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Extraordinary features of Mn site substituted Pr based doped rare earth manganites $Pr_{3/5}Ca_{2/5}Mn_{1-x}Zn_xO_3$(x=0.00 & 0.15)

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After the discovery of Colossal Magneto-Resistance (CMR) in the hole doped manganites, many scientists have carried out a variety of site selective substitutional studies on them to understand the underlying mechanism for this unique behaviour. In this paper, we have studied the fascinating features of Mn site substituted Pr based Doped rare earth Manganites $Pr_{3/5}Ca_{2/5}Mn_{1-x}Zn_xO_3$(x=0.00 & 0.15). The variation of physical properties like grain size, average valence of Mn site were observable and AC susceptibility measurement indicates disappearance of charged ordering. It is due to variable range hopping mechanism and magnetization verses applied field loop taken at 5K for both the compound $Pr_{3/5}Ca_{2/5}Mn_{1-x}Zn_xO_3$(x=0.00 & 0.15).x = 0.00 shows metamagnetic transition and x = 0.15 shows ferromagnetic nature at 5K < T_{co}. This shows increasing the population of hopping electrons and Mn^{3+}/Mn^{4+} ratio are present in this compound.

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Keywords: Colossal Magneto-Resistance (CMR), Hole doped manganites average valence, Metamagnetic transition

1. Introduction

Effect of substitution at the Mn site depends on the nature of the compound on which substitution is undertaken viz Fe, Co, Ni, Cr ion [1-4]. R. Ganguli et. al [5] studied the electrical and magnetic properties of the CMR compound $La_{0.67}$ $Ca_{0.33}$ $Mn_{1-x}Co_xO_3$ $0.00 \leq x \leq 0.40$. They have found that substitution of Co for Mn did not change any crystal symmetry and ferromagnetism got suppressed by dopants. For x = 0.00and 0.05. It showed the ferromagnetic behaviour. The value of Tc and intensity of magnetization were decreased systematically with increase in x. This indicates that oxygen content in compound is stable and remains close to three. But in the Fe doped perovskite viz. $La_{0.67}$ $Ca_{0.33}$ $Mn_{1-x}Fe_xO_3$ [6]. when x = 0.1, the magnetization and Tc were more than Co doped CMR compound and Co doped CMR compound Tc and magnetization were more than Cr doped compound. HS (Higher Spin) and LS (Lower Spin) trivalent Co ions take part in the exchange interaction. The hysteresis loop taken at 5K for the compound $La_{1/2}$ $Ca_{1/2}$ $Mn_{1-x}Cr_xO_3$, compounds shows I-M transition x < 0.10 [7 – 11]. This indicates that Fe, Co, Cr ion were not participating in the D E process. But 10% of Cr supressed I – M transition by retaining the ferromagnetic character because Cr was not participating in the DE process. Zn substituted $La_{2/3}$ $Ca_{1/3}$ $Mn_{1-x}Zn_xO_3$ compounds were studied by many scientists. They concluded that -$La_{1/2}$ $Ca_{1/3}$ MnO_3 is substituted by Zn its resistively transfers from 269K to 112K. For LCMZO when T <112K, $\rho/\rho o$ – T shows its metallic properties. When T >112K, perfect linearity of log $\rho/\rho o$ – $T^{-1/4}$. was observed [12].

2. Experimental

Mn site substituted Pr based Doped Rare Earth manganites were prepared by solid state Reaction method of MnO_2(purity not less than 99%) Zn Oxide (Aldeich, 99.99%) mixed according to desired stoichomety in a silica crucible and prepared in the air at around 1000^{0}C . The mixture is heated by the furnace at 1300^{0}C for 24h. the mixture is heated again for long period of 30h and pressed to convert it into pellet form.

3. Results and discussion

$Pr_{3/5}$ $Ca_{2/5}$ $Mn_{0.85}Zn_{0.15}O_3$ was prepared through the conventional solid state reaction. For comparison bulk $Pr_{3/5}$ $Ca_{2/5}$ MnO_3 was also fabricated simultaneously by the same method.

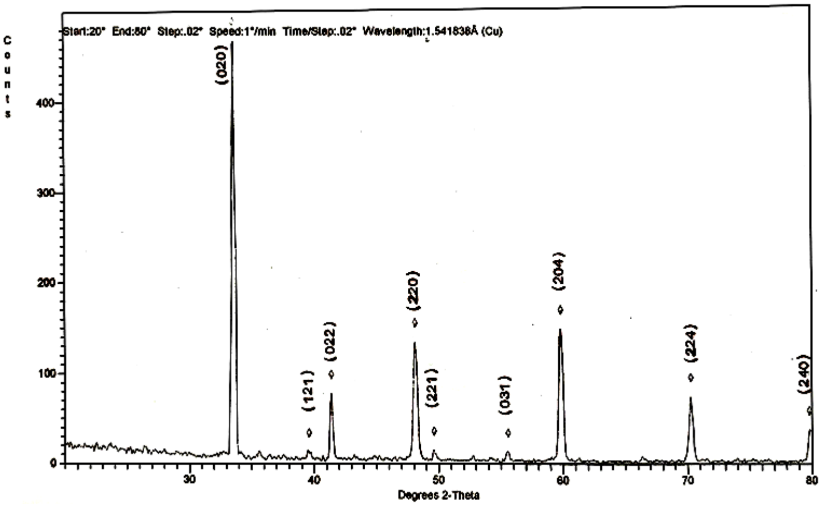

Fig.1. X-ray diffraction pattern of $Pr_{3/5}Ca_{2/5}MnO_3$.

The X – ray diffraction pattern of $Pr_{3/5}$ $Ca_{2/5}$ MnO_3 & $Pr_{3/5}Ca_{2/5}$ $Mn_{0.85}Zn_{0.15}O_3$ are shown in Figs. 1 and 2, respectively. The corresponding tables (I &II) are attached herewith. X-ray diffraction shows the total of 8 peaks are observed in $Pr_{3/5}$ $Ca_{2/5}$ MnO_3, similarly a total of 10 peaks are observed in $Pr_{3/5}$ $Ca_{2/5}$ $Mn_{0.85}Zn_{0.15}O_3$.

Table 1. Shows the diffraction pattern of $Pr_{3/5}$ $Ca_{2/5}MnO_3$.

S. No	Angle	Counts	D space	Rel I	h	k	l
1	33.608	469	2.667	100	0	2	2
2	39.6	13	2.276	3	1	2	1
3	41.394	78	2.181	17	0	2	2
4	48.121	135	1.891	29	2	2	0
5	49.64	15	1.837	3	2	2	1
6	55.58	13	1.654	3	0	3	1
7	59.819	150	1.546	32	2	0	4
8	70.26	75	1.34	16	2	2	4
9	79.82	38	1.202	8	2	4	0

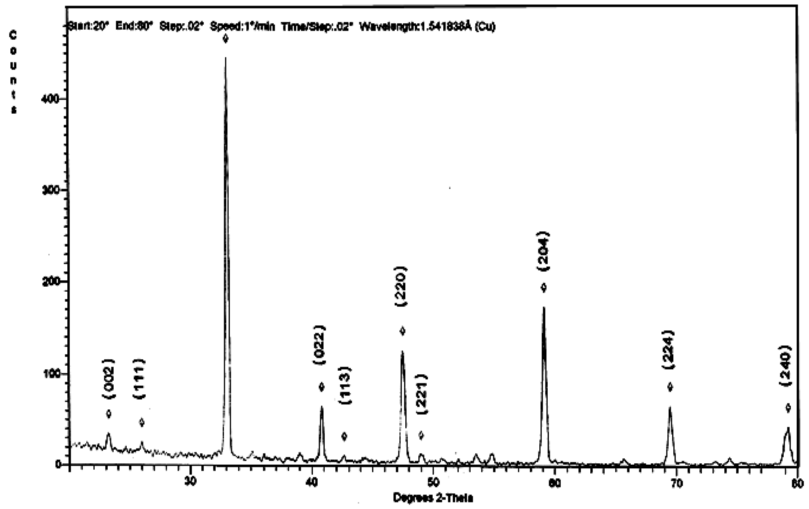

Fig. 2. X-ray diffraction pattern of $Pr_{3/5}Ca_{2/5}Mn_{0.85}Zn_{0.15}O_3$.

Table 2. Shows the diffraction pattern of $Pr_{3/5}\,Ca_{2/5}Mn_{0.85}Zn_{0.15}O_3$.

S. No.	Angle	Counts	D space	Rel I	h	k	L
1	23.24	35	3.827	8	0	0	2
2	25.98	26	3.43	6	1	1	1
3	33.095	445	2.707	100	0	2	0
4	40.82	66	2.211	15	0	2	2
5	4.68	12	2.118	3	1	1	3
6	47.498	126	1.914	28	2	2	0
7	49	13	1.859	3	2	2	1
8	59.14	174	1.562	39	2	0	4
9	69.48	67	1.353	15	2	2	4
10	79.24	44	1.209	10	2	4	0

The X-ray diffraction pattern indicates that both PCMO and PCMZO have single phase & without any other secondary or impurity phase.

All the patterns were indexed on the basis of Pbnm space group.

Table 3.

x	a(A)	b(A)	c(A)	$V(A^3)$
0.00	5.44	5.44	7.615	225.35
0.15	5.3363	5.3363	7.6098	216.697

The Table 3 shows decrease in the value of lattice parameters and lattice volume. It is established that Zn^{2+} occupying the sites of Mn^{3+} ions (0.70A).

XLAT program confirm the above value of lattice parameter and the volume of the unit cell.

There is enough evidence of great influence of Mn ions in these materials.Theoretically speaking, as soon as the average valency of Mn ions are changed, the whole CMR materials get changed.

For example we studied the following materials and the effect of valency changed of Mn ions thereupon:-

First La based manganites

1) $La^{3+}_{2/3}\,Ca^{2+}_{1/3}\;Mn^{V}_{1-x}\,Zn^{2+}_{x}\;O_3^{2-}$
2) $La^{3+}_{2/3}\,Ca^{2+}_{1/3}\;Mn^{V}_{1-x}\,Ga^{3+}_{x}\;O_3^{2-}$
3) $La^{3+}_{2/3}\,Ca^{2+}_{1/3}\;Mn^{V}_{1-x}\,A^{4+}_{x}\;O_3^{2-}$

(1) To find the average valency of Mn ions for material (1) as we know that

(a) Lanthanum (La) has got valency of 3+
(b) Calcium (Ca) has got valency of 2+
(c) Zinc (Zn) has got valency of 2+
(d) Oxygen (O) has got valency of 2-

$$(2/3)\times 3 + (1/3)\times 2 + V(1-x) + 2x - 3\times 2 = 0$$

$$V = \frac{10-6x}{3(1-x)}$$

So we found out that the valecny of Mn ions comes out to be:

$$\frac{10-6x}{3(1-x)}$$

So the value of V depends upon the value of x i.e. composition of divalent ion.

2) For Ga3+ i.e. Galium which is trivalent ion we find that,

For $La^{3+}_{2/3}\,Ca^{2+}_{1/3}\;Mn^{V}_{1-x}\,Ga^{3+}_{x}\;O_3^{2-}$

$$(2/3)\times 3 + (1/3)\times 2 + V(1-x) + 3x - 3\times 2 = 0$$

$$V = \frac{10-9x}{3(1-x)}$$

So we found out that the value of V is definitely dependant upon the value of x.

2) For tetravalent ions i.e. 4+, if we assume to have an ion of A having valency of 4+

$La^{3+}_{2/3}\,Ca^{2+}_{1/3}\;Mn^{V}_{1-x}\,A^{4+}_{x}\;O_3^{2-}$

As earlier, we proceed with the valency

$$(2/3)\times 3 + (1/3)\times 2 + V(1-x) + 4x - 3\times 2 = 0$$

$$V = \frac{10-12x}{3(1-x)}$$

We summarised our finding in a table annexed herewith.

Pr based manganites.

1. $Pr^{3+}_{3/5}\,Ca^{2+}_{2/5}\;Mn^{V}_{1-x}\,Zn^{2+}_{x}\;O_3^{2-}$

2. $Pr^{3+}_{3/5}\ Ca^{2+}_{2/5}\ Mn^{V}_{1-x}\ Ga^{3+}_{x}\ O_3^{2-}$
3. $Pr^{3+}_{3/5}\ Ca^{2+}_{2/5}\ Mn^{V}_{1-x}\ A^{4+}_{x}\ O_3^{2-}$

1. We find the average valency of Mn ions for materials as we know that

a) Preaseodynium (Pr) has got valency of 3^+
b) Calcium (Ca) has got valency of 2+
c) Zinc (Zn) has got valency of 2+
d) Oxygen (O) has got valency of 2-

$$(3/5) \times 3+ \ (2/5) \times 2 + V(1-x) + 2x - 3 \times 2 = 0$$

$$V = \frac{17 - 10x}{5\,(1 - x)}$$

2) For Ga3+ i.e. Galium, which is trivalent ion we find that,

For $Pr^{3+}_{3/5}\ Ca^{2+}_{2/5}\ Mn^{V}_{1-x}\ Ga^{3+}_{x}\ O_3^{2-}$

$$(3/5) \times 3 + (2/5) \times 2 + V(1 - x) + 3x - 3 \times 2 = 0$$

$$V = \frac{17 - 15x}{5\,(1 - x)}$$

3) For tetravalent ions i.e. 4+, if we assume to have an ion of A having valency of 4+

$Pr^{3+}_{3/5}\ Ca^{2+}_{2/5}\ Mn^{V}_{1-x}\ A^{4+}_{x}\ O_3^{2-}$

As earlier, we proceed with the valency

$$(3/5) \times 3 + (2/5) \times 2 + V(1 - x) + 4x - 3 \times 2 = 0$$

$$V = \frac{17 - 20x}{5\,(1 - x)}$$

We summarized our finding in a Tables 4 and 5.

Table 4. Value of average valency 'V' of Mn in La based manganites.

S. No.	Value of x	Divalent (2+) substitution $V = \frac{10 - 6x}{3(1 - x)}$	Trivalent(3+) substitution $\frac{10 - 9x}{3(1 - x)}$	Tetravalent(4+) substitution $\frac{10 - 12x}{3(1 - x)}$
1	0.00	3.33	3.33	3.33
2	0.10	3.48	3.37	3.25
3	0.15	3.57	3.39	3.21
4	0.20	3.66	3.42	3.16
5	0.25	3.77	3.44	3.11
6	0.30	3.90	3.47	3.04
7	0.35	4.05	3.51	2.97
8	0.40	4.22	3.55	2.88
9	0.45	4.42	3.60	2.78
10	0.50	4.66	3.66	2.66

Table 5. Value of average valency 'V' of Mn in Pr based manganites.

S. No.	Value of x	Divalent (2+) substitution $V = \frac{17 - 10x}{5(1 - x)}$	Trivalent(3+) substitution $\frac{17 - 15x}{5(1 - x)}$	Tetravalent(4+) substitution $\frac{17 - 20x}{5(1 - x)}$
1	0.00	3.40	3.40	3.44
2	0.10	3.55	3.44	3.33
3	0.15	3.64	3.47	3.29
4	0.20	3.75	3.50	3.25
5	0.25	3.86	3.53	3.20
6	0.30	4.00	3.57	3.14
7	0.35	4.15	3.61	3.07
8	0.40	4.33	3.66	3.00
9	0.45	4.54	3.72	2.90
10	0.50	4.80	3.80	2.80

Here, too, we infer that the value of V depends in a great deal upon the value of 'x'. The table shows. in the both of case as the value of x increases, the value of V increases, but for the fixed composition, i.e. x remaining constant, the value of V decreases as we go from less valency to high valency (i.e. from divalent to trivalent and from trivalent to tetravalent.)

Tables 6 and 7 show EDXS analysis of the $Pr_{3/5}$ $Ca_{2/5}$ $Mn_{1-x}Zn_xO_3$. x = 0 & 0.15 These show the EDXS analysis of the the $Pr_{3/5}$ $Ca_{2/5}$ MnO_3, $Pr_{3/5}$ $Ca_{2/5}$ $Mn_{0.85}Zn_{0.15}O_3$. It also shows a good homogeneity with experimental error in the composition.

Table 6. EDXS analysis for $Pr_{3/5}$ $Ca_{2/5}MnO_3$.

S. No.	Elements name	Weight percent	Atomic percent	X2
1	Ca	9.60	18.78	37.56
2	Mn	35.53	50.69	101.3
3	Pr	54.87	30.53	61.06

Table 7. EDXS analysis for $Pr_{3/5}$ $Ca_{2/5}Mn_{0.85}Zn_{0.15}O_3$.

S. No.	Elements name	Weight percent	Atomic percent (X)	X2
1	Ca	9.60	18.78	37.56
2	Mn	30.2	42.79	85.58
3	Zn	5.239	7.9	15.8
4	Pr	54.87	30.53	61.06

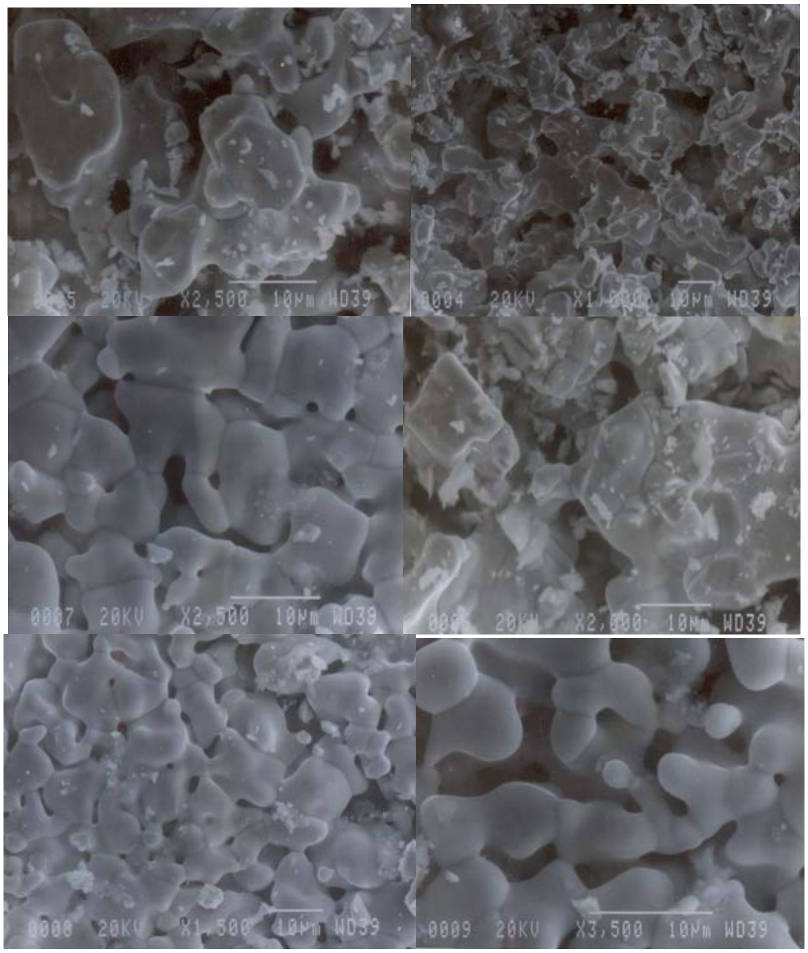

Fig. 3. The scanning electron microscopy under different magnifications 1000 2500,2000 for $Pr_{3/5}Ca_{2/5}MnO_3$ and 2500,1500,3500 magnifications for $Pr_{3/5}Ca_{2/5}Mn_{0.85}Zn_{0.15}O_3$.

Fig. 4 shows χ_{AC} - T data for x = 0.0 a peak around T_{CO} = 230 K Indicate charge ordering (CO) transition x= 0.15 coexisting of AFM and FM ordering charge ordering disappears. It disappears due to variable range hopping mechanism.

Fig. 5 shows the M versus H curves for $Pr_{3/5}$ $Ca_{2/5}$ MnO_3 at 5 K. It exhibits a field induced metamagnetic transition (spin flip) to FM at T < Tco Magnetization is small and monotonically increases up to a certain critical field. It rises sharply before tending toward saturation. This also confirm the presence of Mn^{3+}/Mn^{4+} ratio.

Fig. 6 shows the magnetization versus applied magnetic field loop for the compound $Pr_{3/5}$ $Ca_{2/5}$ $Mn_{0.85}Zn_{0.15}O_3$ taken at 5 K and field ranging between 15T and 15T.

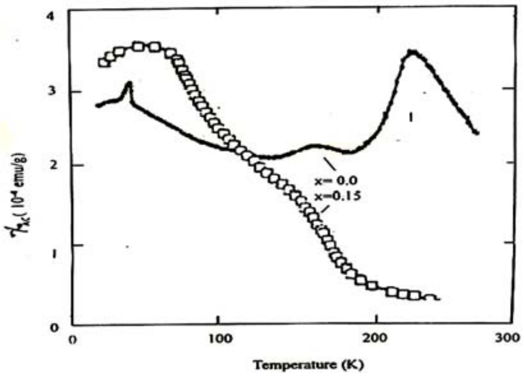

Fig. 4. Temperature dependence of AC susceptibility for $Pr_{3/5}Ca_{2/5}MnO_3$ *&* $Pr_{3/5}Ca_{2/5}Mn_{0.85}Zn_{0.15}O_3$.

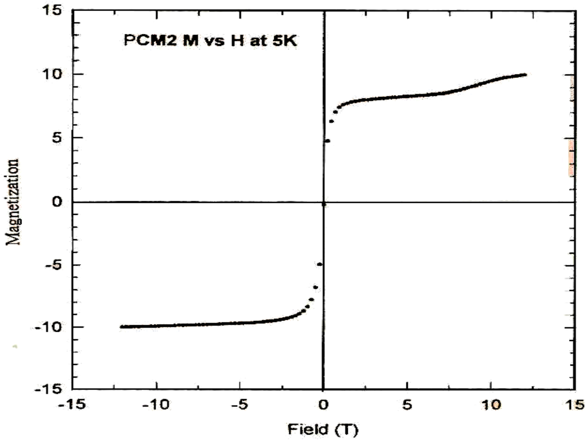

Fig. 5. Magnetization versus applied field loop for $Pr_{3/5}Ca_{2/5}MnO_3$ *at 5K.*

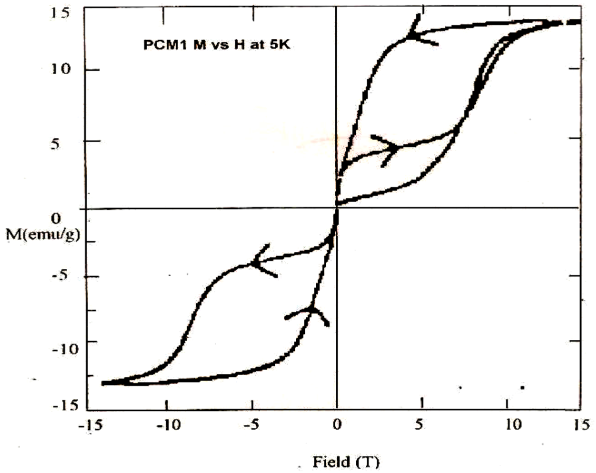

Fig. 6. Magnetization versus applied field loop for $Pr_{3/5}Ca_{2/5}Mn_{0.85}Zn_{0.15}O_3$ *at 5K.*

This curve has been taken in order to study the H dependence of magnetic ordering . When Mn is substituted by Zn the degree of disorder of the system decreases. This doping also causes a depletion of the Mn^{3+}/Mn^{4+} ratio and the increasing population of hopping electron. The compounds are of ferromagnetic nature at 5K<Tco. Coupling constant Jij of the moments decreases. This leads to possible MR being broadened.

References

[1] A. Baranbe, A. Maigan, M. Hervieu, F. Damay, C. Martin, B. Raveau, Appl. Phys. Lett. **71**, 3907 (1997).

[2] B. Raveau, A. Maignan, C. Martin, J. Solid State Chem **130**,162 (1997).

[3] B. Raveau, A. Maignan, C. Martin, J. Solid State Chem. **137**, 365 (1998).

[4] D. Uthra, Bulg. J. Phys. **35**, 125 (2008).

[5] R. Gangoli, I. K. Gopal krishnan, J. V. Yakhmi, Physica **B266**, 332 (1999).

[6] Jian Wang, Cong wang, Bao Gen Chem, Jian Gao Zhao Wen Shan Zhan Appl. Phys. Lett. **71**(12), 1727 (1997).

[7] N. Gayathri, A.K. Roychaudhari, S.K. Tiwari, R. Guddakara A. Arulraj, C.N.R. Rao, Phys. Rev. B **56**, B45 (1997).

[8] M. Rubinstein, D. J. Gillespie, J. E. Snyder, T. M. Tritt, Phys. Rev. B **56**, 5412 (1997).

[9] K. H. Ann, X. W. Wu, K. Liu, C. L. Cwen, Phys. Rev. **B54**, 1 (1996).

[10] S. B. Ogale, R. ShreeKala, S. I. Patil, B. Hannoyer, F. Pettit, G. Marest, Phys. Rev. B **57**, 7841 (1998).

[11] M. Sahana, K. M. Satyalaxmi, M. S. Hegde, V. Prasad, S. V. Subramanyam, Mater. Res. Bull **32**, 831 (1997)

[12] N. F. Mott, Adv. Phys. **21**, 785 (1972).

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