Ni and Fe substitutional effects on Metal Insulator transition in $GdBaCo_2O_{5.5\pm\delta}$ cobaltite

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Abstract. Differential scanning calorimetry (DSC) and DC electrical resistivity measurements have been carried out on GdBaCo2O5.5±δ with Ni and Fe substitution at Co lattice site to probe the variation of metal insulator (MI) transition of the parent compound. XRD results show systematic variation in cell parameters with both substitutions implying that both Ni and Fe substitute at Co lattice. Ni strongly alters MI transition whereas Fe shows less influence. It was observed that Ni substitution suppresses the metal insulator transition temperature at the rate of ~5.05K/ at %. Fe substitution does not alter TMI much but diminishes MI transition.

Keywords: DSC, DC, Ni and Fe substitute.

1 Introduction

This The strong interplay between, electrical, magnetic and structural properties of $REBaCo_2O_{5+\delta}$ (RE - Rare earth) cobaltite is of great research interest nowadays. [1-11]. In particular $GdBaCo_2O_{5+\delta}$ is of great interest because they present intriguing properties such as metal insulator (MI) transition associated with spin state transitions, magnetic transitions like paramagnetic-ferromagnetic (PM-FM) followed by ferromagnetic – weak anti ferromagnetic (FM-AFM) and shows MR effect near later transition [12-16]. The competition among the spin, charge, orbital and lattice degrees of freedom [12-16] drives the system with remarkable properties The oxygen content δ ($0\leq\delta\leq1$) of the system decides the valency of cobalt ions in this system. If δ=0.5, then all the cobalt ions are expected to be in trivalency. Various possible valence states (Co^{2+}, Co^{3+}, and Co^{4+}) and spin states of cobalt ions (Low , high and intermediate spins) are expected in this system because of their small and comparable energy difference among various[7]. These compounds formed by the The stacking of [CoO_2] [BaO] [CoO_2] [GdO_δ] along c-axis, co-ordinate environments such as pyramidal CoO_5 and octahedral CoO_6.

The first systematic study of oxygen deficient $GdBaCo_2O_{5+\delta}$ was carried out by A. Maignan et al has observed that all members of this family with intermediate lanthanides (from Sm to Dy) showed temperature induced Metal – Insulator transition and was very clear that transition temperature depends on R^{3+} ionic radius and varies from 310K- to 360K [2]. Later this MI transition was observed in $GdBaCo_2O_{5.5}$ and $TbBaCo_2O_{5.5}$. Unusual structural changes and magnetic transtitions have been observed in these system across T_{MI} [7,14,17,18].

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Maignan et al suggested a spin state scenario based on the measured effective magnetic moments that there is a co-existence of IS Co^{3+} (pyramidal co-ordinate) and LS Co^{3+} (octahedral co-ordinate) when $T< T_{MI}$ and both states evolving towards HS Co^{3+} in both the environments above T_{MI} [2]. Moritomo et al proposed a model based on the investigations carried out on $TbBaCo_2O_{5+\delta}$ that there is a spin state switching from HS Co^{3+} to IS Co^{3+} across MI leads to $d_{x^2-r^2}$/ $d_{y^2-r^2}$ type orbital ordering (OO) because of the presence of IS Co^{3+}. This OO causes localization of electrons suppresses metallicity [14]. The lateral studies on $GdBaCo_2O_{5.5}$ ruled out the possibility for OO but gives the indication for switching of Co^{3+} LS (Octahedral co-ordination) to HS Co^{3+} (octahedral co-ordination) due to sudden increase in temperature and Co^{3+} IS (pyramidal co-ordination) continues in same spin and environment. It was concluded that the former transition introduces itinerant electron to e_g level leads to conductivity at elevated temperature [6,7,19]. Furthermore, a different picture was proposed based on the oxygen isotopic effect (OIE) of $GdBaCo_2O_{5.5+\delta}$ that this kind of transition was observed in nikelates which was explained on the basis of Jahn- Teller (JT) polaron model and it was not of magnetic origin [20]. So it has been concluded that this MI transition is because of the tendency of IS Co^{3+} in perovskite leads to Jahn- Teller polaron type interaction between the distorted lattice and the delocalized electrons in turn reduces the conduction band- width presents insulating behavior and this was confirmed by density functional calculations [21-24]. This work was aimed on the investigation of the influence of Fe and Ni substitution at Co sublattice on MI transition of the pristine compound by forming the series of $GdBaCo_{2-x}Ni_xO_{5.5+\delta}$ and $GdBaCo_{2-x}Fe_xO_{5.5+\delta}$. DC electrical resistivity and differential scanning calirimetry methods were used as tools to trace the changes in MI transition.

2.Experimental details

Polycrystalline samples of the series $GdBaCo_{2-x}Ni_xO_{5.5+\delta}$ (x=0, 0.05, 0.1, 0.2, 0.3 and 0.4) and $GdBaCo_{2-x}Fe_xO_{5.5+\delta}$ (0, 0.1, 0.2, 0.3 and 0.4) have been synthesized using conventional solid state reaction method. Starting oxides Gd_2O_3, $BaCo_3$, Co_3O_4, NiO and Fe_3O_4 (for Fe doping) were mixed together and decarbonation was done at 850°C for 3hrs in air. Powders were pelletized and sintered at 1050°C for 30hrs in air atmosphere. This procedure was repeated several times for homogeneous samples. Phase purity of the prepared samples were examined by x-ray powder diffraction using STOE diffractometer with Cu Kα line. DC resistivity measurements were carried out using standard van der Pauw four probe method in the temperature range 4.2 – 450K. Differential scanning calorimetry measurements were performed on Ni and Fe series of samples using Mettler DSC 821^e instrument during heating in the temperature range 200-450K with Argon stream was used as protecting gas.

3.Results

3.1 XRD Characterization:

XRD patterns of the samples were recorded at room temperature Primitive orthorhombic structure with Pmmm symmetrywas identified in all the samples prepared. Samples were phase pure for $x\leq0.4$ in both the substitutions. In the case of Ni substitution when $x> 0.4$, a small fraction of Gd_2BaNiO_5 forms, which remains even with repeated grinding and heat treatment. Lattice parameters a,b, and c of the series of samples have been extracted using PCW program. Fig.1 shows the variation of cell parameters as a function of Ni and Fe content.

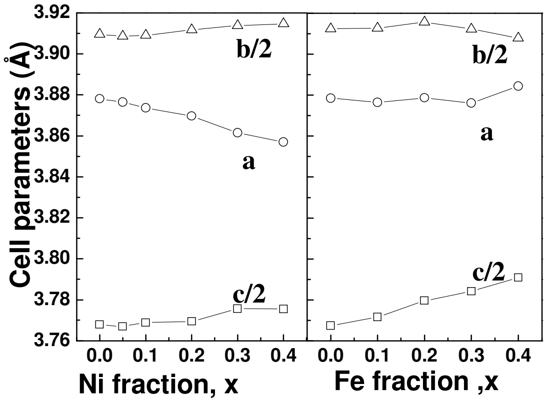

Fig.1: Variation of lattice parameters as a function of Ni and Fe concentration.

It is clear from the figure that a- lattice parameter monotonically decreases with Ni content whereas it remains more or less unaltered with Fe substitution. c-axis increases in both the substitution and b increases slightly with Ni content but remains unaltered with Fe doping.

3.2 DC electrical resistivity:

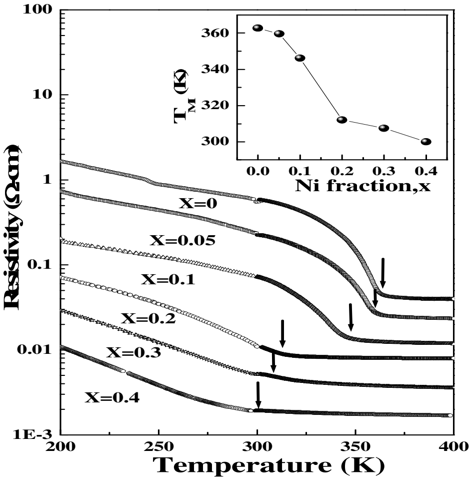

Fig.2: Temperature dependence of resistivity (data shifted along y- axis for better identification) of $GdBaCo_{2-x}Ni_xO_{5.5+\delta}$ for various Ni concentration. Variation of T_{MI} with Ni substitution is given as inset in the graph

Fig. 2 shows the resistivity variation of Ni substituted samples as a function of temperature in the temperature range 200 – 400K. The pristine compound shows insulating behavior up to a certain temperature and resistivity drops at higher temperature which is attributed to insulator to metal transition with T_{MI}=362K. The variation of T_{MI} with Ni content is indicated by arrows at the resistivity jump. It is clear from the variation that T_{MI} decreases and shifts towards lower temperature regime with Ni concentration. The T_{MI} also broader with Ni content increases.

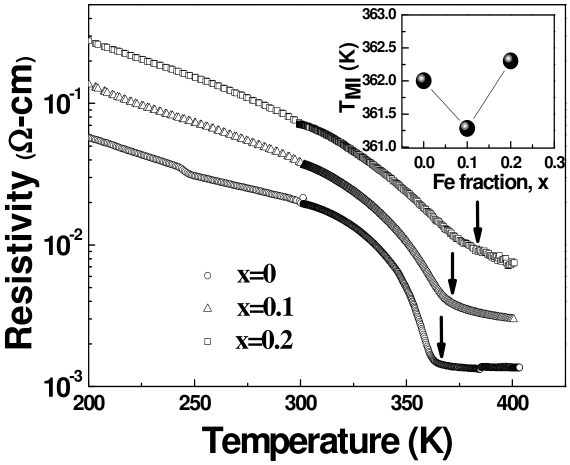

Fig.3: Temperature dependence of electrical resistivity (data shifted along y- axis for better identification) of $GdBaCo_{2-x}Fe_xO_{5.5+\delta}$ for various Fe concentration.. Variation of T_{MI} with Fe substitution is given as inset in the graph

Fig. 3 shows the temperature dependence of resistivity of Fe substituted (x=0,0.1, and 0.2) samples. It is evident from the results that there is no identifiable change in T_{MI} when the system is doped with Fe. T_{MI} is fluctuating within ± 1K. It can be assumed that T_{MI} is not much modified by Fe substitution.

3.3 Differential scanning calorimetry:

Differential scanning calorimetry measurements were carried to trace the substitution effects on metal insulator transition of the parent compound. An evident transition is observed which corresponds to MI transition.

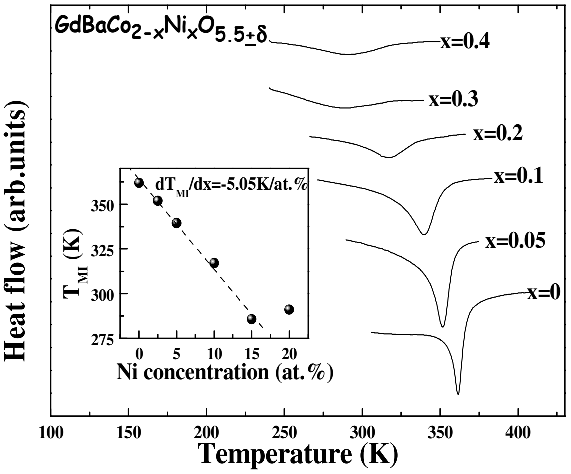

Fig.4: DSC signals of $GdBaCo_{2-x}Ni_xO_{5.5+\delta}$ for various Ni concentration (data shifted along y- axis for better clarity) as a function of temperature. Variation of T_{MI} with Ni content is included as inset of the graph.

Fig.4 shows the DSC signals taken from Ni substituted $GdBaCo_2O_{5.5\pm\delta}$ samples, where the endotherms associated with metal insulator transition are clearly seen. It is evident from the figure that the peaks associated with transition become broader and shifts to lower temperature regime with Ni substitution. Inset of Fig.4 shows the variation of T_{MI} as a function of Ni concentration. Ni substitution alters T_{MI} from 360K to ~ 300k with a suppression rate of T_{MI} ~5.05K/at%.

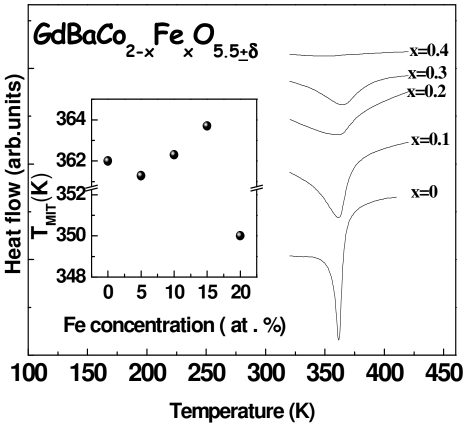

Fig.5: DSC signals of $GdBaCo_{2-x}Fe_xO_{5.5+\delta}$ for various Fe concentration (data shifted along y- axis for better clarity) as a function of temperature. Variation of T_{MI} with Fe content is included as inset in the graph.

Fig.5 shows the DSC signals taken from the Fe substituted samples. Endotherms are associated with MI transition. It is clear that MI transition of the parent system is less altered by Fe substitution. This substitution also leads to broadening of MI transition peaks.

4.Discussion

In this work we have summarized the changes in metal insulator of the pristine sample $GdBaCo_2O_{5.5\pm\delta}$ upon Ni^{3+} and Fe^{3+} substitution would results in electron and hole doping. The MI transition was observed at T_{MI}=360K in both resistivity and DSC measurements. XRD results confirm that both Ni and Fe substituted samples were phase pure till x=0.4. It was observed that a- lattice parameter decreases and b lattice increases upon Ni substitution results in increased orthorhombicity since it is defined as (b/2-a)/(b/2+a). Iodometry titration done on the samples has been reported elsewhere [25] showed that there is no much variation in the oxygen content implies that both Ni and Co both are in the same valence state. Substituted Ni^{3+} can occupy in both the environments.

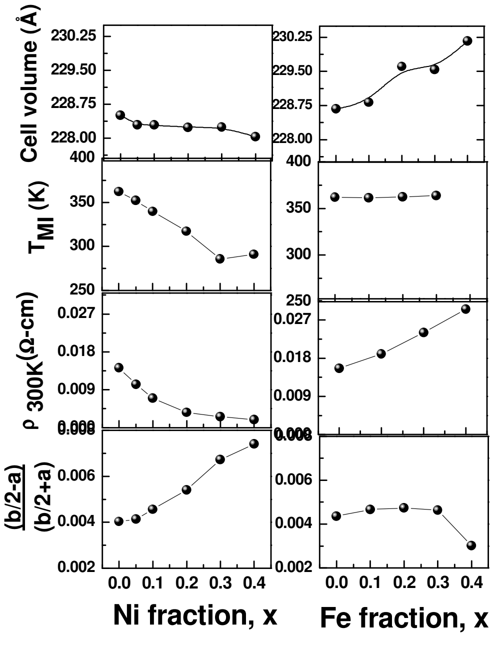

Fig.6: Variation of over all cell volume, TMI, ρ_{300K}, and orthorhombic distortion as a result of Ni and Fe substitution at Co site in $GdBaCo_2O_{5.5+\delta}$.

Fig.6 summarizes the variation of orthorhombicity, cell volume, room temperature resistivity and TMI and indicates that there is a strong correlation among them results in varying T_{MI} upon Ni substitution. Substituting Ni^{3+} having the spin configuration

t_{2g}^{6}, e_{g}^{1}, S=1/2 introduces one e_g electron such that it adds Co^{2+} (HS) to the system thereby it makes the system electron doped. Though room temperature resistivity decreases upon Ni doping, low temperature resistivity shows insulating behavior. This can be explained on the basis of spin blockade mechanism [26]. According to this electron hopping is restricted if it moves in the environment of Co^{3+}(LS) and Co^{3+} (IS) and this could be the reason for insulating behavior at lower temperature. This is shown in Fig.7.

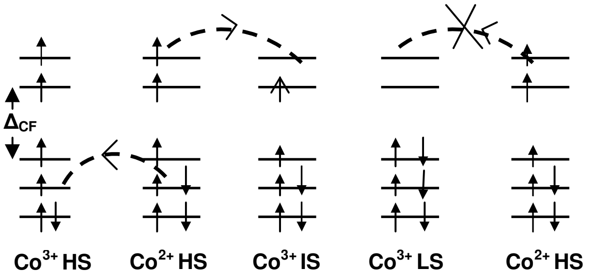

Fig. 7: Spin blockade mechanism in the case of Ni substitution.

The structural change arises due to the increased orthorhombicity could alter the crystal field splitting energy Δ_{CF}. Hence the energy required for the spin state transition reduces in turn shifting the MI transition towards lower temperature regime and also reducing the room temperature resistivity upon Ni substitution.

XRD results reveal that both a and b lattice parameters remain more or less unchanged with Fe doping and there is a huge increase observed in c-axis leads to overall increase in volume of the unit cell. Mossbauer studies on the samples gives the idea that Fe substitutes as Fe^{3+} and occupies octahedral environment [27] . Doping of Fe in the perovskite $LaCoO_3$ leads to around 30% increase in volume and it has been confirmed that Fe^{3+} takes high spin state (HS) rather low spin (LS) [28]. Iodometry titration performed on the samples shows that there is a systematic increase in oxygen content implies that there is a increase in Co^{4+} due to the addition of Fe^{3+} in order to maintain charge balance [27]. This can be considered as this Fe substitution introduces holes in to the system and making the system to be hole doped. It is evident from the fig.6 that there is no noticeable variation in orthorhombicity tells that effect of Fe doping on MI is not of structural change origin. According to A. A. Taskin et al $GdBaCo_2O_{5.5\pm\delta}$ doped with holes by increasing the value of δ direct the system to be metallic. This was explained by spin- blockade mechanism wherein the exchange of spins possible when Co^{4+} (LS) is moving in an environment of Co^{3+} (LS) and Co^{3+} (IS) mixture leads to increased conduction. But in our observation though we introduce Co^{4+} in to the system by adding Fe^{3+}, Co^{4+} does not favors conduction. Instead it increases the room temperature resistivity and this could be explained by spin blockade mechanism. The movement of Co^{4+} in the mixture of Co^{3+} (LS) and Co^{3+} (IS) could leads to conduction. Co^{4+} has also been introduced in the system is due to the addition of Fe^{3+} and always there is a possibility that this could form FeO_6 occupies either in octahedral or in pyramid co-ordination. But the carriers hopping among Fe^{3+} and a mixture of Co^{3+} (LS) and Co^{3+} (IS) is completely restricted. This is clearly explained in the Fig. 8a and 8b.

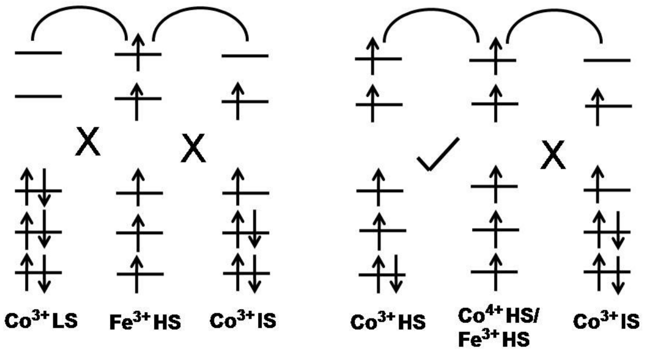

Fig.8a, 8b: spin blockade mechanism in the case of Fe substitution.

As a whole there may not be any net conduction due to the addition of Fe. But there is an another signature of increased volume as a function of Fe content could be the reason for increased resistivity at room temperature. Because volume expansion is normally expected to localize the charges by increasing the excitation gap. Many models have been propped so far to understand this kind of first order MI transition and it was believed that switching of spin states from LS to HS due the addition of thermal energy will introduce an extra electron in e_g orbital in turn causes metallicity. It is very clear from our observations that MI more or less unaffected because of Fe substitution. This can again be understood by spin blockade explained in figure.6. Increase in temperature leads to switching of Co^{3+} (LS) to Co^{3+} (HS) in the octahedral network and Co^{3+} (IS) available in the pyramidal chain remain in the same state. In such a case that Co^{4+} (LS) can also be switched over to Co^{4+} (HS) because Δ_{CF} can be override by thermal excitation. Exchange of spins between Co^{4+} (HS) (Fe^{3+}) and Co^{3+} (HS) is possible but the transfer between Co^{4+} (HS)(Fe^{3+}) and Co^{3+} (IS) is restricted. Finally there will be a cancellation of conduction by means of restriction of spin transfer may lead to very less influence of Fe substitution on TMI. The reduction in enthalpy seen in DSC as a function of Fe and Ni doping is not clear yet and needs further investigation.

5.Summary and Conclusion

Ni and Fe have been substitutedat Cosite in $GdBaCo_2O_{5.5\pm\delta}$ and the influence of the substitution on metal insulator transition has been investigated. Both electron and hole doping showed different effect on MI transition. Ni substitution influences the MI and shits towards lower temperature. This was understood by the structural change which is evidenced by the increase in orthorhombicity. But no remarkable change was observed in MI transition upon Fe substitution and was understood by spin blockade mechanism.

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