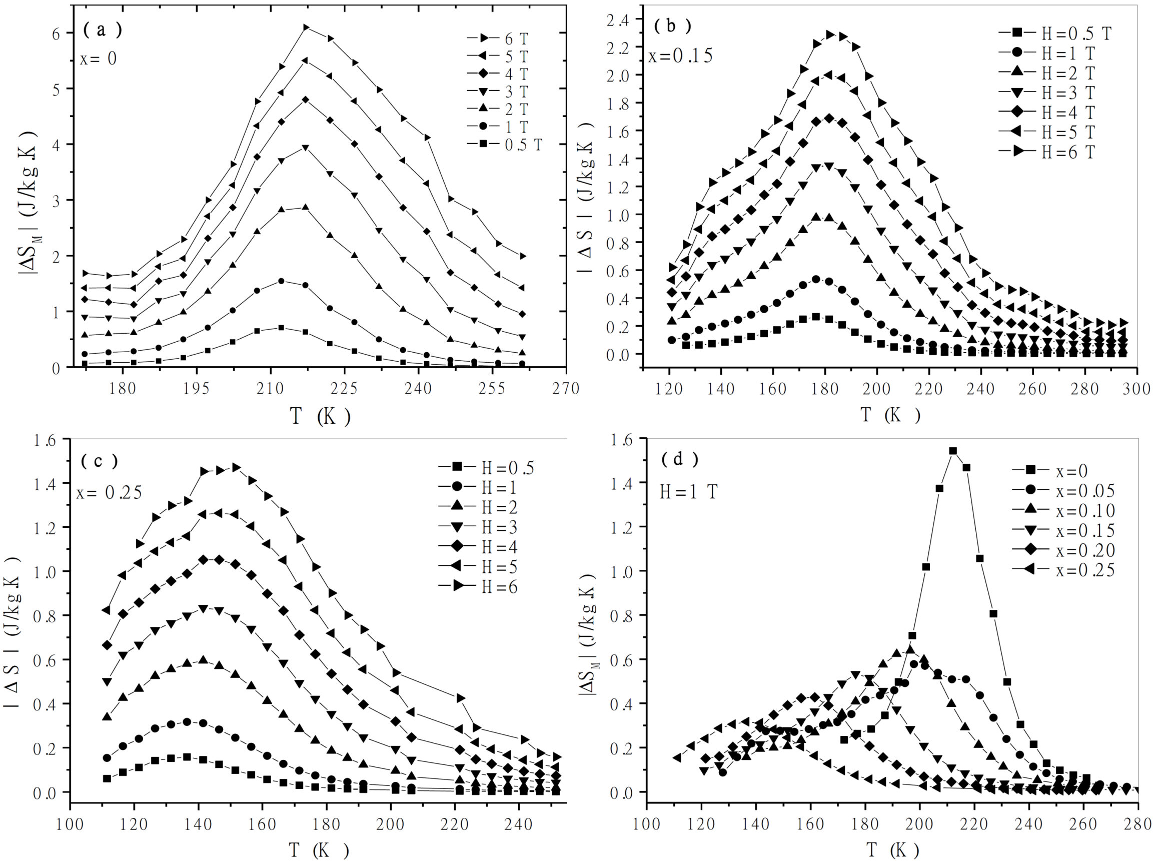

Fig. 5. The temperature dependence of magnetic entropy change for (a) $x = 0$, (b) $x = 0.15$, and (c) $x = 0.25$ at various magnetic fields. (d) The magnetic entropy change for $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$) compounds at 1 T magnetic field.

In magnetic entropy change $|\Delta S_m|$ the decrease may be due to ferromagnetic dilution with increased Cr doping. As discussed above, depending on the ferromagnetic dilution, saturation magnetization (M_s) decreased from 86.13 emu/g for $x = 0$ to 35.69 emu/g for $x = 0.25$. In this case it is one of the conditions for a sample to have a very large magnetic entropy change.

The refrigeration capacity (RC) was calculated by taking the direct product of the maximum entropy change and the full width at half maximum of the peak ($= |\Delta S_m| \delta T_{\mathrm{FWHM}}$). The calculated values of RC at 5 T magnetic field change were given in Table I. The refrigeration capacities vary from 264.53 J/kg for $x = 0$ to 100.41 J/kg for $x = 0.25$. The values of $|\Delta S_m|$ and RC for our compounds are large enough for considering as a magnetic refrigerant.

4. Conclusion

In this study, the structural, magnetic, and magnetocaloric properties of $La_{0.94}Bi_{0.06}Mn_{1-x}Cr_xO_3$ ($x = 0$, 0.05, 0.1, 0.15, 0.2, 0.25) compounds were investigated. X-ray analysis indicated that the substitution of Mn by Cr produced no considerable structural change and only the diffraction peaks for orthorhombic symmetry were obtained for all samples. It was found that the Curie temperature (from 209 K for $x = 0$ to 127 K for $x = 0.25$) and saturation magnetization (from 86.13 emu/g for $x = 0$ to 35.69 emu/g for $x = 0.25$) decrease with increase of Cr content and are attributed to weakening of the ferromagnetism in Cr doped samples. The maximum value of the magnetic entropy change was determined to decrease from 1.54 J/(kg K) for $x = 0$ to 0.31 J/(kg K) for $x = 0.25$ at 1 T magnetic field. The decrease in peak value of $|\Delta S_m|$ could be attributed to decrease in saturation magnetization with increase of Cr content.

Acknowledgments

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