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The interaction between Co and Mn ions on the magnetic frustration and the inducement of the double-exchange mechanism in hole-doped $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ (x = 0–1.0) cobaltite

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This study investigates the interaction between Co and Mn ions on spin state behaviour and magnetic frustration in hole-doped $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ (x = 0–1.0) cobaltite. It aims to understand the inducement of the double-exchange (DE) mechanism in this system. The samples were synthesised using the conventional solid-state synthesis method, and their crystal structure and magnetic properties were analysed. Rietveld refinement of X-ray diffraction data confirmed that $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}O_3$ (x = 0.0 and 0.2) samples had rhombohedral crystals structure with $R\bar{3}c$ space group. An orthorhombic (*Pbnm*) perovskite structure was observed for the $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ (x = 0.4 –1.0) accompanied by increasing cell volume in the samples as the substitution level of Mn increases. Temperature dependence of resistivity $\rho(T)$ shows semiconducting behaviour in the whole temperature and composition range of x = 0.0–0.8. However, further substitution with x = 0.9 and x = 1.0 give remarkable induced MI behaviour where the MI transition temperature (T_{MI}) increased from 75 K and 132 K, respectively. The result suggests that Mn ions play an important role in the magnetic properties of the cobaltite, and the system can be tuned by adjusting the Mn concentration.

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Keywords: Manganites, DE mechanism, A–site disorder, Perovskite

1. Introduction

Rare earth cobaltite of the general formula $La_{1-x}A_xCo_{1-y}B_yO3$ (A = alkaline earth, B = transition metal) is one of the most popular family members of cobaltite perovskite system that excites researchers' interest because of its various behaviour of electrical and magnetic properties. The behaviour can be manipulated by influencing the spin states of the system. Intriguingly, the cobaltite system mixed spin states namely the low spin (LS: $t^6_{2g}e^0_g$ for Co^{3+} and $t^5_{2g}e^0_g$ for Co^{4+}), intermediate spin (IS: $t^5_{2g}e^1_g$ for Co^{3+} and $t^4_{2g}e^1_g$ for Co^{4+}) and high spin (HS: $t^4_{2g}e^2_g$ for Co^{3+} and $t^3_{2g}e^2_g$ for Co^{4+})[1]. Undoped $LaCoO_3$ showed a nonmagnetic insulator at low temperatures and shifted to metal-insulator behaviour (T_{MI} ~ 500 K) and at T>650 K the system became a good conductor[2]. The spin states also exhibit a crossover from the low spin to the intermediate spin or the high spin as temperature increases[3].

In addition to temperature, the ionic radius and valence state can give significant changes on spin states hence on properties of $LaCoO_3$ systems[4]. The spin state transitions can be controlled by substitution either at A or B cation site[1]. Various cobaltite shows metallicity and ferromagnetism depending on the composition and the size of the A-site[5]. This has been observed in the behaviour of $La_{1-x}Sr_xCoO_3$ wherein spin-glass behaviour (0.0≤ x ≤0.18) shifted to cluster-glass behaviour (0.18≤ x ≤0.5)[5]. Previous reports also suggested that the decreased magnetisation and increased electrical resistivity of four series of rare earth cobaltates of the formula $La_{0.7-}$

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${}_{x}Ln_{x}Ca_{0.3}O_3$ with Ln = Pr, Nd, Gd and Dy are strongly related to the increased in x or decreased in average radius $<r_A>$ [5]. In addition, the Ca-substituted cobaltates were more likely to exhibit phase separation and related effects because of their smaller $<r_A>$ or e_g bandwidth compared to the Sr-substituted materials[5].

Meanwhile, the study of hole-doped $La_{0.8}Sr_{0.2}Co_{1-x}V_xO_3$ (x = 0.00, 0.02, 0.04 and 0.06) showed that the substitution of V and Sr suppressed the ferromagnetic order with the existence of spin glass behaviour and caused the presence of mixed valence of Co^{3+}/Co^{4+} valences wherein both are in intermediate spin states, thereby suggesting the double exchange between Co^{3+} and Co^{4+} as the origin for the ferromagnetic order [6]. However, $La_{0.7}Sr_{0.3}Co_{1-x}Mn_xO_3$ (x = 0-0.5) shows unusual magnetic and electrical properties. Mn substitutions (x~10%) in the system have been reported that interaction between Mn and Co ions is antiferromagnetic super-exchange and not caused by the ferromagnetic double exchange. The system showed insulating spin glass (SG) behaviour at x = 0.1. Further substitution of Mn ions ($x \geq 0.2$) revived ferromagnetism caused by the double exchange interactions between Mn ions but did not induce metallic conductivity[7]. In addition, it is important to study how the uniqueness of the Mn spin state which is always in their high spin state ($t^3_{2g}\,e^1_g$ and t^3_{2g}) can influence the electrical and magnetic properties of cobaltite systems[7].

Thus, it is interesting to study the contributions of hole doping resulting from Mn substitutions in $LaCoMnO_3$ on the revival of the ferromagnetic region and spin glass behaviour. Furthermore, the interaction between Mn-Co ions is expected to give meaningful results given that their relationships remain questionable either leading to the revival of double exchange interaction or magnetic frustration. In addition, it may contribute knowledge about the role played by the high spin state of Mn ions on spin state transition hence on electrical and magnetic properties of the system. Moreover, the nature of spin glass and cluster glass can be further elucidated given that antiferromagnetic (AF) super exchange interactions arising from Co^{3+} - Co^{3+} are also expected. Thus, it is interesting to study how the substitution of HS state Mn ions can influence the spin state transition in a hole-doped cobaltite system as the magnetic mechanism remains unclear. This is because Mn-doped cobaltite is expected to create mixed valence Co^{3+}/Co^{4+} and Mn^{3+}/Mn^{4+} which can also reflect the double exchange mechanism. Conversely, the existence of antiferromagnetic (AF) super exchange interactions arising from Co^{3+} - Co^{3+} is also expected which in turn causes magnetic frustration phenomenon[8].

2. Experimental Details

A starting composition of $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ (x = 0–1.0) samples was synthesised via conventional solid-state synthesis method with appropriate amounts of high-purity (> 99.99%) oxides. Lanthanum oxide La_2O_3, Dysprosium Oxide Dy_2O_3, Calcium Carbonate $CaCO_3$, Cobalt (IV) Oxide Co_4O_3 and Manganese (IV) oxide MnO_2 powders as the raw material were then weighed in stoichiometric amounts by using an electronic balance. Subsequently, these powders were mixed and ground for 2 h before calcination in air at 950 °C for 24 h with intermediate grinding. Finally, the powder was pressed into pellets (diameter, 13 mm; thickness of approximately 3 mm) under a pressure of around 5 tonnes and sintered in air at 1100 °C for 36 h.

The phase of the samples was characterised by using the X-ray diffraction (XRD) technique using a PAN analytical model Xpert PRO MPD diffractometer with Cu -Kα radiation emitted by copper, whose characteristic wavelength for the Cu-Kα radiation is 1.5418 Å. Magnetisation measurements versus temperature, M(T) and versus magnetic applied field, M(H) were carried out using the Physical Property Measuring System (PPMS) in the temperature range 5–300 K and in the magnetic field ± 4 T. The electrical resistivity and magnetoresistance (MR) behaviours were investigated using the standard four-point probe technique as a function of temperature (30–300 K) in a Janis model CCS 350ST cryostat under external magnetic fields of around 0.8 T.

3. Results and Discussion

Powder XRD patterns for $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}O_3$ (x = 0.0 and 0.2) samples at room temperature are presented in Figure 1. The data were analysed by the Rietveld method using the GSAS program and EXPGUI package crystal structures were visualised using the program VESTA. In all XRD patterns of all samples, the structural transition occurred with no trace of secondary phase detectable. The analysed data in Figure 1 showed that $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}O_3$ (x = 0.0 and 0.2) samples had a rhombohedral crystal structure with $R\bar{3}c$ space group belonging to the hexagonal setting where $a = b \neq c$[1]. An orthorhombic (*Pbnm*) perovskite structure with $a \neq b \neq c$ was observed for the $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ (x = 0.4 –1.0) accompanied by increasing cell volume in the samples as the substitution level of Mn increases. Figure 2 shows the final refinement fits for x = 0.2 and x = 0.4 samples. All peaks are sharp, clear and well-defined thus suggesting the samples are well crystallised.

The refined lattice parameters, bond angle and bond length are summarised in Table 1. As shown, structural parameters a and b decreased from 5.4113 Å (x = 0) to 5.398 Å (x = 0.2), while c slightly increased from 13.1839 Å (x = 0) to 13.2719 Å (x = 0.2) with Mn substitution. In addition, the unit cell volume, V, increased from 334.33 Å^3 (x = 0) to 334.7 Å^3 (x = 0.2) for the rhombohedral crystal structure. For Mn (x = 0.4, 0.6, 0.8 and 1.0), it causes a structural transition from rhombohedral structure to orthorhombic structure. For orthorhombic structure, the results of structural parameters reveal the increase in lattice parameters a, b and c, as shown in Table 1. The value of lattice parameter, a, for x = 0.4–1.0 samples showed a significant increment from a = 5.3971, a = 5.4083, a = 5.4238, to a = 5.4381. The same trend was observed for the b lattice parameter of b = 7.6333, b = 7.6829 b = 7.7146 and b = 7.7518. Mn substitutions also cause lattice parameter c measured elongated with the values of c = 5.4172, c = 5.4314, c = 5.4496 and c = 5.479 for x = 0.4–1.0 samples. The obtained reliabilities χ^2 for rhombohedral structure (x = 0.0 and 0.2) were 1.173 and 3.643, respectively. Meanwhile, for orthorhombic structure, the reliabilities χ^2 of 1.016, 1.040, 1.130 and 2.714 were obtained for x = 0.4, 0.6, 0.8 and 1.0 compounds, respectively. These χ^2 values showed good reliability of results. Upon Mn substitution, the Mn–O–Mn bond angle decreased from 177.07^o (x = 0.2) to 164.094^o (x = 1.0), whereas the Mn–O bond length slightly increased from 1.91130 (x = 0.2) to 1.96044 (x = 1.0). This result shows how Mn ions are responsible to play a role to alter and distort the Mn–O–Mn bond angle and Mn–O bond length. The observed behaviour is justified because a larger ionic radius of Mn^{3+} (0.785 Å) is substituted into smaller Co^{3+} (0.75 Å) ions[6], which possibly induced the lattice expansion in both a and b direction. Variation of lattice parameters, increasing cell volume in the sample, distortion and structural phase transition in the sample were because of the average ionic radii of Mn and Co ions.

Table 1. Structure parameters obtained by Rietveld refinement; metal-insulator transition temperature, T_{MI} *at 0 T; Curie temperature* T_c *of* $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ *for (x = 0.0–1.0) samples.*

Sample (x)	0.0	0.2	0.4	0.6	0.8	1.0
a (Å)	5.4113	5.3968	5.3971	5.4083	5.4238	5.4381
b (Å)	5.4113	5.3968	7.6333	7.6829	7.7146	7.7518
c (Å)	13.183	13.271	5.4172	5.4314	5.4496	5.4790
Volume, V (Å^3)	334.33	334.76	223.175	225.68	228.027	230.97
T_c (K)	116	50	57	71	128	133
T_{MI} (K)	-	-	-	-	-	132
χ^2	1.173	3.643	1.016	1.040	1.130	2.714
Bond length, <Mn-O>	-	1.91130	1.94008	1.95242	1.96044	1.96921
Bond angle, <Mn-O-Mn> (^{o})	-	177.067	164.153	164.114	164.114	164.094
Rwp (%)	0.0817	0.1676	0.0783	0.0870	0.1017	0.2010
Rp (%)	0.0625	0.1013	0.0663	0.0676	0.0777	0.1464

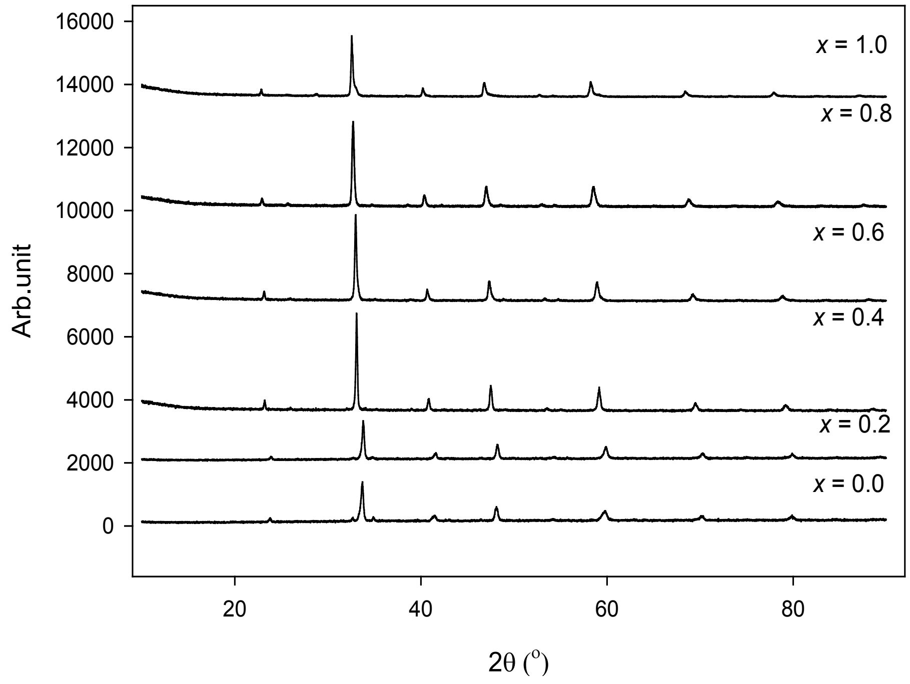

Fig. 1. XRD patterns of $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}O_3$ *(x = 0.0-1.0) samples.*

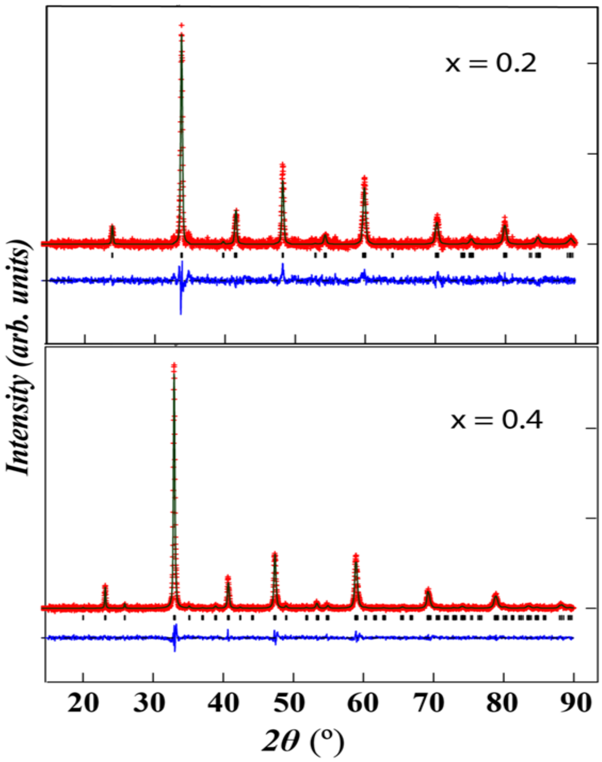

Fig. 2. Rietveld refinement of the XRD patterns for $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}O_3$ *(x = 0.2 and 0.4) The solid red line represents the observed data, the black line corresponds to the calculated data, whilst the blue lines correspond to the difference between the observed and calculated data.*

Temperature dc resistivity was measured in the temperature range of 20 K–300 K for $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ (x = 0–1.0) samples to determine the effect of Mn substitution on the conduction mechanism, as presented in Figure 3. Temperature dependence of resistivity $\rho(T)$ shows semiconducting behaviour in the whole temperature and composition range of x = 0.0–0.8. At H = 0 T, the sample with x = 0–0.8 exhibited a strong insulating behaviour and did not show insulator to metallic transition as temperature decreased. However further substitution with x = 0.9 and x = 1.0 give remarkable induced MI behaviour where the MI transition temperature (T_{MI}) increased from 75 K to 132 K, as presented in Table 1. In addition, the resistivity decreases with the increase in the Mn substitutions. The $La_{1-x}Ca_xCoO_3$ compound over a doping range of $0< x <0.3$ shows an FM insulator behaviour[9]. Hence, it is suggested because of the presence of dominant double exchange (DE) interaction between the Mn ions[1]. By referring to the simple valence calculation, it is also strongly suggested that the observed transport behaviour is caused by the mixed-valence Co^{3+}/Co^{4+} and Mn^{3+}/Mn^{4+} which can also induce the double exchange interaction.

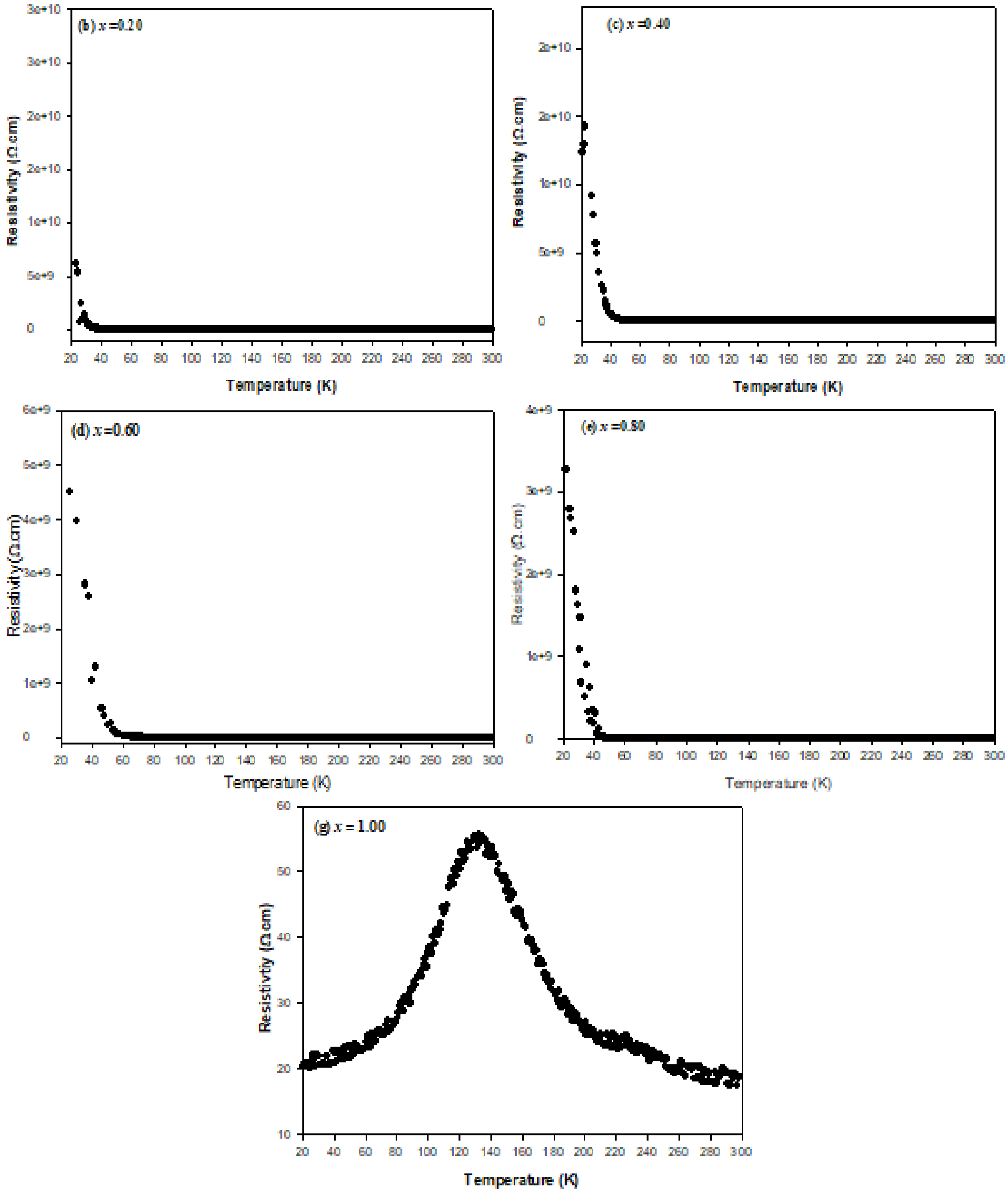

Fig. 3. Temperature dependence of resistivity $\rho(T)$ in the temperature range of 20 K – 300 K for $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ (x=0–1.0) samples

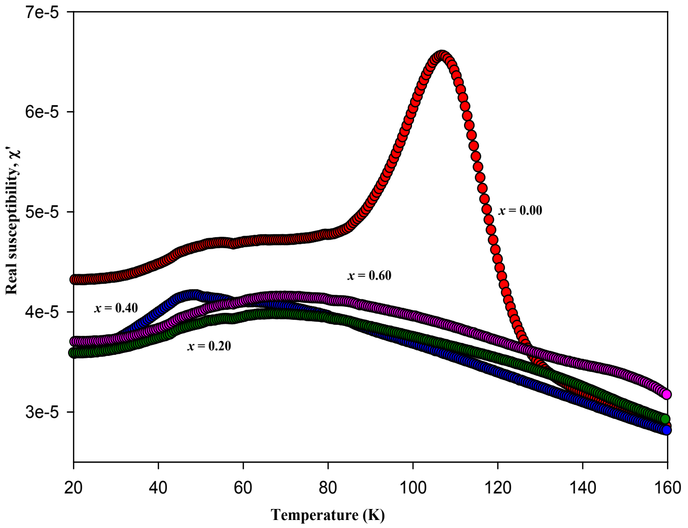

Fig. 4. AC susceptibility (real part) versus temperature plots for the compounds in the temperature range of 20 K–300 K for $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ *(x = 0.0–0.60) samples.*

Figure 4 shows the AC susceptibility (real part) versus temperature plots for the compounds in the temperature range of 20 K–300 K for $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ (x = 0–1.0) carried out under an AC field of 2 Oe and frequency of 325 Hz. The temperature in which the transition of ferromagnetic to paramagnetic state (FM–PM) occurs, known as Curie temperature (T_c), was determined based on the temperature corresponding to the minimum value from the derivative of magnetisation (dM/dT) versus T plot. The dM/dT versus T plot for the x = 1.00 sample is shown in Figure 5[10]. On the one hand, with the increase in x, x = 0.0–0.4, the AC susceptibility data not only shows weak magnetic susceptibility but also derives Curie Temperature (T_c) to lower temperature from 116 K to 57 K. On the other hand, further substitution of Mn causes T_c to increase with higher magnetic susceptibility. Maximum T_c of 158 K was observed at x = 0.9 which underwent a transition from paramagnetic (PM) to ferromagnetic (FM) phase with slightly lower magnetic susceptibility as compared to the compound of x = 0.8. Interestingly, Mn substitutions revived both ferromagnetism and metallic conductivity at x = 0.9. Meanwhile, the maximum susceptibility with T_c = 133 K was observed at x = 1.0 when Mn ions are fully substituted in the system as shown in Figure 6.

This is consistent with a previous study that reported the interaction between magnetic elements Mn–Co in super exchange antiferromagnetic (AFM-SE), as observed in $La_{0.7}Sr_{0.3}Co_{1-x}Mn_xO_3$. Furthermore, 10% substitutions of Mn in the cobaltite system suppressed the ferromagnetic because antiferromagnetic (AFM) super exchange interactions arise from Co^{3+}-Co^{3+}. The existence of antiferromagnetic (AMF) super exchange interactions arising from Co^{3+}-Co^{3+} is suggested which in turn causes magnetic frustration phenomenon[8]. By Mn substitution, antiferromagnetic (AFM) interaction is suggested to increase and ferromagnetic (FM) fraction phase decreased[1]. The competition between FM-DE and AFM-SE interaction in these compounds leads to a more disordered spin. In addition, further substitution of Mn ions ($x \geq 0.2$) revived ferromagnetism because of the double exchange interactions between Mn ions but did not induce metallic conductivity[7].

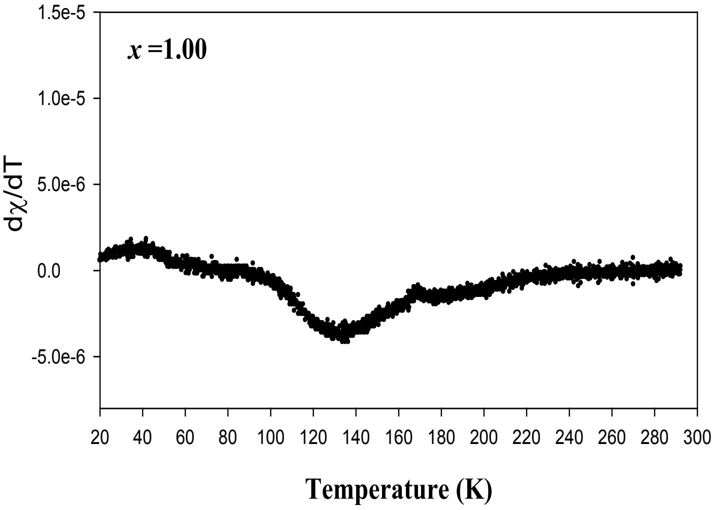

Fig. 5. The dM/dT versus T curve for x = 1.00.

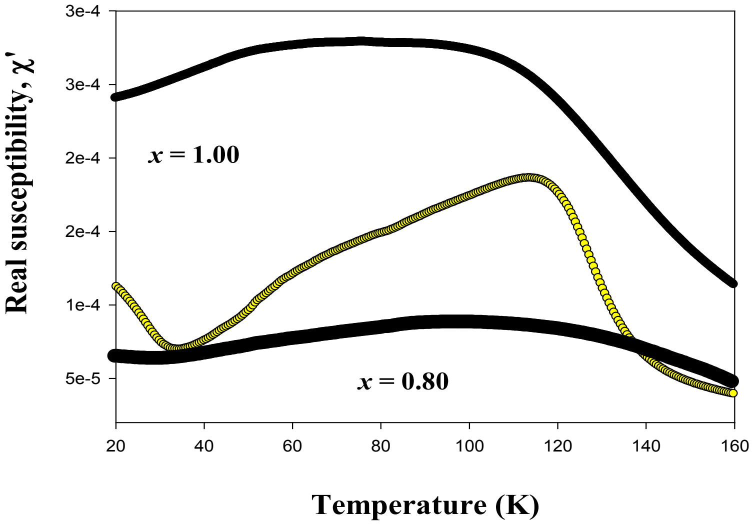

Fig. 6. AC susceptibility (real part) versus temperature plots for the compounds in the temperature range of 20 K – 300 K for $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ (x = 0.80 – 1.0) samples

4. Conclusions

In conclusion, this study investigated the interaction between Co and Mn ions in hole-doped $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ cobaltite to understand the behaviour of spin states and magnetic frustration, with a focus on the induction of the double-exchange (DE) mechanism. The X-ray diffraction analysis confirmed that the $La_{0.6}Dy_{0.1}Ca_{0.3}Co_{1-x}Mn_xO_3$ samples with $x = 0.0$ and 0.2 exhibited a rhombohedral crystal structure with a specific space group. However, as the Mn substitution level increased ($x = 0.4$–1.0), an orthorhombic perovskite structure (*Pbnm*) was observed, accompanied by an increase in cell volume. The temperature-dependent resistivity measurements demonstrated semiconducting behaviour across the entire temperature and composition range of $x = 0.0$–0.8. Notably, further substitution with $x = 0.9$ and $x = 1.0$ exhibited a remarkable metal-insulator (MI) transition behaviour. The results also revealed that the substitution of Mn ions for Co ions triggered a transition from a high spin state to a low spin state, resulting in magnetic frustration. However, the presence of Mn partially alleviated this frustration by inducing the DE mechanism. The magnetic properties of the samples exhibited strong dependence on the concentration of Mn. At $x = 0.9$, a maximum transition temperature (T_c) of 158

K was observed, indicating a transition from the paramagnetic (PM) to the ferromagnetic (FM) phase. Although the compound at $x = 0.9$ displayed slightly lower magnetic susceptibility compared to the compound at $x = 0.8$, it was interesting to note that the Mn substitutions at $x = 0.9$ revived both ferromagnetism and metallic conductivity. These findings underscore the significant role played by Mn ions in determining the magnetic properties of the cobaltite system.

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