Chapter 1

Phase transitions in double perovskite GdBaCo$_2$O$_{5+\delta}$

The present thesis is focussed mainly on the oxygen deficient layered double perovskite GdBaCo$_2$O$_{5+\delta}$. To set the stage for the contents of the thesis, in this chapter, an overview of the description of the system that includes the structure, electronic and magnetic properties is provided. The various phase transitions exhibited by the system that includes the metal insulator transition, paramagnetic to ferromagnetic and antiferromagnetic transitions are described. An outline of the thesis contents is provided at the end of the chapter.

1.1 The layered double perovskite LnBaCo$_2$O$_{5+\delta}$

Perovskite materials have attracted much attention in the last twenty five years. The most famous examples are the high-temperature cuprate superconductors [1] and the colossal-magnetoresistance (CMR) manganites [2]. More recently, a class of layered double perovskite LnBaCo$_2$O$_{5+\delta}$ (Ln= lanthanides; 0 ≤ δ ≤ 1) were synthesized in the search for cobalt analogous of both the layered cuprate superconductors and the perovskite colossal-magnetoresistance manganites. Many interesting behaviors, such as giant magnetoresistance, large Seebeck coefficient, charge ordering, spin blockade, metal-insulator transition, and metamagnetic transformation have been observed in these compounds [2-16]. The crystal structure of the LnBaCo$_2$O$_{5+\delta}$ compounds is closely related to the YBaFeCuO$_5$-type [17]. It consists of a sequence of [CoO$_2$]-[BaO]-[CoO$_2$]-[LnO$_\delta$] layers along the c axis, including a doubling of the original perovskite cell in c direction (a$_p$ x a$_p$ x 2a$_p$ unit
cell, where $a_p$ is the cubic perovskite cell parameter) [18]. The excess-oxygen atoms fill LnO$_6$ layers and have a strong tendency to order into channels along the $a$ direction. Depending on the value of $\delta$, the Co ion coordination changes from purely CoO$_5$-pyramidal ($\delta = 0$) to a coexistence of both CoO$_5$-square pyramidal and CoO$_6$-octahedral ($\delta > 0$). In LnBaCo$_2$O$_{5.5}$ only Co$^{3+}$ ions are present, equally distributed in CoO$_5$ pyramidal and CoO$_6$ octahedral oxygen environment. Figure 1.1 depicts various unit cells of LnBaCo$_2$O$_{5+\delta}$ with different values of $\delta$.

Figure 1.1: Schematic crystallographic structure of LnBaCo$_2$O$_{5+\delta}$ (a) $\delta=0$ with $a_p \times a_p \times 2a_p$ structure, where a mixture of Co$^{2+}$ and Co$^{3+}$ ions are in unique square pyramidal environment (b) $\delta=0.5$ with $a_p \times 2a_p \times 2a_p$ structure, where all Co$^{3+}$ ions are equally distributed in pyramidal and octahedral environment (c) $\delta=1$ with $a_p \times a_p \times 2a_p$ structure, where a mixture of Co$^{3+}$ and Co$^{4+}$ ions are in octahedral unique environment. From Conder et al [19].

In addition to the charge, spin, and orbital degrees of freedom also observed in manganites and cuprates, the phenomenon of spin-state transitions is unique in cobaltites. Spin-state transitions occur due to the near equality of Hund’s intra-atomic exchange and the energy splitting of the cobalt 3d terms caused by crystal fields. Therefore, it is possible to thermally excite a Co ion to a higher spin state. Co$^{2+}$, Co$^{3+}$ and Co$^{4+}$ ions can all exist in multiple spin states. For instance, it is known that Co$^{3+}$ ions are diamagnetic in the low-spin (LS) state $t_{2g}^0 \ e_g^0$ (S=0), while they are paramagnetic in the intermediate-spin (IS) $t_{2g}^5 \ e_g^1$ (S=1) and high-spin (HS) $t_{2g}^4 \ e_g^2$ (S=2) states. Besides, the cobalt ion in the IS and HS configurations is a typical Jahn-
Teller ion, like e.g., Mn\(^{3+}\) \((t_{2g}^3 e_g^1)\) or Cu\(^{2+}\) \((t_{2g}^6 e_g^3)\). Consequently, a cooperative orbital ordering is probable in the compounds containing IS/HS Co\(^{3+}\) ions.

1.2 Metal insulator transition in LnBaCo\(_2\)O\(_{5+\delta}\)

The metal insulator transition (MI) was observed for the first time by Martin et al [3] for both EuBaCo\(_2\)O\(_{5.4}\) and GdBaCo\(_2\)O\(_{5.4}\) at T\(_{MI}\) ~ 360 K. The resistivity curves of these new oxygen deficient perovskites show that a metal insulator (MI) transition occurs at T\(_{MI}\) ~ 360 K separating a nearly constant \(\rho\) region (~10\(^{-3}\) \(\Omega\)-cm values for T\(_{MI}\) > 360K) from an insulating region below 360 K [3] as shown in Figure 1.2(a). The MI transition is in fact related to the paramagnetic to ferromagnetic transition, as shown by the plot of inverse susceptibility in Figure 1.2(b). Such a magnetic transition in the vicinity of MI was explained by spin-state transition [3]. The ac susceptibility studies by Martin et al [3] also noted a steep increase in \(\chi'\) as T decreases associated with the paramagnetic to ferromagnetic transition, a cusp occurs at 275 K as shown in Figure 1.2(c). The sharp decrease in \(\chi'\) below this indicates the ferromagnetic to anti-ferromagnetic transition. In the same work it was shown that the resistivity at T\(_{MI}\) can be tuned with magnetic field leading to a giant negative magnetoresistivity effect (GMR) leaving, however, MI transition unaffected. A large negative magneto resistance of ~ 10 % was observed below 250 K [3].

Following these behavior, several systems have been investigated to look for metal insulator transitions. It was observed that the MI transition only appears for the intermediate lanthanides, i.e., Ln= Sm to Dy [5]. For the larger lanthanides (Ln= Pr, Nd), a semimetallic behaviour is observed in the 100 - 400 K temperature range, whereas for the smaller lanthanide (Ln=Ho) a semiconducting-like behaviour is observed. This study demonstrated a very important role of the oxygen stoichiometry as MI transition was always observed at \(\delta\) ~ 0.5.

The correlation between the metal insulator transition (MIT) and structural parameters was revealed in several synchrotron and neutron diffraction measurements [for example, [7]]. Synchrotron radiation x-ray powder diffraction measurements on...
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Figure 1.2: (a) Temperature dependence of the resistivity $\rho$ of EuBaCo$_2$O$_{5.4}$ (1) and GdBaCo$_2$O$_{5.4}$ (2). (b) Temperature dependence of the inverse of the susceptibility $\chi^{-1}(T)$ for EuBaCo$_2$O$_{5.4}$ (1) and GdBaCo$_2$O$_{5.4}$ (2). In the high temperature paramagnetic region, the effective magnetic moment of EuBaCo$_2$O$_{5.4}$ was found to be 4.7 $\mu_B$ that is close to the theoretical value of 4.9 $\mu_B$ per high spin (HS) state of Co$^{3+}$. (c) Temperature dependence of the real part of the susceptibility $\chi'$ for EuBaCo$_2$O$_{5.5}$ (1 Hz, 0.3 mT). Inset: Enlargement around $T_{\text{cusp}}$ of the $\chi'(T)$ curves registered with f=1, 10, 100 Hz. Although they show large divergence below 280 K, they do not exhibit a clear shift of $T_{\text{cusp}}$ indicating that some magnetic frustration probably exists between ferro and antiferro magnetic interactions but without any signature of a spin-glass state [20]. Taken from Martin et al [3].

TbBaCo$_2$O$_{5.5}$ [7] have been carried out to investigate the changes in the structural parameters across the MIT. These studies revealed that with decrease of temperature, lattice constants show a discontinuous change that indicate a shrinking in the CoO$_5$ pyramids (by ~ 3 %) an (by ~ 5 %) elongation in the CoO$_6$ octahedron. Based on these observations, a significant JT-type distortion was found in the insulating phase ($\leq T_{\text{MI}}$), suggesting a $d_{3x^2-r^2}/d_{3y^2-r^2}$-type orbital alternation along the $b$ axis. Based on these studies, the possible scenario for MIT was constructed. In the high temperature metallic phase with HS Co$^{3+}$ ions, both the octahedral and pyramidal sites
shift from the basal plane towards the apical oxygen. This movement destabilizes the \( d_{3z^2-r^2} \) orbital and causes a spin-state transition of the Co\(^{3+} \) ions from the HS \( (t_{2g}^4 e_g^2) \) to IS \( (t_{2g}^5 e_g^4) \) states. Accordingly the produced orbital degree of freedom couples with the JT instability, and results in a cooperative chain-like distortion. Figure 1.3 illustrates the correlation between MIT and the structural changes in TbBaCo\(_2\)O\(_{5.5}\) based on synchrotron and neutron diffraction measurements [7].

Figure 1.3: (a) Temperature dependence of lattice parameters \( a, b \) and \( c \) of TbBaCo\(_2\)O\(_{5.5}\). Circles and squares are data obtained from x-ray and neutron powder patterns respectively. \( T_{\text{MI}} \) stands for critical temperature for the MI transition. (b) and (c) Temperature dependence of the Co-O bond lengths in CoO\(_3\) pyramids and CoO\(_6\) octahedra of TbBaCo\(_2\)O\(_{5.5}\). \( d_{(Co-O)} \) (i=a, b and c) represent the Co-O bond length along the respective axis (d) Schematic crystal structure and \( d_{3z^2-r^2} / d_{3y^2-r^2} \) orbital ordering in TbBaCo\(_2\)O\(_{5.5}\). Taken from Moritomo et al [7].
On the other hand, the lattice parameters $a$, $b$ and $c$ obtained for GdBaCo$_2$O$_{5.5}$ using ultra-high resolution synchrotron x-ray powder diffraction (SXRPD) \[9\] exhibit different values and thermal evolution in contrast with values reported for TbBaCo$_2$O$_{5.5}$ \[7\]. On cooling through the transition, $b$ and $c$ lattice parameters exhibit sudden shrinking while $a$ lengthens at $T_{MI}$ [see Figure 1.4 (a)] in strong contrast with those reported for TbBaCo$_2$O$_{5.5}$, where $a$ shrinks at $T_{MI}$ and $b/2$ lengthens. Another important difference is the deformation of the octahedra and the pyramids below and above MIT in both the compounds [see Figure 1.4(b) and(c)]. It was found in GdBaCo$_2$O$_{5.5}$ that pyramids and octahedra are deformed in both the insulating and metallic phases; long and short bonds alternate along the $b$ axis at both sides of the transition [see Figure 1.4(d)]. This is different to the evolution reported for TbBaCo$_2$O$_{5.5}$, where such an alternation was only observed below $T_{MI}$ which suggests that the basal plane deformation in pyramids and octahedra vanishes above $T_{MI}$. Hence, the observation on GdBaCo$_2$O$_{5.5}$ discards the stabilization of a $d_{3x^2-r^2}/d_{3y^2-r^2}$ type orbital ordering below $T_{MI}$ as the physical mechanism for the MI transition in GdBaCo$_2$O$_{5.5}$. Based on these observations along with the effective magnetic moment $\mu_{eff}$ obtained using Curie-Weiss fitting to the temperature dependence of inverse susceptibility [see Figure 1.4(e)], it was concluded that the driving force for the MI transition is a spin state switch in the Co$^{3+}$ ions located at the octahedra. They suddenly switch from LS ($t_{2g}^6 e_g^0$) to HS states at $T_{MI}$. Thereby, the metallic conductivity in this family of oxides (full Co$^{3+}$) seems related with the injection of electrons in the conduction band that accompanies the stabilization of a HS ($t_{2g}^4 e_g^2$) state in the CoO$_6$ octahedra. The volume expansion observed here is another confirmation of the transition to the high spin state [see Figure 1.4(f)]. Such a kind of spin state transition was proposed as a most probable scenario for the MI transition [21-23].
Figure 1.4: Temperature dependence of (a) lattice parameters (b) Co-O, bond distances for the CoO$_5$ pyramids (Co-O stands for the bond lengths along i=a, b and c axes) (c) Co-O$_5$ bond distance for the CoO$_6$ octahedra (d) average Co-O distances for the CoO$_6$ and CoO$_5$ polyhedra (e) inverse of the susceptibility $\chi$ Co (the straight lines show the Curie fits above and below $T_{MI}$); (f) unit – cell volume of GdBaCo$_2$O$_{5+\delta}$. Taken from Frontera et al [9].

1.3 Magnetic properties and spin structure of GdBaCo$_2$O$_{5+\delta}$

Extensive magnetization measurements have been reported on single crystals of GdBaCo$_2$O$_{5+\delta}$ by Taskin et al [10] to understand the nature of the magnetic
transitions involved in these systems and a possible magnetic structure has been proposed based on the results. The magnetization of untwinned GdBaCo$_2$O$_{5.5}$ single crystals measured along $a$, $b$ and $c$ axes in the field –cooling process reveals that below 300 K, a net ferromagnetic component appears in the Co sublattice and suddenly vanishes at ~260 K, indicating successive PM-FM-AF transitions [2,4,5,7,8,24] as shown in Figure 1.5(a). A remarkable feature of the FM state is not only the narrow temperature window where it shows up, but is also associated with a very strong anisotropy. It was found that the net FM moment appears only along the $a$-axis, and even the high magnetic field (for example 7 T) is not enough to turn over the magnetic moment along the $b$ or $c$ axis. This behavior suggests the spin system in GdBaCo$_2$O$_{5.5}$ to be Ising like.

Another interesting aspect is that the balance of FM and AF ordering in GdBaCo$_2$O$_{5+x}$ was found to be quite delicate and can be easily affected by temperature, magnetic fields, or even subtle variation in stoichiometry. Magnetic fields applied along the spin easy $a$ axis stabilize the FM state and shift the FM-AF transition to lower temperatures as shown in Figure 1.5(b). If this switching were originating from equally strong and competing AF and FM exchange interactions, spin fluctuations would inevitably be enhanced in the vicinity of the FM-AF phase boundary, smearing the transition. Although the FM-AF balance is subtle, and fairly weak fields (~1.5 T at 240 K) are capable of recovering the FM order, the AF-FM transition remains always sharp, showing that thermal fluctuations are irrelevant here. This behaviour clearly indicates that the observed AF-FM switch occurs within the ordered spin state and is governed by the reorientation of spins in one of the weakly coupled sublattices. A strong ferromagnetic interaction aligns spins within each sublattice, while a much weaker antiferromagnetic (at $T < 260$ K) interaction provides a subtle coupling between the sublattices, which can be broken by an applied field. Based on these results, the saturated net magnetic moment was found to be ~ 1$\mu_B$ / Co which corresponds to 1:1 mixture of low-spin $S=0$ and intermediate-spin $S=1$ states. In fact, a similar conclusion, that Co$^{3+}$ ions exhibit a 1:1 mixture of LS and IS spin states below $T_{\text{MIT}}$ based on the Curie-Weiss fitting of the PM susceptibility [2,8,10] in the temperature range as well as based on the structural data [9] can be inferred.
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Figure 1.5: (a) Magnetization of an untwinned GdBaCo$_2$O$_{5.5}$ crystal measured in H= 0.1 T applied along one of the crystal axes. Inset: raw magnetization data for field applied along $a$ axis, where the solid line shows the Curie-Weiss contribution of Gd$^{3+}$ ions. (b) Magnetization of GdBaCo$_2$O$_{5.5}$ measured in different magnetic fields applied along $a$ axis. Kinks at $T = 360$ K correspond to the metal-insulator transition. Taken from Taskin et al [10].

Based on these observations, a picture of the magnetic ordering in GdBaCo$_2$O$_{5.5}$ has been proposed by Taskin et al [10] which is illustrated in Figure 1.6(a). The alternating filled and empty oxygen chains create two types of structural environment, octahedral and pyramidal, for Co$^{3+}$ ions; the former favors the nonmagnetic LS ground state, while the latter makes the IS state preferable. At high temperatures, the entropy keeps the cobalt ions in octahedral positions in the HS state, and the compound behaves as a paramagnet composed of IS and HS Co$^{3+}$ ions. Upon cooling below $T_{MIT} < 360$ K, the octahedral cobalt ions cooperatively switch into the LS state, and thus the CoO$_2$ planes develop a spin-state order consisting of alternating rows of Co$^{3+}$ ions in the LS and IS states. Consequently, the magnetic cobalt ions form two-leg ladders extended along the $a$ axis and separated from each other by nonmagnetic CoO$_2$ $ac$ layers along the $b$ axis and by paramagnetic GdO$_{0.5}$ layers along the $c$ axis as shown in Figure 1.6 (a).
Figure 1.6: (a) A sketch of the crystal and magnetic structure of GdBaCo$_2$O$_{5+\delta}$ [10]. Owing to the ordering of oxygen (small shaded spheres) into alternating empty and filled chains, the Co ions become non-equivalent and exhibit either an IS state (black spheres, where occupied $d_{x^2-y^2}$ or $d_{z^2}$ orbitals are shown), or a LS state (shaded spheres). Ba and Gd are not shown. (b) The $b$-axis interaction of IS-Co$^{3+}$ ions mediated by LS-Co$^{3+}$ results in AF ordering. (c) Excited (Co$^{2+}$) ions switch the $b$-axis interaction into the FM one. Taken from Taskin et al [10].

The magnetic ordering in insulators is known to be predominantly caused by the superexchange (SE) interaction [25,26]. The FM spin order in ladders explained by the orbital ordering among IS Co ions is shown in Figure 1.6(a). Owing to the reduced dimensionality (quasi-1D/2D) of the ladders, the FM order develops quite gradually upon cooling. Eventually, FM-ordered ladders with spins aligned along the $a$ axis are formed. The interaction between different FM ladders, mediated by spinless-Co-O layers [Figure 1.6(b)], turns out to be antiferromagnetic, bringing about the AF ground state. The interladder coupling is weak, and switching from the ground-state AF order to the FM one can be induced by magnetic fields or temperature. Upon heating, a certain amount of LS Co$^{3+}$ ions become Co$^{2+}$, Co$^{4+}$, or change their spin state. In either case, each excited ion acquires a nonzero spin and replaces the weak SE interaction between two IS Co ions on the neighbouring ladders with usual SE
interactions, providing a strong bridge between spin-ordered ladders [Figure 1.6(c)]. Regardless of whether the excited spin couples ferro or antiferromagnetically with the spins in ladders, the symmetry of the bridge makes it certain that the additional coupling between the ladders is FM. Therefore, thermally excited spins should inevitably induce an AF-FM transition.

1.4 Transport properties of GdBaCo$_2$O$_{5\pm\delta}$: Electrical resistivity

LnBaCo$_2$O$_{5\pm\delta}$ compounds are interesting due to the fact that the concentration and sign of the charge carriers are easily controlled by changing the oxygen concentration. If $\delta=0.5$, all cobalt ions are in the Co$^{3+}$ state. By varying the oxygen concentration, the CoO$_2$ planes can be doped with either electrons (Co$^{2+}$ states) or holes (Co$^{4+}$ states). In addition to controlling the degree of band filling with charge carriers, it is also possible to vary its width by using rare-earth elements with different ionic radii. Considering the specific case of GdBaCo$_2$O$_{5.5}$, the parent compound, where all the Co ions are nominally in the 3+ state. The limiting phases $x = 0$ and $x = 1$ in GdBaCo$_2$O$_{5+x}$ should correspond to the 1:1 mixtures Co$^{2+}$/Co$^{3+}$ and Co$^{3+}$/Co$^{4+}$, respectively, or in other words to the doping levels of 0.5 electrons and 0.5 holes per Co ion. It would not be surprising, if the $x = 0.5$ composition were insulating, and a metallic behaviour emerging when the oxygen content deviates from $x=0.5$ towards lower or higher values. The actual behaviour of GdBaCo$_2$O$_{5+x}$, however, turns out to be more complicated. It never becomes a true metal, even though the doping level could vary from 0.5 electrons per Co ($x = 0$) up to 0.27 holes per Co ($x = 0.77$) [12]. It is to be noted that the highest oxygen concentration achieved for the ceramic GdBaCo$_2$O$_{5+x}$ samples is 0.77, since it required annealing at low temperatures where oxygen diffusion is inhibited [12]. At low temperatures, the in-plane resistivity $\rho_{ab}$ exhibits an insulating behaviour throughout the whole accessible range of $x$. It shows a sharp transition at $T \approx 360$ K. In addition to the MIT, a clear, small kink is seen at $T_N$ on the resistivity curve which is related to a change in activation energy due to magnetic ordering which will be discussed in the subsequent section.

The resistivity behaviour of GdBaCo$_2$O$_{5+x}$ in the concentration range $0.45 < x < 0.55$ [15] is illustrated in Figure 1.7(a). Although all $\rho(T)$ curves demonstrate
insulating behaviour in the \(0.45 < x < 0.55\) concentration range, an introduction of charge carriers into the system changes the absolute value of resistivity, and this change is different for both electrons and holes. The difference in the doping response of holes and electrons is presented in Figure 1.7 (b). The most striking feature is an asymmetry for electron and hole doping: while the hole doping leads to a steady decrease in resistivity (for example, \(\rho\) changes by almost 5 orders of magnitude at 60 K as \(x\) increases from 0.50 to 0.55), the electron doping causes little change in resistivity.

![Figure 1.7](image_url)

**Figure 1.7:** (a) Temperature dependence of the in-plane resistivity \(\rho(T)\) of GdBaCo$_2$O$_{5+x}$ samples \(x\) close to 0.5. (b) Doping dependence of the in-plane resistivity \(\rho(x)\) of GdBaCo$_2$O$_{5+x}$ samples measured at various temperatures. Taken from Taskin et al [15].

The parent compound GdBaCo$_2$O$_{5.5}$ exhibits a simple activation behavior \(\rho_{ab} \alpha \exp(\Delta/T)\) with \(\Delta \approx 70\) meV [12] which is well consistent with the narrow-gap insulator. However, when the oxygen content deviates from \(x = 0.50\), the resistivity behaviour immediately switches into the 3d variable range hopping (VRH) [27] \(\rho_{ab} \alpha \exp[(T_0/T)^{1/4}]\). This type of conduction is typical for disordered systems where the charge carriers move by hopping between localized electronic states. Initially, at the oxygen composition of \(x=0.50\), GdBaCo$_2$O$_{5+x}$ possesses a well ordered structure, where the oxygen ions form perfect filled and empty chains alternating along the \(b\)-axis [see Figure 1.1]. When the oxygen content deviates from \(x = 0.5\), this results
either in vacancies emerging in the filled chains, or in oxygen ions that fill the empty chains. While these oxygen defects inevitably generate electrons or holes in the CoO planes, they also produce a poorly screened Coulomb potential that may well localize the generated charge carriers, so that some of the adjacent Co ions acquire the Co\(^{2+}\) or Co\(^{4+}\) states. Hence, the conductivity occurs through the hopping of such localized charge carriers, thus leading to variable range hopping behaviour. Another interesting aspect is that, the slope of the resistivity curves monotonically decreases with increasing x (x > 0.5), implying that the localization length of holes (Co\(^{4+}\)) is comparatively larger than that of electrons. For x < 0.45, the temperature dependence of the resistivity follows Efros-Shklovskii type conduction [28] which is usually observed when the Coulomb interaction starts to play a role in carriers hopping. Various low temperature resistivity behaviours such as the activation, variable range hopping and Efros-Shklovskii of GdBaCo\(_2\)O\(_{5+x}\) with different oxygen content are illustrated in Figure 1.8 (a) - (c).

![Figure 1.8: Low temperature resistivity behaviors in GdBaCo\(_2\)O\(_{5+x}\) for different values of x. (a) activation behavior for x=0.50. (b) 3D variable range hopping behavior for x=0.45 - 0.525. (c) Efros-Shklovskii behavior for x=0.165 - 0.440. From Taskin et al [12].](image)

### 1.5 Activation energies in AFM and FM ordered states

The charge transport in these systems turns out to be very sensitive to both the FM and AF ordering, and magnetic fields readily induce a giant magnetoresistance by affecting the subtle AF-FM balance [8,10]. The c-axis resistivity of a twinned
GdBaCo$_2$O$_{5.50}$ crystal measured at $H = 0$ and 14 T is shown in Figure 1.9. In zero field, the FM-AF transition at $< 260$ K brings about a steplike increase of the resistivity $\rho_c$ indicating two different activation energies for charge carriers in FM and AF states. A 14 T field applied along the $ab$ plane shifts the magnetic transition towards lower temperatures and wipes out the resistivity increase, thus causing the resistivity to drop by several times. The charge carriers, therefore, have different activation in the FM and AF states, and the MR originates from the reduction in this activation energy. As soon as the magnetic field becomes insufficient to maintain the FM order, the system switches into the AF state at $T = T_N$ (14 T), and the resistivity jumps to its zero-field value.

**Figure 1.9:** Temperature dependence of $\rho_c$ measured at $H = 0$ and 14 T applied along the $ab$ plane. The dashed lines show simple activation fits $\rho_c \propto \exp (\Delta/\Theta)$ for both the AF and FM states, and $T_N$ indicates the temperature of the FM-AF transition that is shifted to lower temperatures by the applied field. (b) A linear-scale view of the high temperature region, illustrating a step-like increase of $\rho_c$ at $T_N$. Taken from Taskin et al [12].

The reorientation of weakly coupled ladders affects the charge transport, bringing about a giant magnetoresistance. The MR mechanism was explained in the following way: GdBaCo$_2$O$_{5.5}$ appears to be a narrow-gap insulator, where the carrier generation goes through the formation of Co$^{2+}$ - Co$^{4+}$ pairs, and the excitation energy for these states may well depend on the magnetic order. Indeed, in a low-spin Co-O layer, each
thermally excited state strongly couples with two adjacent spin-ordered ladders, providing them with a FM bridge; correspondingly, if the ladder moments are AF oriented, the resulting frustration should increase the energy of the excited state. Thus, the relative ordering of adjacent FM ladders is capable of significantly changing the insulating-gap size. Applied magnetic fields align the FM ladders and reduce the insulating gap, which results in step like increase in the number of carriers and decrease in resistivity.

1.6 Thermoelectric power in GdBaCo$_2$O$_{5+\delta}$

A characteristic feature of cobaltites that makes them stand out from the rest of the transition metals, is the high thermoelectric power or Seebeck coefficient. The oxygen deficient perovskites LnBaCo$_2$O$_{5+\delta}$ with $\delta = 0.5$ exhibit a simultaneous ordering of the Ln$^{3+}$ and Ba$^{2+}$ cations on one side and of the oxygen vacancies on the other side, and are of great interest due to their metal insulator transition (MIT) [Refer Section 1.2] which appears to be strongly correlated with the spin-state transitions [2,5,9,23,29].

Thermoelectric power measurements have been performed on oxygen-deficient layered perovskite HoBaCo$_2$O$_{5.5}$ [13] to identify the coupling of charge and spin degrees of freedom, which is an intrinsic feature of these strongly correlated oxides. The temperature dependent Seebeck coefficient $S$ shows a clear change of the conduction regime at the metal insulator transition. The temperature dependence of Seebeck coefficient $S$ (T) without magnetic field shows that above $T_{MI}$ (~ 280 K), $S$ is negative with a small absolute value ($S \sim 2 \mu V/ K$). At $T_{MI}$, $S$ changes sign between 285 and 290 K, jumping by more than 10 $\mu V/ K$ in less than 5 K. Then $S$ value keeps on increasing as $T$ decreases, reaches a maximum value $S= +170 \mu V/ K$ at 75 K, and finally, $S$ decreases down to $+90 \mu V/ K$ at 15 K. The hysteresis is evidenced, which is persisting up to ~ 220 K. The negative magnetothermoelectric power was observed to persist down to the lowest temperature values. Temperature dependence of the thermopower of HoBaCo$_2$O$_{5.5}$ along with the negative magnetothermoelectric power is shown in Figure 1.10.
The sign change of \( S \) from \( S < 0 \) to \( S > 0 \) was explained assuming that a spin state transition occurs at \( T_{MI} \) [13]. In the metallic state, \( \text{Co}^{2+} \) \( e_g \) electrons are moving in a broad band on the background of high or intermediate spin \( \text{Co}^{3+} \) ions. In contrast, the insulating behavior may result from the \( \text{Co}^{3+} \) spin state transition to a low-spin \( \text{Co}^{3+} \) occurring in the octahedra. In this phase the transport would occur by hopping of the low-spin \( \text{Co}^{4+} \) holes, whereas the high-spin \( \text{Co}^{2+} \) electrons become immobilized due to the mechanism called spin blockade in which the charge transport depends on the spin states \( \text{Co}^{3+} \) ions [13]. Thus in the high temperature phase of \( \text{LnBaCo}_2\text{O}_{5.5} \), consisting predominantly of HS and IS \( \text{Co}^{3+} \), there will be a rather high conductivity carried out by electrons in a relatively broad \( e_g \) band, whereas in the low temperature state, the presence of LS \( \text{Co}^{3+} \) sheets (octahedral layers) would suppress the transport of electrons, and only much weaker hole hopping would remain. This is consistent with the experimental observations (see Figure 1.10) that the thermopower is small and negative at \( T > T_{MI} \), typical for metal with electrons as the main carriers, whereas it becomes positive and much larger at \( T < T_{MI} \). The increase of \( S \) with decreasing \( T \) may be connected with the localization of heavy \( t_{2g} \) holes due, for instance, to disorder.

**Figure 1.10:** Temperature dependence of Seebeck coefficient \( S \) measured along cooling and warming cycles. Inset: Comparison of \( S (T) \) curves collected upon cooling in 0 T and 7 T. Taken from Maignan et al [13].
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The thermoelectric power is another transport property that can distinguish between electrons and holes. Figure 1.11(a) shows the temperature dependence of the Seebeck coefficients ($S$) in GdBaCo$_2$O$_{5+x}$ [30]. The MIT has a spectacular manifestation in the thermoelectric properties of GdBaCo$_2$O$_{5+x}$ similar to what is observed in HoBaCo$_2$O$_{5.5}$ [13]. At high temperatures, $S$ is very small and negative for both electron and hole doped crystals [12]. On the other hand, at low temperatures the thermoelectric power is very sensitive to the type of charge carriers: $S > 0$ for hole doped samples and $S < 0$ for electron doped samples which are evident in the figure. The most prominent feature of the doping dependence of the $S$ is shown in Figure 1.10 (b). A sharp divergence is evident at $x=0.5$ for $T=100$ K. Its absolute values $|S|$ are extremely large for $x$ which is very close to $x=0.5$, reaching ~ 800 $\mu$V/K, and decreases rapidly as $x$ deviates from 0.5, though in a different way for electrons and holes. Based on these observations, it is clear that both the temperature and doping dependence of the Seebeck coefficient clearly deviate from the behavior of conventional band gap materials.

![Figure 1.11](image)

Figure 1.11: (a) Temperature dependence of the Seebeck coefficient $S(T)$ of GdBaCo$_2$O$_{5+x}$ samples with $x$ close to 0.5. (b) The doping dependence of the absolute value of the Seebeck coefficient $|S|$ in GdBaCo$_2$O$_{5+x}$ at $T=100$ K. Taken from Taskin et al [30].

The temperature dependence of the Seebeck coefficient $S(T)$ do not follow a simple insulating behavior either for holes or electrons doped samples [12]. Figure
Chapter 1: Phase transitions in double perovskite GdBaCo$_2$O$_{5+x}$

Figure 1.1: Inverse temperature dependence of the thermopower of GdBaCo$_2$O$_{5+x}$, where the slope is reflecting the activation energy for charge carriers $\Delta s$, $S(T)=k_B/e(\Delta s/k_B T)$. It becomes immediately clear that the only composition that exhibits a conventional semiconducting behavior with the activation energy $\Delta s \approx 70$ meV is the parent compound GdBaCo$_2$O$_{5.5}$ [12]. A subtle deviation of the oxygen concentration from $x=0.5$, changes the thermopower behavior from the conventional semiconducting behavior as seen in figure. It is clear that $S$ becomes almost temperature independent at $\sim 100$ K, indicating that the electron behavior is no longer governed by the band gap. This behavior is very similar to the resistivity where the thermal activation behavior switches to VRH mode as discussed in the previous section.

Figure 1.12: Inverse temperature dependence of thermoelectric power of GdBaCo$_2$O$_{5+x}$ for different oxygen concentrations. Note that the sample with $x=0.5$ only follows the simple activation behavior, whereas the samples with $x$ other than 0.5 deviate from this behavior. Taken from Taskin et al [12].

From the hopping character of the charge transport in GdBaCo$_2$O$_{5+x}$, it can be assumed that a large part of the thermopower comes from the entropy, which is
carried by each electron and hole along with the charge [30]. According to Koshibae and Maekawa et al [31], the spin-orbital degeneracy of charge carriers plays an important role in systems with correlated hopping transport. In GdBaCo$_2$O$_{5+x}$, there are two kinds of lattice sites for Co ions depending on the oxygen content [Figure 1.1], x octahedra and (1-x) pyramids, which provide different spin–orbital states for introduced electrons (Co$^{2+}$), holes (Co$^{4+}$), or host Co$^{3+}$ ions. It is known that Co$^{3+}$ ions can adopt three different spin states depending on the ratio between $\Delta_{CF}$ and the $J_H$. It is believed that in the parent compound GdBaCo$_2$O$_{5+x}$ at low temperatures, the Co$^{3+}$ ions adopt LS state in the octahedral and IS states in the pyramids [8,12,32]. For Co$^{2+}$, the $\Delta_{CF}$ is weaker than for the Co$^{3+}$ and thus Co$^{2+}$ adopts the HS state, while for Co$^{4+}$, $\Delta_{CF}$ is stronger favoring the LS state. Any state with non-zero spin $S$ has the spin degeneracy $2S+1$. In addition to this spin degeneracy, there can be orbital degeneracy as well. The thermopower $S$ is the entropy per charge and the entropy is given $S = k_B \ln g$, where $g$ is the spin-orbital degeneracy or the number of configurations of charge without doubly occupied states and degeneracy of spin [31]. The entropy contribution of charge carriers that includes spin-orbital degeneracy can be accounted for the doping dependence of Seebeck coefficient and its remarkable divergence at $x = 0.5$. This explains the larger thermopower of the electron-doped samples in comparison with the hole-doped samples. The larger degeneracy of HS-Co$^{3+}$ (electrons) when comparing to LS Co$^{4+}$ (holes) could be the reason why electron doping enhances the thermopower of GdBaCo$_2$O$_{5+x}$ than the hole doped samples.

1.7 Phase diagram of GdBaCo$_2$O$_{5+x}$

An empirical phase diagram has been generated by Taskin et al [12] based on the structural, transport and magnetic studies on the single crystal of GdBaCo$_2$O$_{5+x}$ as a function of the oxygen concentrations as discussed in earlier sections. Figure 1.13 shows the phase diagram of GdBaCo$_2$O$_{5+x}$ as a function of oxygen content, $x$.

At the lowest oxygen content, $x=0$, GdBaCo$_2$O$_{5+x}$ is an antiferromagnetic insulator [AFI (1)]; its low-temperature phase should most likely correspond to a charge-ordered G-type antiferromagnet. An increase in the oxygen content $x$ is found to immediately result in the formation of isolated ferromagnetic clusters embedded in
Chapter 1: Phase transitions in double perovskite GdBaCo$_2$O$_{5+x}$

the antiferromagnetic [AFI(1)] matrix. With further increasing oxygen content in GdBaCo$_2$O$_{5+x}$ (up to $x = 0.45$), the FM clusters smoothly grow in size, reaching percolation, and at low temperatures develop an intrinsic instability towards a new type of AF ordering [AFI(2)], which is the ground state of the parent compound GdBaCo$_2$O$_{5.5}$ [10]. GdBaCo$_2$O$_{5+x}$ is being composed of nanoscopic phases mixed together over a wide composition of $0 < x < 0.45$.

![Phase diagram](image)

**Figure 1.13:** Phase diagram of GdBaCo$_2$O$_{5+x}$ as a function of $x$. This includes regions of a paramagnetic metal (PMM), paramagnetic insulator (PMI), ferromagnetic metal (FMM), ferromagnetic insulator (FMI), and antiferromagnetic insulator (AFI). Note that GdBaCo$_2$O$_{5+x}$ seems to have a few stable phases such as $x=0$, $x \approx 0.5$, $x \approx 0.7$, while intermediate compositions always tend to phase separate on a nanoscopic or mesoscopic scale. Taken from Taskin et al [12].

Compounds GdBaCo$_2$O$_{5+x}$ with $0.45 \leq x \leq 0.55$ possess plenty of attractive transport and magnetic behaviors that may turn them into model systems. This region with the richest behaviors occupies the center of the phase diagram around the “parent” compound GdBaCo$_2$O$_{5.5}$. In this doping range, the crystal structure is macroscopically orthorhombic up to rather high temperatures due to the ordering of oxygen into alternating full and empty chains that run along the a-axis (see Figure 1.1). Owing to this structural order, broad magnetic and transport features are emerging and GdBaCo$_2$O$_{5+x}$ demonstrates a series of sharp transitions upon
cooling: first, from a paramagnetic metal (PMM) to a paramagnetic insulator (PMI) at \( T_{\text{MIT}} \) which is also accompanied with a spin state transition, then to a ferromagnetic insulator (FMI) at \( T_C \) and, finally, to an antiferromagnetic insulator (AFI(2)) at \( T_{\text{FM-AF}} \).

When \( x \) exceeds 0.55, GdBaCo\(_2\)O\(_{5+x}\) develops a new phase possessing considerably lower temperatures ferromagnetic transitions and the FM-AF transition. Until \( x \) reaches \( \approx 0.7 \), this mesoscopic phase is mixed with the \( x \approx 0.5 \) phase, and only at \( x \geq 0.68-0.70 \), the system recovers its homogeneity. In the \( x \approx 0.7 \) region, the series of successive PM-FM-AF transitions occur similar to that at \( x \approx 0.5 \) but comparatively at lower temperatures.

**1.8 Spin states and electronic structure of Co in LnBaCo\(_2\)O\(_{5+\delta}\): A theoretical approach**

It is well known that the physical properties of cobalt oxides are closely related to the Co spin state and the corresponding electronic structure. Several spin-state models have been proposed to explain these electronic and magnetic phase transitions involved in these systems and the consolidation of these models can be found in Ref. [33]. However, great controversy has arisen regarding the issue of the Co spin state of LBaCo\(_2\)O\(_{5.5}\) and the explanation of the rich physical properties. Maignan et al [5] proposed, on the basis of the measured effective magnetic moments, that a spin-state ordering is most probable in LBaCo\(_2\)O\(_{5.5}\) below \( T_{\text{MI}} \) with low-spin (LS) octahedral Co1 and intermediate-spin (IS) pyramidal Co2, while both the spin states evolve towards a high-spin (HS) state above \( T_{\text{MI}} \). Moritomo et al [7] suggested, based on an investigation of the varying crystal structure of TbBaCo\(_2\)O\(_{5.5}\) with temperature (T), that the \( T_{\text{MI}} \) is induced by a spin-state transition from the \( d_{x^2-y^2}^{2-r^2}/d_{y^2-r^2}^{2} \) orbital-ordered IS state below \( T_{\text{MI}} \) to the HS state above \( T_{\text{MI}} \). However, a later structural study of GdBaCo\(_2\)O\(_{5.5}\) performed by Frontera et al [9] ruled out orbital ordering and indicated that the \( T_{\text{MI}} \) is driven by a sudden electron excitation in the octahedral Co1 ions from the LS to the HS states, while the pyramidal Co2 ions remain in their IS state. Meanwhile, the lattice anomaly at \( T_{\text{MI}} \) was ascribed to the Co1 LS–HS transition.
In strong contrast, Wu et al argued [34], on the basis of density functional calculations [35], that the AFM–FM-like transition and $T_{MI}$ originate from the $pd\sigma$ hole delocalization in the almost HS state [36]. In this work, some more evidence was found to support this distinct mechanism of the AFM–FM transition, $T_{MI}$, and lattice anomaly in LBaCo$_2$O$_{5.5}$ ($L =$ Sm, Eu, Gd, Tb, Dy, Y), from LSDA + $U$ (the local spin-density approximation plus electron-correlation correction) calculations for GdBaCo$_2$O$_{5.5}$ (for which structural data are available and the results applicable to the isostructural LnBaCo$_2$O$_{5.5}$ class). This study provides a unified explanation for a number of experimental findings on LnBaCo$_2$O$_{5.5}$ [5,7,9,12,37,39]

1.9 Doping studies on LnBaCo$_2$O$_{5+\delta}$

Apart from the study by varying the oxygen content [12], many doping studies have been undertaken to gain insight into the understanding of the mechanism involved in transport and magnetic behaviors of the parent compound LnBaCo$_2$O$_{5.5}$ ($Ln$ being lanthanides). The doping studies involve substituting different cations (differing either in valence or in size) at lanthanide ($Ln$) or alkaline earth (Ba) or transition metal (Co) site of LnBaCo$_2$O$_{5+\delta}$. Following table lists representative different doping studies on various systems and other relevant aspects.

Table 1: List of various observations on the results of representative doping studies on LnBaCo$_2$O$_{5+\delta}$ by chemical substitutions at lanthanide ($Ln$), alkaline earth (Ba) and transition metal (Co) sites. Note that the table briefs only few substitutional studies.

<table>
<thead>
<tr>
<th>Doped system</th>
<th>Objective</th>
<th>Significant observations</th>
</tr>
</thead>
</table>
| Studies on LnBaCo$_2$O$_{5+\delta}$ with different lanthanides | Influence of oxygen stoichiometry on the structure, metal insulator transition and competition between ferromagnetism and antiferromagnetism by having different rare earths in LnBaCo$_2$O$_{5+\delta}$ | • Larger (Pr and Nd) and smaller (Dy and Ho) lanthanides stabilize in tetragonal structure, whereas intermediate lanthanides (Sm, Eu, Gd, Tb) exhibit orthorhombic structure  
• MIT appears only for intermediate lanthanides  
• $T_{MIT}$ decreases with the size of the lanthanide |

| LnBaCo$_2$O$_{5+\delta}$ (Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho) Maignan et al [5] | |  |
Chapter 1: Phase transitions in double perovskite GdBaCo$_2$O$_{5+\delta}$

- $T_C$ increases as the size of the lanthanide decreases

**Doping studies on LnBaCo$_2$O$_{5+\delta}$ by the cationic substitution at Ln site**

<table>
<thead>
<tr>
<th>Ln$_{1-x}$Ca$_x$BaCo$<em>2$O$</em>{5.5+\delta}$ (Ln=Y, Gd, Sm)</th>
<th>Effect of local lattice distortions on the physical properties of LnBaCo$<em>2$O$</em>{5.5+\delta}$ by substituting smaller lanthanide by larger size divalent Ca and keeping the Co valence constant</th>
<th>Samples remain orthorhombic with no significant change in lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.M.Seikh et al [40] see also [41 - 44]</td>
<td>Samples remain orthorhombic with no significant change in lattice parameters</td>
<td>No change in $T_C$ for the compound with Ln=Y</td>
</tr>
<tr>
<td></td>
<td>$T_C$ increases for intermediate lanthanides along with increases in the window of existence of FM phase</td>
<td>$T_C$ increases for intermediate lanthanides along with increases in the window of existence of FM phase</td>
</tr>
<tr>
<td></td>
<td>Substitution of Ca destabilizes the ferromagnetic state for smaller lanthanides Ln= Ho and Dy</td>
<td>Substitution of Ca destabilizes the ferromagnetic state for smaller lanthanides Ln= Ho and Dy</td>
</tr>
<tr>
<td></td>
<td>No remarkable change in $T_{MIT}$ for intermediate lanthanides Ln=Y, Gd, Sm and Eu</td>
<td>No remarkable change in $T_{MIT}$ for intermediate lanthanides Ln=Y, Gd, Sm and Eu</td>
</tr>
<tr>
<td></td>
<td>No $T_{MIT}$ observed for Ln=Ho and Dy</td>
<td>No $T_{MIT}$ observed for Ln=Ho and Dy</td>
</tr>
</tbody>
</table>

**Doping studies on LnBaCo$_2$O$_{5+\delta}$ by the cationic substitution at Ba site**

<table>
<thead>
<tr>
<th>Y(Ba$_{1-x}$Ca$_x$)$_2$Co$<em>2$O$</em>{5.5}$</th>
<th>Role of cationic disorder and size effects by substituting smaller cation at the Ba-site</th>
<th>Samples remain orthorhombic for $0 \leq x \leq 0.05$, above which there is a coexistence of orthorhombic and tetragonal phases though oxygen content remains unaltered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aurelio et al [45] see also [46 - 48]</td>
<td>Samples remain orthorhombic for $0 \leq x \leq 0.05$, above which there is a coexistence of orthorhombic and tetragonal phases though oxygen content remains unaltered</td>
<td>$T_C$ is unaffected</td>
</tr>
<tr>
<td></td>
<td>AFM phase is destabilized</td>
<td>$T_C$ is unaffected</td>
</tr>
<tr>
<td></td>
<td>$T_{MIT}$ decreases with Ca substitution and lattice distortions are shown to be concomitant with MIT</td>
<td>AFM phase is destabilized</td>
</tr>
</tbody>
</table>

**Doping studies on LnBaCo$_2$O$_{5+\delta}$ by the cationic substitution at Co site**

<table>
<thead>
<tr>
<th>TbBaCo$_{2-x}$Fe$<em>x$O$</em>{5.5}$</th>
<th>Replacing one transition metal (TM) ion in LnBaCo$<em>2$O$</em>{5.5}$ by another one could have a great impact on magnetic properties</th>
<th>Samples are orthorhombic for $x \leq 0.1$ above which there is a coexistence of orthorhombic and tetragonal phases. For $x \geq 0.12$, tetragonal phase stabilizes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Troyanchuk et al [49] see also [50 - 54]</td>
<td>Samples are orthorhombic for $x \leq 0.1$ above which there is a coexistence of orthorhombic and tetragonal phases. For $x \geq 0.12$, tetragonal phase stabilizes</td>
<td>Unit cell volume increases with Fe doping</td>
</tr>
</tbody>
</table>
| | • Oxygen content decreases with Fe
• $T_C$ increases and $T_N$ decreases for $x \leq 0.1$, orthorhombically distorted samples
• A small increase in $T_{MIT}$ for $x \leq 0.1$
• FM component disappears for $x > 0.1$ |

1.10 Overview of the thesis

Based on the above substitutional studies, it is clear that cationic substitution in this class of compounds could lead to a variety of interesting at the same time complex behavior. This thesis is aimed at investigating the doping effects of GdBaCo$_2$O$_{5.5}$ by chemically substituting different cations at Co and Gd sites without altering the total oxygen content of the parent compound. This study involves the substitution of Ni and Fe at Co site expecting electron and hole doping into GdBaCo$_2$O$_{5.5}$. It also involves the substitution of Ce and Sr at Gd site equivalent to doping of electrons and holes into the parent compound. Experimental techniques such as electrical resistivity, thermopower and Differential Scanning Calorimetry have been used to study the transport behavior and metal insulator transition involved in the system of investigation. Fourier Transform Infrared Spectroscopy is a sensitive probe to identify the local changes associated with metal insulator transition that has also been used in the present study. This thesis is organized as,

Chapter 2: Experimental techniques
• This chapter provides an overview of different experimental techniques that were employed in this thesis

Chapter 3: Electrical transport and Metal Insulator transition studies on Ni and Fe substituted GdBaCo$_2$O$_{5.5+\delta}$
• This chapter aims at to get insight into the substitutional effects on the transport properties and metal insulator transition (MIT) of GdBaCo$_2$O$_{5.5+\delta}$ by chemically substituting Ni and Fe at Co site

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Chapter 4: Electrical transport and Metal Insulator transition studies on Sr and Ce substituted GdBaCo$_2$O$_{5.5+\delta}$

- This chapter deals with investigations of substitutional effects on transport properties and the metal insulator transition of GdBaCo$_2$O$_{5.5+\delta}$ by substituting Sr and Ce at Gd site

Chapter 5: Infrared spectroscopy study of MIT in Ni doped GdBaCo$_2$O$_{5.5+\delta}$

- This chapter presents the detailed experimental investigation to probe the changes in the phonon modes across the metal insulator transitions in GdBaCo$_{2-x}$Ni$_x$O$_{5.5+\delta}$ samples using Fourier Transform Infrared (FTIR) Spectroscopy

Chapter 6: Summary and outlook

- This chapter summarises the thesis with a general discussion on the results presented throughout the report. It ends with the comments on how the study could be continued for better understanding of the results presented

Appendix: Probing Metal Insulator transition in Ni doped Na$_{0.75}$CoO$_2$ using FTIR spectroscopy

- Though this work is not included in the main part of this these, this work carried out by me pertains to the use of infrared spectroscopy in the study of phonon behaviour across the T$_{MIT}$ in Ni doped Na$_{0.75}$CoO$_2$. 
References


Chapter 1: Phase transitions in double perovskite GdBaCo$_2$O$_{5+\delta}$


24. D. Akahoshi and Y. Ueda, *Oxygen Non-stoichiometry, Structures, and Physical Properties of YBaCo$_2$O$_{5+x}$ (0.00\(\leq x \leq 0.52\))*, Journal of Solid State Chemistry 156 (2001) 355

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