Chapter-2

Preparation of Ca$_3$Co$_4$O$_9$ and study its microstructure, electrical, optical and magnetic properties

2.1 Introduction of Ca$_3$Co$_4$O$_9$

Metal oxides, particularly those containing one or more transition elements, for many years have been the foundation of solid-state inorganic chemistry. Here, the synthetic skill to manipulate the reactivity of diverse chemical elements, often at extreme temperatures and pressures, hand-in-hand with developments in structural characterization, including both spectroscopic and diffraction methods. A very good, and indeed already well-documented example, is the case of the cuprate superconductors, discovered in the early 1980s, which led to increasing complex structural chemistry and which continues to push the frontiers of knowledge and electronic properties of the solid-state. The interplay between the synthetic and structural work of chemists and the property measurement and theory of physicists led to the rapid development in understanding of a unique group of materials. When one also considers the role of the materials scientist in device fabrication of such electronic materials, the area is seen to be truly interdisciplinary. Oxides continue to be the focus of much attention, and increasingly the area is driven by target properties. In this volume we have been largely concerned with properties arising from electronic structure but other applications, in catalysis or in optical media, are equally as important and are researched equally actively. The role of the chemist in synthesis is still paramount, and indeed it is very apparent that the scope for novel compositions and structures is far from being exhausted. More than ever the goal of a particular desirable property and the need to understand structure–property relationships is always in mind in contemporary research.

Thermoelectric oxides have attracted considerable attention in recent years as potential waste heat conversion candidate materials not only because of their promising thermoelectric properties, but also because of the stability of oxides at high temperature. Two specific compounds in the Ca-Co-O family, namely, the low-dimension cobaltates...
Ca$_3$Co$_2$O$_6$ and Ca$_3$Co$_4$O$_9$ showed promising thermoelectric properties. Energy demands have driven the search for both improved utilization of our fossil energy and new alternative energy resources. These new energy technologies are preferably cleaner, cheaper, smaller and more efficient than those currently being employed, for instance fuel cells, lithium-ion batteries, thermoelectric. Nanocrystalline oxide conductors may exhibit significantly altered physical properties, which offer opportunities for technological innovations. This is particularly true in the oxide semiconductors, which have unusual optical, electrical, and magnetic properties. In addition, the size and morphology play a critical role in the electrical, diffusive and defect properties of electro ceramics. We consider the size dependence of the defect formation, electrical conductivity, thermopower, and magnetization in several technologically important oxides for energy conversion and storage system.

Inorganic structures with one-dimensional (1D) atomic arrangements are in the limelight because of their unique electronic and magnetic properties. Investigations into the nature of the magnetism in these materials have proved particularly rewarding because of the combination of highly anisotropic structures and phenomena such as ferromagnetism (F), antiferromagnetism (AF), and more complex magnetic behavior. Low-dimensional materials are currently in the focus because of their technological significance. For example, magnetoresistance effects have been evidenced in layered Bi-based cobaltites and a high figure of merit for the conversion of thermoelectric energy is found in the two dimensional Ca$_3$Co$_4$O$_9$. A large number of oxides have been synthesized with 1D structures.

However, most of their physical properties and the theoretical interpretations about them remain largely unexplored because of their complex crystal and magnetic structures. The density-functional full-potential calculations is expected to open up new avenues where new materials of fundamental and technological significance. In this we report electronic structure and magnetic properties of pure and Yttrium substituted 1D Ca$_3$Co$_4$O$_9$. We show that Ca$_3$Co$_4$O$_9$ transforms into a half-metallic ferromagnet by application of magnetic fields as well as by substituting Y for Ca. When the concentration of Y increases, the system prefers to be an insulator. The different possible
oxidation states of cobalt in cobalt oxides together with its various spin configurations such as low spin (LS), intermediate spin, and high spin (HS) are responsible for various phenomena such as temperature-/hole-doping-induced spin-state transitions.

2.2 Structure of Ca$_3$Co$_4$O$_9$

Layered cobaltate materials have been the focus of many recent studies due to the wide variety of electrical, magnetic, and structural properties they exhibit. Among the different layered cobaltate systems, the Ca$_3$Co$_4$O$_9$ stands out as the only system containing one cation with nominally different oxidation states, namely Co$^{2+}$ in the rock salt buffer layers Ca$_2$CoO$_3$ and Co$^{4+}$ in the octahedral CoO$_2$ layers, which makes it an ideal system for studying effects such as charge transfer, orbital ordering, and spin state transitions on the material’s electrical behavior [G. Yang et al., (2008)]. Ca$_3$Co$_4$O$_9$ can be denoted as [Ca$_2$CoO]$_{rs}$[CoO$_2$]$_{1:61}$ to indicate two misfit layered monoclinic symmetry subsystems; a distorted rock-salt type layer (RS) Ca$_2$CoO$_3$ located between two CdI$_2$ type CoO$_2$ layers. The two subsystems have same lattice parameters for a=4.8339Å, c=10.8346 Å and β=98.14° but with b$_1$=2.8238 Å and b$_2$=4.5582Å. The number 1:61 indicates ratio of the two incommensurate b lattice parameters. The outer CdI$_2$ type CoO$_2$ triangular lattices consist of edge-sharing CoO$_6$ octahedrons [A. C. Masset et al., (2000); Y. Miyazaki et al., (2002)]. Fig.2.1 shows crystal structure of the system. Natural (CCO-349) super lattice exhibits thermally activated semiconductor-like behavior with hole as its charge carrier.

Fig.2.1. shows crystal structure of the Ca$_3$Co$_4$O$_9$ system [Y. Miyazaki et al., (2004)]
Role of the dielectric rock-salt type subsystem is to effectively shorten phonon mean free path thus lowering thermal conductivity. It also provides charge carriers by transferring holes to the CoO₂ layer. The CdI₂ type subsystem is responsible for the electrical conductivity through hopping of holes between Co³⁺ and Co⁴⁺ sites along the layer [H. Muguerra et al., (2008)].

2.3 Physical Properties of Ca₃Co₄O₉

Ca₃Co₄O₉ ceramic is considered to be a promising candidate p-type thermoelectric material for high temperature power generator, which has excellent thermal and chemical stability [Wang et al., (2010)]. For practical use their thermoelectric performance must be further improved. One approach is partial substitution for Ca or Co site by metals such as rare earth metals, Ag and transition metal. Ca₃Co₄O₉ composite doped with Lu and Ag by solid-state reaction and spark-plasma-sintering (SPS) techniques. The maximum Z could reach 5.55×10⁻⁴ at 1100 K which is the highest value reported for the polycrystalline Ca₃Co₄O₉ system so far. However, the feature of these materials is that they contain rare earth metal Lu which is a scarce element in the crust of the earth. The price of Ca₃Co₄O₉ based thermoelectric may be raised sharply by doping with Lu. Compared with Lu, Y is much cheaper. It has been reported that the thermoelectric performance of Ca₃Co₄O₉⁺ₓ could be improved effectively by doping with Yttrium [Wang et al., (2010)]. And the optimize composition (Y₀.₂Ca₂.₈Co₄O₉) is the same to that of Lu doped Ca₃Co₄O₉. In addition, the solid-state reaction method presents several serious drawbacks, such as high reaction temperature, large particle sizes, limited degree of chemical homogeneity and low sintering ability. Sol-gel method could conquer these drawbacks. In this method, the reactant cations are intimately mixed on an atomic scale, so the rate of the reaction will be increased, leading to lower synthesis temperatures [Mathur et al., (2002)].

(i) Literature review of Ca₃Co₄O₉

Recently, oxide thermoelectric and magnetic materials have received attention since [Terasaki et al., (1997)]. Reported high thermopower and low resistivity in NaₓCoO₂. This material has performance comparable with that of thermoelectric
compounds, and there is no performance degradation due to oxidation. Furthermore, high thermoelectric performance has been reported for calcium cobalt oxide $\text{Ca}_3\text{Co}_4\text{O}_9$ [Masset et al., (2000)]. Attempts at further improvements in the thermoelectric properties of calcium cobalt oxide have included the substitution of other elements into the calcium and cobalt sites to produce $\text{Ca}_{3-x}\text{M}_x\text{Co}_4\text{O}_9$ and $\text{Ca}_3\text{Co}_{4+y}\text{M}_2\text{O}_9$ oxides. Calcium cobalt oxide has two phases, $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_3\text{Co}_2\text{O}_6$. $\text{Ca}_3\text{Co}_4\text{O}_9$ has lower resistivity over a wide temperature range and a Seebeck coefficient greater than 100 $\mu\text{V/K}$ at or above room temperature.

Calcium cobalt oxides are of great interest from a physics point of view as shown by their electrical and magnetic properties. $\text{Ca}_3\text{Co}_4\text{O}_9$ was studied as they are more prospects for the practical thermoelectric application than sodium cobaltite because of the high sodium volatility at elevated temperature. The layered cobalt oxides seem interesting candidates due to their chemical stability and absence of hazardous elements such as Te, Se and Pb [I. Terasaki et al., (1997); H. Muguerra et al., (2010)]. $\text{Ca}_3\text{Co}_4\text{O}_9$ was first synthesized in 1968 and their structures are described by two monoclinic subsystems alternating along the c-axis [T. M. Tritt et al., (2001); E. Woermann et al., (1970)]. The single crystal of this was grown by Woermann et al in 1970. A structural model of cobaltite was reported as “misfit” alternating layers of a triple rock salt-type ($\text{Ca}_2\text{CoO}_3$) subsystem and a single CdI$_2$-type ($\text{CoO}_2$) subsystem stacked along the c-axis [S. Bhattacharyaa et al., (2005)]. These two subsystems have common a- and c-lattice parameters and $\beta$ angles but different b-lattice parameters causing a misfit along the b-axis [S. Li et al., (1999)]. X-ray powder diffraction patterns are closely similar with that of $\text{Ca}_2\text{Co}_2\text{O}_5$, which is in layer structure with ordered oxygen vacancies. $\text{Ca}_3\text{Co}_4\text{O}_9$ undergoes evaluation from a low temperature insulator to a strongly correlated fermi liquid to an incoherent metal and finally to a semiconductor at elevated temperature. The electrical resistivity of cobaltite was depended on the $\text{Co}^{4+}$ content while the kind of the relevant cations entering that layered compound (Na or Ca) did not influence the electrical resistivity. Cobaltite having layered $\text{CoO}_2$ planes and the charge carriers can vary over a remarkable wide range by doping so that effective valence of Cobalt ions can changes from $\text{Co}^{2+}$ to $\text{Co}^{4+}$ in these materials.
The magnetic properties of Ca$_3$Co$_4$O$_9$ are very complicated because the valence state of cobalt is either 3+ or 4+ due to the misfit between two subsystems in the unit cell [G. Yang et al., (2008); An M et al., (2007); J. Heitmanek et al., (2012)]. When super-exchange and double-exchange interactions between Co$^{3+}$ and Co$^{4+}$ ions are considered as coexisting in the system, the ferrimagnetisms in the system are mainly caused by the interlayer coupling between the CoO$_2$ and Ca$_2$CoO$_3$ subsystems [R. Moubah et al., (2009); J. Sugiyama et al., (2002); S. Demirel et al., (2013); G.D. Tang et al., (2010)].

2.4. Synthesis and Characterization of Pure and Substituted Ca$_{3-x}$M$_x$Co$_4$O$_9$ (M = Y)

Many complex oxides are synthesized by MSS methods at relatively low temperature compared to conventional ceramic method. Although numerous compounds within this class of oxides have been synthesized as polycrystalline powders by traditional solid state techniques, a major breakthrough in the synthesis and structural characterization of perovskite related oxides was realized by the ability to grow single crystals from molten salts or fluxes. This method has the advantage of lower reaction temperatures and the stability of unusual oxidation states, yet does not have the stoichiometric control often associated with solid state methods. As in all solvents for crystallization, one has a choice, and examines the desirable characteristics necessary for each reaction. These qualities include melting point, volatility, solubility of reactants, cost, toxicity and ease of separating the final product. Considering these criteria, some possible candidates are carbonates, halides and hydroxides.

This chapter is about the synthesis and characterization of pure and yttrium substituted Ca$_{3-x}$Y$_x$Co$_4$O$_9$ (M = Y) prepared via novel MSS method for the first time using potassium carbonate and potassium chloride (mixed flux). This Ca$_3$Co$_4$O$_9$ are also synthesized by co-precipitation (precursor) and sol-gel methods. Synthesized compounds are characterized by Thermal analysis (TG/DTA), powder - XRD, FT-IR, Raman spectroscopy and Scanning Electron Microscope (SEM) for phase identification and morphological study. MSS method preparation in alkali carbonate and chloride salts is used as supportive to affirm the reactive nature of Ca$_{3-x}$Y$_x$Co$_4$O$_9$ in water based atmosphere. Literature on (CCO-349) is briefed in this chapter including of optical,
electrical and magnetic properties to explain our results. Briefly physical properties and crystallographic aspects of this cobaltite are also given.

2.4.1. Preparation of Ca₃₋ₓYₓCo₄O₉ by molten flux technique

CaCO₃, Y₂O₃, Co₃O₄, KCl and K₂CO₃ are analytical grade reagent used without further purification. Polycrystalline samples Ca₃₋ₓYₓCo₄O₉ (x=0.0-1.0) have been prepared by molten flux synthesis. CaCO₃, Y₂O₃ and Co₃O₄ were taking stoichiometry amount were ground in an agate mortar. The grounded powder was added to the mixed flux (7g of K₂CO₃+ 1 g of KCl) in a recrystallized alumina crucible and then sintering the crucible at 895°C in the air for 5 hours after the reaction was finished then slowly cooled to room temperature. The black crystals were separated from the flux by washing in hot distilled water repeatedly then dried at room temperature. The removal of potassium could be tested by flame photometry and it was confirmed by EDX.

2.4.2. Characterization Technique

The powders were characterized by X-ray diffraction technique (XRD, Bruker D8 Advance, by CuKα radiation, kα = 1.5406Å). The surface morphology and the microstructure were studied by a scanning electron microscope (HRSEM FEI Inspect F50) instrument. The chemical composition was determined with an EDX analyzer attached with a (HRSEM FEI Inspect F50) instrument. Optical band gap obtained by using Jasco V-670-UV-Visible diffused reflectance spectrometer. Electrical resistivity is measured from Dc Four probe setup, electrical resistivity play a major role in technical applications. The magnetic properties were studied by using Quantum Design PPMS system.

2.4.3 Results and discussion

2.4.3.1 XRD analysis

Fig.2.3. shows the powder XRD pattern of Ca₃₋ₓYₓCo₄O₉ (x=0.0-1.0) diffraction peaks in the samples can be indexed and lattice parameters are consistent with those reported in JCPDS card No 21-0139. The lattice parameters of Ca₃₋ₓYₓCo₄O₉ sample are calculated in monoclinic symmetry based on its diffraction patterns by a standard least squares refinement method as listed in Table-2.1, where b_RS corresponds to the b-axis.
length of Ca$_2$CoO$_3$ layers. The diffraction peak (004) shifts from a low angle to a high angle due to the introduced Y$^{3+}$ doped into the calcium site of Ca$_{3-x}$Y$_x$Co$_4$O$_9$ indicating the formation of single-phase compounds. All the diffraction peaks in the patterns can be indexed by the Ca$_{3-x}$Y$_x$Co$_4$O$_9$ phase, and there is not any detectable impurity peak, which indicates the formation of single-phase compounds, yttrium doping on calcium site of this system. As described in Fig.2.2, the substitution of Y for Ca does not affect the crystalline structure, but from the following analyses, we will see that Y doping strongly influences the magnetic properties in this system [Yang Wang et al., (2010); J.Hejtmanek et al., (2012)].

**Fig.2.2** Schematic structural view of Ca$_{3-x}$Y$_x$Co$_4$O$_9$, where Ca$^{2+}$ sites are partially occupied by Y$^{3+}$ ions [Yang Wang et al., (2010)]

Using the XRD diffraction data, the crystallite sizes of samples were able to be estimated using the Scherer equation (2.1).

$$D = \frac{K\lambda}{\beta\cos\theta}$$  \hspace{1cm} (2.1)

In this equation, $D$ is the crystallite size (nm); $K$ is the so-called shape factor, which usually takes a value of about 0.9; $\lambda$ is the X-ray wavelength; $\beta$ the full width at half maximum of the diffraction peak at $\theta$ is the diffraction angle. Since the peak from the (004) plane is the most intense among all of the planes and this diffraction, was selected to calculate the average crystallite size as 150-300nm.
Fig. 2.3. XRD patterns of $\text{Ca}_{3-x}\text{Y}_x\text{Co}_4\text{O}_9$ ($x=0.0-1.0$)
Table- 2.1. Lattice parameters of Ca$_{3-x}$Y$_x$Co$_4$O$_9$

<table>
<thead>
<tr>
<th>Composition (X)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
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<td>0.0</td>
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<td>4.562</td>
<td>10.851</td>
</tr>
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<td>0.4</td>
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<td>10.864</td>
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<tr>
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<td>0.8</td>
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<td>1.0</td>
<td>4.834</td>
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<td>10.873</td>
</tr>
</tbody>
</table>

2.4.3.2 Scanning Electron Microscope (SEM) analysis- Morphological observations

SEM photographs of the sample prepared by the molten flux technique under the optimum condition in Fig.2.4. Here Fig.2.4. (a,b) it shows and the Ca$_3$Co$_4$O$_9$ platelet shape with a large grain crystalline shape of 20µm not well aligned grains and 5µm image show the agglomerate particle shape. Fig.2.4. (c,d) Ca$_{3-x}$Y$_x$Co$_4$O$_9$ (x=0.4) shows the number of particles increases and its 5µm image shows the spongy spread on the platelet grain shape. Fig.2.4. (e,f) Ca$_{3-x}$Y$_x$Co$_4$O$_9$ (x=1.0) shows the agglomeration increases and its 5µm image and more spongy thread like nature increases on the platelet shape. From these micrograph particles, hexagonal diffused grain crystalline nature its size range from 150nm to 300nm. SEM image shows the yttrium doping increases the spongy nature of particles increases.

2.4.3.3 EDX analysis

EDX spectra of Ca$_{3-x}$Y$_x$Co$_4$O$_9$ (x=0.0-1.0) is shown in Fig.2.5. The spectrum clearly ascertains the presence of calcium, cobalt, yttrium and oxygen in the synthesized samples. However, the atomic ratio of yttrium site increase and calcium decrease from this spectrum it clearly indicates the doping of Y$^{3+}$ in Ca$^{2+}$. Ca$_3$Co$_4$O$_9$ parent analysis shows that the ceramics are formed by Ca, Co and O whose atomic percentage varies locally with an average value of 25.8%, 18.7% and 55.5% for Co, Ca and O, respectively. Ca$_{3-x}$Y$_x$Co$_4$O$_9$ (x=0.2). In this Y$^{3+}$ present as 1.00% and for (x=0.6) doping atomic percentage as 1.34% then (x=1.0) for this compound 4.55% of yttrium observed in the spectra.
Fig. 2.4 SEM analysis of $\text{Ca}_{3-x}\text{Y}_x\text{Co}_4\text{O}_9$ ($X = 0, 0.4, 1.0$) lower and high magnifications
Fig. 2.5 EDX spectra of Ca$_{3-x}$Y$_x$Co$_4$O$_9$ (x=0.0, 0.2, 0.6, 1.0) for elemental composition.
2.4.3.4 Diffuse Reflectance spectroscopy studies

Fig.2.6. shows the optical property of Ca$_3$Co$_4$O$_9$ was studied by UV-Visible DRS absorption spectra. The spectra were recorded between 200 to 800 nm wavelength regions at room temperature. It contains major peaks at wavelengths of 204, 234 nm and other minor broad peak at 340 nm due to the presence of Ca-O, Co-O stretching bonds. The filling of the conduction band by electrons will generally result in blue shift, which is clearly observed in the absorbance spectra. Therefore, the augmentation of carrier concentration may be attributed, on one hand, to the substitution of Y$^{3+}$ ions for Ca$^{2+}$ ions as their ionic radii match resulting in two more free electrons, and Ca$_3$Co$_4$O$_9$ Oxide is a p-type conductive material in which many of the intrinsic defects (oxygen vacancies, interstitial) exist. The spectrum can be explained in terms of charge transfer in transition metal (TM) oxides. The relationship between the absorption coefficients $\alpha$ is an incident photon energy $h\nu$. In order to calculate the optical band gap of sample by using Tauc’s relation in equation (2.2)

$$ (\alpha h\nu)^n = A(h\nu - E_g) $$

where $\alpha$ denotes the absorption coefficient, $A$ is constant, $E_g$ is band gap and exponent $n$ depends on the type of transition. For directly allowed transitions, indirect allowed transition and direct forbidden transition, $n$ is 1/2, 2 and 3/2, respectively.

For the sample under investigation, the conduction process can be attributed to the presence of two types of charge carriers, that is, p type, as a hole exchange between Co$^{4+}$, Co$^{3+}$ and Co$^{2+}$ and transfer of O$^{2-}$ between filled side with vacant oxygen side. The following equation (2.3), (2.4) and (2.5) can explain the mechanism as follows

$$ \text{Co}^{4+} \rightarrow \text{Co}^{3+} + h^+ $$

(2.3)

$$ \text{Co}^{3+} \rightarrow \text{Co}^{2+} + h^+ $$

(2.4)

$$ 1/2\text{O}_2 + \text{V}^{2+} \rightarrow \text{O}^{2-} $$

(2.5)
Fig.2.7. shows the optical band gap was calculated using Tauc relation by plotting \((ah\nu)^2\) against \(h\nu\), by extrapolating the curve to photon energy axis. Calcium cobaltite prepared in this work, cobalt exists in the octahedra of oxygen ions with Co\(^{3+}\) (high spin \(e_g^2\ t_{2g}^4\) / low spin \(e_g^0\ t_{2g}^6\)) ions occupying tetrahedral and octahedral sites, respectively [H.F. Jiang et al., (2009); Jinmei Wang et al., (2011); S.K. Jaiswal et al., (2011); S. S. Pawar et al., (2013)]. The optical absorption plot shows energy band gap as 2.10eV due to the ligand to metal charge transfer (LMCT) takes place from O\(^{2-}\) to Co\(^{3+}\).

DRS spectrum explains the crystal field transitions in transition metal (TM) oxides. As a consequence, d\(^n\) configuration splits into multiplet levels which, in turn, further split by the crystal field such that the ‘3d’ band extends beyond the O(2p)–Co(4s) gap. An obvious blue shift of the absorption edges can also be observed in the system and the measured optical band gap for different composition as shown in Table-2.2. Hence d-d charge transfer takes place in the Ca\(_3\)Co\(_4\)O\(_9\) system it shows p-type semiconducting material by yttrium doping it becomes insulator.

Table-2.2. DRS energy band gap estimate from Fig. 2.7.

<table>
<thead>
<tr>
<th>Composition (X)</th>
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<tr>
<td>0.8</td>
<td>4.50</td>
</tr>
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<td>1.0</td>
<td>4.54</td>
</tr>
</tbody>
</table>
Fig. 2.6. UV-Visible absorbance spectra of Ca$_{3-x}$Y$_x$Co$_4$O$_9$
Fig. 2.7. DRS optical band gap for $\text{Ca}_{3-x}\text{Y}_x\text{Co}_4\text{O}_9$
2.4.3.5 Electrical resistivity measurement

Fig.2.8. shows the electrical resistivity measured by DC four probe method. Ca$_{3-x}$Y$_x$Co$_4$O$_9$ sample pressed into a pellet with a diameter of 12mm and sintered at 800°C for 12 hours. The pellet used as a sample for electrical resistivity measurement by four probe method, applied current (I) is 8mA and the resistance is measured in the temperature range of 300-473K. This method can eliminate the effects of contact resistance between the sample and electrical contacts and therefore is most suitable for low and accurate resistance measurements [Yadunath Singh (2013)]. The resistivity of the material is obtained from the equation (2.6). Using ohm’s law, after passing a constant current through a material the voltage generated can be measured at different temperature.

$$\rho = \left(\frac{V}{I}\right) 2\pi S \Omega \text{cm}$$

(2.6)

Where, $\rho =$ resistivity of the material, $V=$voltage (volts), $I=$current (Amp.), $S=$ distance between the probe (=0.1875).

The electrical resistivity decreases with increasing temperature as shown in Fig.2.8. The materials have negative temperature coefficient of resistance semiconductor. Yttrium content increase its resistivity also increases due to the impurity compensation effect decreases the mobility and concentration of the hole with increasing resistivity. The graph was drawn between resistivity vs. temperature is plotted.

If we increase the temperature, however thermal agitation increases and some valence electron gain energy greater than $E_a$ and then jump to the conduction band. The activation energy of the material is calculated from the relation in equation (2.7), where k is Boltzmann constant.

$$E_a = \frac{2.303 \times 2k \times \text{Slope}}{2}$$

(2.7)
Fig. 2.9. shows the graph is plotted between $\log_{10}\rho$ versus $T^{-1}$ shows higher electrical resistivity at room temperature as the temperature increases the resistivity decreases due to hopping conduction mechanism. The slope value is calculated from the graph and it is substituted in equation 7, to calculate the activation energy is 0.06eV of $\text{Ca}_{3-x}\text{Y}_x\text{Co}_4\text{O}_9$ (x=1.0) increases with increasing yttrium content.

For these $\text{Ca}_{3-x}\text{Y}_x\text{Co}_4\text{O}_9$ pellets, the resistivity is measured from room temperature 295K to 470K and represented in Table-2.3.

**Table-2.3 Electrical resistivity of $\text{Ca}_{3-x}\text{Y}_x\text{Co}_4\text{O}_9$**

<table>
<thead>
<tr>
<th>Composition (X)</th>
<th>Electrical resistivity ($\rho$) (at room temperature) m.ohm.cm</th>
<th>Electrical resistivity ($\rho$) (at 200°C) mohm.cm</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
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<td>0.0141</td>
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<td>0.0448</td>
</tr>
<tr>
<td>1.0</td>
<td>0.257</td>
<td>0.1320</td>
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</tbody>
</table>
Fig. 2.8 Electrical resistivity as a function of temperature for Ca$_{3-x}$Y$_x$Co$_4$O$_9$

Fig. 2.9 log$_{10}$ρ versus $T^{-1}$ shows Activation energy for Ca$_{3-x}$Y$_x$Co$_4$O$_9$
2.4.3.6 Magnetic Measurement

Fig. 2.10 shows the magnetic properties of Ca$_{3-x}$Y$_x$Co$_4$O$_9$ were obtained by using Quantum Design PPMS system. The graph plotted between the magnetization versus applied magnetic field (M-H curves) at a temperature of 5K. It exhibits clearly ferrimagnetic hysteresis loop at 5K with low coercivity values. M-H curve shows hysteresis loop with the increase of temperature the hysteresis curve change to a straight line it proves the material has a ferrimagnetic to paramagnetic phase transition.

Fig. 2.11. shows the variation of saturation magnetization $M_s$ and coercivity $H_c$ with increasing content of Yttrium in Ca$_{3-x}$Y$_x$Co$_4$O$_9$. The saturation magnetization decreases with respect to rare earth yttrium doped on calcium site because the trivalent ($Y^{3+}$) substitute on divalent (Ca$^{2+}$), it creates the oxygen vacancy this leads to mixed oxidation state of cobalt ions present in the substituted sample.

Hence for Ca$_{3-x}$Y$_x$Co$_4$O$_9$ (x=1) saturation magnetization attain a low value of 5x10$^{-4}$. The coercivity ($H_c$) decreases with respect to rare earth yttrium doped on calcium site because the trivalent ($Y^{3+}$) substitute on divalent (Ca$^{2+}$) increase in magneto-crystalline anisotropy is related to the increase in low spin Co$^{2+}$ ions concentration at the octahedral site. Hence for Ca$_{3-x}$Y$_x$Co$_4$O$_9$ (x=0-1) coercivity decreases finally attains zero, this reveals it becomes paramagnetic material.
Fig. 2.10. Magnetic field dependence of magnetization at room temperature for the Ca$_{3-x}$Y$_x$Co$_4$O$_9$ samples.

Fig. 2.11. Variation of saturation magnetization $M_s$ and coercivity $H_c$ with increasing content of Yttrium in Ca$_{3-x}$Y$_x$Co$_4$O$_9$.
2.4.3.7 Conclusion

$\text{Ca}_{3-x}\text{Y}_x\text{Co}_4\text{O}_9$ (x=0.0-1.0) have been prepared by one step molten salt synthesis. By this flux method highly crystalline product is achieved by short time duration process. The higher electrical resistivity for Yttrium doped samples attributes to the impurity compensation effect. An optical study proves the band gap increases from 3.6 to 4.54eV with $\text{Y}^{3+}$ doping due to p-type semiconductor-insulator transitions occurred. This compound having interesting electrical properties of materials can be better improved at higher Yttrium doping. The magnetic results reveal that the rare earth ions, doped in $\text{Ca}_{3-x}\text{Y}_x\text{Co}_4\text{O}_9$ behave as a paramagnetic material. M-H curve shows hysteresis loop with saturation magnetization ($M_s$) and coercivity ($H_c$) reveals the presence of soft magnetic material.

2.4.4. Sol-gel combustion synthesis of $\text{Ca}_3\text{Co}_4\text{O}_9$

$\text{Ca}_3\text{Co}_4\text{O}_9$ are synthesized by a solid state reaction between the individual component oxide powders. This method generally requires repeated mechanical mixing and extensive heat treatment at high temperatures to achieve the desired phase purity. It has been accepted that the wet-chemical process offers advantages of good mixing of the starting materials and excellent chemical homogeneity of the final product [M. Sopicka Lizer et al., (2005); L.B. Wang et al., (2002); P.S. Liu et al., (2008)]. Sol-gel method could conquer these drawbacks. In this method, the reactant cations are intimately mixed on an atomic scale, so the rate of the reaction will be increased, leading to lower synthesis temperatures [S. Mathur et al., (2002)]. By contrast with traditional solid state reaction, the sol–gel method is an efficient way to decrease the atom diffusion distance and to obtain the new pure phase in a lower temperature range [J.M. Zheng et al., (2011)]. In sol-gel method, the reactant cations are intimately mixed on the atomic scale, so the rate of the reaction will be increased; leading to lower synthesis temperatures and smaller particles [J. Pei et al., (2009)].
2.4.4.1 Experimental Procedure

Polycrystalline samples of Ca$_3$Co$_4$O$_9$ were synthesized by the sol-gel cum combustion method using starch [$(C_6H_{10}O_5)_n$] as a gelling agent and combustion fuel. The starting materials were analytical-grade starch, Ca(NO$_3$)$_2$.4H$_2$O and Co(NO$_3$)$_2$.6H$_2$O. Aqueous solutions 50ml of 3M of calcium nitrate and 50ml of 4M of cobalt nitrate the reactants were mixed by using the magnetic stirrer attached with hot plate (Magnetic stirrer- REMI -1MLH model) and then add 50ml of 7M starch solution added into the mixed metal nitrate solution. The resulting pink transparent solution was heated to a temperature in the range 353-393K in the mean time the temperature was checked by using thermometer with constant stirring to obtain the pink gel. Subsequently, it was decomposed at 623K for 0.5 h in a preheated silica carbide furnace (INDFUR furnace heating rate 10°C/min), resulting in a large voluminous fluffy mass of black precursor. This precursor was then heated at 1073K for 12h to obtain the single phase product by removing carbonaceous material.

2.4.4.2 Characterization Technique

Thermogravimetry differential thermal analysis of precursor was carried out with a SDT Q600 V20.9 model. The powders were characterized by X-ray diffraction technique (XRD, Bruker D8 Advance, by CuK$_\alpha$ radiation, $\lambda_{\alpha}$ = 1.5406Å). FTIR spectrums were examined using JASCO 400 Infrared spectrometer. The surface morphology and the microstructure were studied by a scanning electron microscope (HRSEM FEI Inspect F50) instrument. The chemical composition was determined with an EDX analyzer attached with a (HRSEM FEI Inspect F50) instrument. Optical band gap obtained by using Jasco V-670-UV-Visible diffused reflectance spectrometer. Electrical resistivity is measured from Dc Four probe setup, electrical resistivity play a major role in technical applications. Dielectric measurements were studied by a LCR meter (HIOKI 3532-50LCR meter HITESTER) dielectric studies in the frequency range from 50Hz to 5MHz for variation of temperature. The magnetic properties were studied by using Quantum Design PPMS system.
2.4.4.3 Results and Discussion

2.4.4.4 Thermal analysis

Thermogravimetric analysis (TGA) is an important tool to determine the stable product formation and decomposition step of carbonaceous organic compound present in the precursor. Fig. 2.12. shows the TGA-DTA results of pink gel precursor powder. TGA graph shows three decomposition step, first step the weight loss of about 12.32% due to evaporation of adsorbed water at 313-373K (40-100°C). The endothermic peak appears to be due to the initiation of starch melting 586K (the melting point is 213°C) (C. Suciu et al., 2008; J.M. Zheng et al., 2011). When second step weight loss 7.6% in the temperature range of 423-533K (150-260°C) due to decomposition of polymeric metal-starch ligand containing the hydroxyl bonds broken it losses hydrogen and oxygen removed as gaseous compounds. The second endothermic peak at 954K (681°C) due to decomposition of nitrogen compounds as nitrous oxide and carbon dioxide as organic material it leads to form CaCO₃ and Co₃O₄. Finally, the third step weight loss of 20.26% due to decomposition of carbonates to oxide by loss of carbon dioxide in the temperature of 1073K it forms the Ca₃Co₄O₉ stable product. The following Eq.(2.8) represents the overall weight loss 42.70% due to the decomposition of organic compounds and carbonates into oxide, it could be further proved by XRD.

\[
\begin{align*}
3\text{Ca(NO}_3\text{)}_2\cdot4\text{H}_2\text{O} + 4\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} + 7\text{[(C}_6\text{H}_{10}\text{O}_5\text{)]}_n} & \quad \text{1023K} \\
\text{Ca}_3\text{Co}_4\text{O}_9 + 14\text{NO}_2_{(g)} + 36\text{ H}_2\text{O}_{(g)} + x\text{O}_2_{(g)} + n\text{CO}_2_{(g)} + (nC+nH_2) & \quad \text{Decomposition step these gaseous phases removed}
\end{align*}
\]
Fig. 2.12. TGA-DTA pattern of precursor decompose to Ca$_3$Co$_4$O$_9$
2.4.4.5 XRD analysis

Fig.2.13. shows the XRD pattern of the product calcined at various temperatures. The sol gel combustion 623K precursor product XRD pattern shows the presence of corresponding metal carbonates. After calcinations at 873K for 2 hours, CaCO₃ phases and Co₃O₄ are detected. Increasing the temperature to 973K for 2 h, calcium carbonate decomposed it form an amorphous Ca₃Co₄O₉ phase. Further increase the temperature to 1073K for 12h the XRD pattern proves the Ca₃Co₄O₉ stable single phase formed as monoclinic crystal system and its lattice parameters a=b=4.8251Å, c=10.8506Å were consistent with those reported in JCPDS (card No 21-0139). Using the XRD diffraction data, the crystallite sizes of samples were able to be estimated using the Scherer Eq.(2.9).

$$D = \frac{K\lambda}{\beta\cos\theta}$$  \hspace{1cm} (2.9)

In this equation, $D$ is the crystallite size (nm); $K$ is the so-called shape factor, which usually takes a value of about 0.9; $\lambda$ is the X-ray wavelength; $\beta$ is the full width at half maximum of the diffraction peak at $\theta$ is the diffraction angle. Since the peak from the most intense (004) plane diffraction was selected to calculate the average crystallite size of Ca₃Co₄O₉ as ~ 150-300nm.

2.4.4.6 FTIR Studies

FTIR absorption band in the range of 4000-400cm⁻¹ are usually assigned to vibration of ions in the crystal lattice were recorded using KBr disc method. Fig.2.14. shows the FTIR spectra of the sol gel combustion precursors of 673K product shows the presence of organic compounds and carbonate peaks. As illustrated in the band at 3480cm⁻¹ could be assigned to absorbed water and two bands appear at 1440 and 850cm⁻¹ were assigned to the stretching vibration of carbonate peak which decreases, with calcinations increase from 873K to 973K. From the FTIR spectra illustrated at 1073K that the carbonate decomposed and the bands appear at 690 cm⁻¹ and 520 cm⁻¹, 440 cm⁻¹ due to the vibration of Ca-O and Co-O groups (Jie Xu et al., 2010; J. Pei et al., 2009; V. A. M. Brabers et al., 1969; Y. F. Zhang et al., 2006).
Fig. 2.13. XRD pattern of Ca$_3$Co$_4$O$_9$
Fig. 2.14. FTIR spectra of Ca$_3$Co$_4$O$_9$. 

![FTIR spectra of Ca$_3$Co$_4$O$_9$](image-url)
2.4.4.7 SEM Micrograph analysis

Fig.2.15. shows the SEM image of Ca₃Co₄O₉ ceramic prepared by the sol gel combustion method. The figures represent several magnifications. In order to investigate the morphology evolution of the samples Using the Image J program the diameter values of the spheres were obtained from 150 to 300 nm, the material shows a micro porous sphere like morphology and is composed of agglomerated assembled spheres indicate a good connectivity between the grains.

2.4.4.8 EDX analysis

Fig.2.16. shows the energy dispersive X-ray spectroscopy (EDX) used to quantify the elements exist in the prepared sample by taking a selective portion of SEM image in the form peaks. The EDX pattern confirms the findings of XRD pattern and shows the combination of Ca₃Co₄O₉.

2.4.4.9 Diffuse Reflectance spectroscopy studies

Fig.2.17. shows the optical property of Ca₃Co₄O₉ was studied by UV-Visible DRS absorption spectra. The spectra were recorded between 200 to 800 nm wavelength regions at room temperature. It contains major peaks at wavelengths of 204, 234 nm and other minor broad peak at 340 nm due to the presence of Ca-O, Co-O stretching bonds. The spectrum can be explained in terms of charge transfer in transition metal (TM) oxides. The relationship between the absorption coefficients α is an incident photon energy hυ. In order to calculate the optical band gap of sample by using Tauc’s relation in equation (2.10)

\[(ahυ)^n = A(hυ−Eg)\]  

(2.10)

where α denotes the absorption coefficient, A is constant, \(E_g\) is band gap and exponent n depends on the type of transition. For directly allowed transition, indirect allowed transition and direct forbidden transition, n is 1/2, 2 and 3/2, respectively. Fig.2.18. shows the optical band gap was calculated using Tauc relation by plotting \((ahυ)^2\) against \(hυ\), by extrapolating the curve to photon energy axis.
Fig. 2.15. SEM images of Ca$_3$Co$_4$O$_9$
Fig. 2.16. EDX spectra for elemental composition of $\text{Ca}_3\text{Co}_4\text{O}_9$
Calcium cobaltite prepared in this work, cobalt exists in the octahedra of oxygen ions with Co\(^{3+}\) (high spin \(e_g^2 t_{2g}^4\) / low spin \(e_g^0 t_{2g}^6\)) ions occupying tetrahedral and octahedral sites, respectively [H.F. Jiang et al., (2009); Jinmei Wang et al., (2011); S.K. Jaiswal et al., (2011); S. S. Pawar et al., (2013)]. The optical absorption plot shows energy band gap as 2.10 eV due to the ligand to metal charge transfer (LMCT) takes place from O\(^2-\) to Co\(^{3+}\).

DRS spectrum explains the crystal field transitions in transition metal (TM) oxides. The interactions of 3d-transition metal electrons with the surrounding oxygen ions form localized states which spread out over an energy range due to strong repulsion among the d-electrons themselves. As a consequence, \(d^n\) configuration splits into multiplet levels which, in turn, further split by the crystal field such that the ‘3d’ band extends beyond the O(2p)–Co(4s) gap. Hence d-d charge transfer takes place in the Ca\(_3\)Co\(_4\)O\(_9\) system it shows p-type semiconducting material.

2.4.4.10 Electrical Resistivity Measurements

Ca\(_3\)Co\(_4\)O\(_9\) ceramic powder was pelletized using a hydraulic press technique employing a pressure of 7tons and it compressed to form a pellet was 12mm in diameter and 1mm in thickness. Ca\(_3\)Co\(_4\)O\(_9\) pellet was sintered at 1073K for 12 hours. The pellet used as a sample for electrical resistivity measurement by four probe method, applied current (I) is 8mA and the resistance is measured in the temperature range of 300-473K. The method can eliminate the effects of contact resistance between the sample and electrical contacts and therefore is most suitable for low and accurate resistance measurements [Yadunath Singh (2013)]. The resistivity of the material is obtained from the formula equation (2.11)

\[
\rho = \left(\frac{V}{I}\right) 2\pi S \Omega \text{ cm}
\]

where S is the distance between probe S= 0.1875, V is the obtained voltage across the two inner contacts, I is the current passing through the sample.
Fig. 2.17. UV-DRS absorption spectra of Ca$_3$Co$_4$O$_9$

Fig. 2.18. DRS band gap spectra of Ca$_3$Co$_4$O$_9$

Fig. 2.19. shows the relation between resistivity of material with increasing temperature. Ca$_3$Co$_4$O$_9$ p-type semiconductor must have a narrower band gaps so that appreciable number of charge carriers are in the valance and conduction bands at room
temperature. The maximum electrical resistivity (0.002mΩcm) was exhibited by Ca$_3$Co$_4$O$_9$ that was decreased to 0.0012mΩ cm. Temperature were increased from 300K to 473K. If we increase the temperature, however thermal agitation increases and some valance electron gain energy greater than $E_a$ and then jump to conduction band. The activation energy of the material is calculated from the relation in Eq.(2.12), where k is Boltzmann constant.

$$E_a = \frac{2.303 \times 2k \times \text{Slope}}{2} \quad (2.12)$$

**Fig.2.20.** shows the graph is plotted between log$_{10}\rho$ versus $T^{-1}$ shows higher electrical resistivity at room temperature as the temperature increases the resistivity decreases due to hopping conduction mechanism. The slope value is calculated from the graph and it is substituted in equation 4, to calculate the activation energy of Ca$_3$Co$_4$O$_9$ is 0.99eV.

### 2.4.4.11 Temperature Dependence Dielectric Studies

Ca$_3$Co$_4$O$_9$ ceramic powder was pelletized using a hydraulic press technique employing a pressure of 7tons and it compressed to form a pellet was 12mm in diameter and 1mm in thickness. The pellet was finely polished by electronic grade silver paints were applied on top and bottom faces of pellet to make a capacitor. LCR meter (HIOKI 3532-50 LCR meter HITESTER) was used to carry dielectric studies in the frequency range from 50Hz to 5MHz for variation of temperature. The control, measurements and analyses were maintained through the computer with indigenously developed software. The dielectric constant ($\varepsilon'$) is calculated from the formula equation.(2.13)

$$\varepsilon' = \frac{C_p t}{A \varepsilon_0} \quad (2.13)$$

Where $C$ is the capacitance obtained from the analysis, $t$ is the thickness of the pellet, $\varepsilon_0$ is the permittivity of the free space, $A$ is the area of the pellet [Banwari Lal et al (2004)].
Fig. 2.19. Electrical resistivity as a function of temperature for Ca$_3$Co$_4$O$_9$.

Fig. 2.20. log$_{10} \rho$ versus $T^{-1}$ shows Activation energy for Ca$_3$Co$_4$O$_9$.
Fig. 2.21. shows the temperature dependence of dielectric constant (ε’) versus temperature of at different frequencies. Strong relaxation of ε’ is observed in the investigated frequency range where the temperature range is maximum. The dielectric constant increases with temperature increases. The intense peak is observed from the graph between dielectric constant and temperature which corresponds the phase transition temperature (T_m). In this temperature structural phase transition takes place from polar to non-polar phase at 420K due to the polarization from two different types of charge carriers [A.L. Kholkin et al., 2001; N. Rezlescu et al., 1974; H. M. Zaki et al., 2005]. For the sample under investigation, the conduction process can be attributed to the presence of two types of charge carriers, that is, p type, as a hole exchange between Co^{4+}, Co^{3+} and Co^{2+} and transfer of O^{2-} between filled side with vacant oxygen side. The following Eq. (2.14), (2.15) and (2.16) can explain the mechanism as follows

\[
\begin{align*}
\text{Co}^{4+} & \rightarrow \text{Co}^{3+} + h^* \\
\text{Co}^{3+} & \rightarrow \text{Co}^{2+} + h^* \\
\frac{1}{2}\text{O}_2 + V^{2+} & \rightarrow \Theta^2
\end{align*}
\]  

(2.14), (2.15), (2.16)

The ac conductivity is calculated from the equation. (2.17), (2.18)

\[
\sigma_{ac} = \omega \varepsilon_0 \varepsilon' \tan \delta \quad (2.17)
\]

\[
\omega = 2\pi f \quad (2.18)
\]

where \( f \) is the applied ac frequency. The activation energy is obtained from the graph \( \sigma_{ac} \) versus inverse of temperature in kelvin.

\[
\sigma = \sigma_0 \exp \left( \frac{E_a}{kT} \right) \quad (2.19)
\]

where \( k \) is Boltzmann constant and \( T \) is the temperature.

Fig. 2.22. shows the temperature dependence of dielectric loss (or) tan δ also increases with increasing temperature. The major reason for increasing dielectric loss due to the domain wall density increases, resulting in the decrease of the dielectric constant.
Fig. 2.23. shows the temperature dependence of $\sigma_{ac}$ for Ca$_3$Co$_4$O$_9$ at frequency of 5 kHz. The Figure shows that $\sigma_{ac}$ increases gradually with temperature up to 423 K after which a rapid increase is obtained. The conductivity gets decreases with increased temperature (D. Szwagierczak et al., 2005). The activation energies were calculated by curve fitting Eq.(2.19) the activation energy is $E_a = 0.96$ eV. The low activation energy suggests an intrinsic conduction due to the contribution of space charge carriers and holes.

Fig. 2.24. Shows the diffuse phase transition graph plot between ln($\varepsilon_m'/\varepsilon'$) Vs ln $(T-T_m)$ at frequency of 5KHz can be obtained from the following Vogel-Fulcher Eq. (2.20)

$$\frac{\varepsilon_m'}{\varepsilon'(T)} = 1 + \frac{[T-T_m(f)]^\gamma}{2\delta^2} \quad (1 \leq \gamma \geq 2) \quad (2.20)$$

where $\varepsilon_m'$ maximum dielectric constant at $T_m$, $T_m$ is the phase transition temperature, $\varepsilon'$ dielectric constant, $\gamma$ is the degree of dielectric relaxation, $\delta$ is the degree of diffuseness $T$ is the absolute temperature in kelvin. The degree of dielectric relaxation can be obtained from the slope of the graph, ($\gamma=1.96$) is $> 1$, express more relaxor ferroelectric behaviour of transition. The intercept of graph is the degree of diffuseness ($\delta=0.63$) resulted in a lower degree of diffuseness and weaker relaxor behaviour [Chien-Chih Huang et al (2007)].

2.4.4.12 Temperature dependence Magnetic Measurement

Fig. 2.25. Shows the magnetic moment of Ca$_3$Co$_4$O$_9$ proves the temperature dependent magnetic behavior. It behaves as ferromagnetic at 5K as the temperature increases above 50K, phase transition take place between ferrimagnetic to paramagnetic behavior.
Fig. 2.21. Variations of Dielectric constant (ε') as a function of temperature for Ca$_3$Co$_4$O$_9$.

Fig. 2.22. Variations of Dielectric loss (tan δ) as a function of temperature for Ca$_3$Co$_4$O$_9$. 

Fig. 2.23. Variations of AC conductivity for Ca$_3$Co$_4$O$_9$ with absolute temperature at a frequency of 5 KHz for Ca$_3$Co$_4$O$_9$.

Fig. 2.24. Diffuse phase transition graph plot between ln($\varepsilon_m'/\varepsilon'$) Vs ln (T-$T_m$) at frequency of 5KHz for Ca$_3$Co$_4$O$_9$. 

\[ E_a = 0.96 \text{eV} \]

\[ \gamma = 1.96 \]
Fig. 2.25. Magnetic moment Vs Field (Gauss) for Ca₃Co₄O₉
In this Ca₃Co₄O₉ system interaction takes place mainly due to the presence of cobalt ions. The transfer of electron between Co³⁺ and Co²⁺ double layer interaction in the rock salt-type (Ca₂CoO₃) subsystem and a single CdI₂-type (CoO₂) subsystem of sandwiched layer structure of Ca₃Co₄O₉ (Yanan Huang et al., 2012; S. Demirel et al., 2013).

Fig.2.25. shows the magnetic properties of Ca₃Co₄O₉ were obtained by using VSM. The graph plotted between the magnetization versus applied magnetic field (M-H curves) at temperature of 300K. It exhibit clear ferrimagnetic hysteresis loop with low coercivity values. M-H curve reveals the presence of soft magnetic material.

2.4.4.13 Conclusion

Starch assisted sol gel combustion as a simple and efficient method to synthesize of pure Ca₃Co₄O₉ ceramic powder. X-ray diffraction pattern confirmed the formation of single phase Ca₃Co₄O₉. Thermal analysis proves the Ca₃Co₄O₉ phase formation temperature of 1073K. SEM image indicates the obtained samples are diffused micro porous sphere like morphology and its grain size will be in the range of 150-300nm. Optical properties of Ca₃Co₄O₉ ceramic shows a band gap in the energy range of 2.10eV. The maximum electrical resistivity (0.002mΩ cm) was exhibited by Ca₃Co₄O₉ that was decreased to (0.0012mΩ cm) due to temperature were increased from 300K to 473K. The temperature dependent electrical property of Ca₃Co₄O₉ material proves as the temperature increases phase transitions occur. Dielectric test observed for the function of temperature from room temperature to 673K indicates the space charge polarization contributes the conduction mechanism. Ca₃Co₄O₉ material shows the dielectric relaxation with activation energy 0.96eV. Ferrimagnetic to paramagnetic phase transition occur because of the interlayer coupling between Ca₂CoO₃ and CoO₂ two sub systems arranged in the rock salt manner with the increase of temperature in M-H curve. Room temperature (300K) shows hysteresis loop reveals the presence of soft magnetic material.

2.4.5. Co precipitation precursor Synthesis and characterization of Ca₃Co₄O₉

The composition and microstructure of oxide ceramics plays an important role to optimize the efficiency of the electrical and magnetic properties. Although a lot of methods have been reported to be efficient to produce well aligned bulk materials, in
these or in similar anisotropic systems, such as spark plasma sintering, laser floating zone melting (LFZ), template grain growth (TGG), microwave texturing, hot uniaxial pressing etc. Ca$_3$Co$_4$O$_9$ powders were mostly synthesized by the solid-state reaction process [Kohei obata et al., (2013); G. Xu et al., (2002); S.W. Li et al., (2001)]. Although in solid state process has more disadvantage as high reaction temperatures, low chemical homogeneity and long time process. The advantage of precursor method is maintaining the metals ratio in a homogenous form and the product formed in low temperature compare to other ceramic methods. The solid solution precursor method for preparation of mixed metal oxides as the method reported in [K. Vidyasagar et al., (1984)]. Cobalt oxide can also be used in biomedical application as fibrous textile possessing enhanced antimicrobial properties are prepared by the deposition or interstitial precipitation of cobalt (II, III) oxide (Co$_3$O$_4$) crystals. This chapter deals with precursor synthesis of Ca$_3$Co$_4$O$_9$ and objective of our present work is to study its semiconducting behavior and the first time reporting its antibacterial activity against Klebsiella pneumonia and Escherichia coli.

2.4.5.1 Preparation of Ca$_3$Co$_4$O$_9$

Ca$_3$Co$_4$O$_9$ was synthesized using a co precipitation carbonate process as described in detail [K. Vidyasagar et al., (1984)]. In this work stoichiometry ratios of metal nitrates were dissolved in deionized water under constant stirring at 80°C. For the precipitation 2M sodium carbonate was dripped into the mixed salt solution under mild stirring until the pH value of the salt solution reached 8.5. The suspension was stirred for 30 minutes to attain homogenization. The precipitated carbonate was washed with distilled water and dried at 80°C for 4h. The colorless filtrate was tested for residual metal ions to determine the complete precipitation. Then the carbonate precursor can be further decomposed to 800°C for 3 hours the presence of air, it forms the single phase Ca$_3$Co$_4$O$_9$ as a product.

2.4.5.2 Characterization Techniques

Thermogravimetry differential thermal analysis of precursor was carried out with a SDT Q600 V20.9 model. The powders were characterized by Powder X-ray diffraction technique (XRD, Bruker D8 Advance, by CuKα radiation, kα = 1.5406Å). FTIR spectrums were examined using JASCO 400 Infrared spectrometer. The surface
morphology and the microstructure of $\text{Ca}_3\text{Co}_4\text{O}_9-\delta$ were studied by a scanning electron microscope (HRSEM FEI Inspect F50). The chemical composition was determined with an EDX analyzer attached with a (HRSEM FEI Inspect F50) instrument. Oxygen content estimation was also determined by thermogravimetric analysis and iodometric titration. Optical band gap obtained by using Jasco V-670-UV-Visible diffused reflectance spectrometer. The antibacterial activity of $\text{Ca}_3\text{Co}_4\text{O}_9-\delta$ was studied by agar well diffusion method.

2.4.5.3. Results and Discussion

2.4.5.4. Thermal analysis

The decomposition mechanism of carbonate precursor and product formation was investigated by TGA-DTA. Thermogravimetry differential thermal analysis was carried out from room temperature to 900°C in an oxygen atmosphere at a heating rate of 4°C/min. Fig.2.26. shows the thermal analysis of carbonate precursor. The first weight loss 6.1% due to the evaporation of residual water. The possible stepwise weight loss of metal carbonate precursor as shown below scheme-1. The two endothermic peak at 217°C and 621°C due to loss of carbon dioxide then it forms oxycarbonates, further decompose at high temperature 800°C it forms stable product of $\text{Ca}_3\text{Co}_4\text{O}_9-\delta$ the overall weight loss 35.05% and phase identification by XRD it proves the product formation.

**Scheme-1 Plausible stepwise decompositions**

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Temperature</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Ca}_3\text{Co}_4(\text{CO}_3)_7 + \text{O}_2 \rightarrow \text{Ca}_3\text{Co}_4\text{O}_3(\text{CO}_3)_4 + 3\text{CO}_2$</td>
<td>250-600°C</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$\text{Ca}_3\text{Co}_4\text{O}_3(\text{CO}_3)_4 + \text{O}_2 \rightarrow \text{Ca}_3\text{Co}_4\text{O}_6(\text{CO}_3) + 3\text{CO}_2$</td>
<td>600-700°C</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$\text{Ca}_3\text{Co}_4\text{O}_6(\text{CO}_3) \rightarrow \text{Ca}_3\text{Co}_4\text{O}_9-\delta + \text{CO}_2$</td>
<td>800°C</td>
<td></td>
</tr>
<tr>
<td>Overall decomposition step</td>
<td>$\text{Ca}_3\text{Co}_4(\text{CO}_3)_7 + \text{O}_2 \rightarrow \text{Ca}_3\text{Co}_4\text{O}_9-\delta + 7\text{CO}_2$ (purple colour)</td>
<td>800°C</td>
<td>(black colour)</td>
</tr>
</tbody>
</table>
Fig. 2.26. TGA-DTA pattern for the formation of Ca$_3$Co$_4$O$_{9.8}$. 
2.4.5.5 XRD analysis

Fig.2.27. shows the XRD pattern of the product calcined at various temperatures. The precursor XRD pattern shows the presence of corresponding metal carbonates. After calcinations at 600°C for 2 hours, CaCO$_3$ phases and Co$_3$O$_4$ are detected. Increasing the temperature to 700°C for 2 h, calcium carbonate decomposed it form an amorphous Ca$_3$Co$_4$O$_9$-δ phase. Further increase the temperature to 800°C the XRD pattern proves the Ca$_3$Co$_4$O$_9$-δ stable single phase formed as monoclinic crystal system and its lattice parameters a=b=4.8261Å , c=10.8516Å  were consistent with those reported in JCPDS (card No 21-0139). Using the XRD diffraction data, the crystallite sizes of samples were able to be estimated using the Scherer equation (2.21).

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2.21)

In this equation, $D$ is the crystallite size (nm); $K$ is the so-called shape factor, which usually takes a value of about 0.9 ; $\lambda$ is the X-ray wavelength; $\beta$ is the full width at half maximum of the diffraction peak at $\theta$ is the diffraction angle. Since the peak from the most intense (004) plane diffraction was selected to calculate the average crystallite size of Ca$_3$Co$_4$O$_9$-δ as ~ 160-400nm.

2.4.3.6 FTIR Studies

Fig.2.28. shows the FTIR spectra was recorded for the carbonate precursor as obtained and after calcinations at different temperature. As illustrated in two bands at 3480 and 1630cm$^{-1}$ can be assigned to absorbed water which decreased with calcinations. When the precursor was calcined at 600°C, two bands appear at 1440 and 850cm$^{-1}$ are assigned to the stretching vibration of carbonate peak. From the spectra illustrated at 700°C that the carbonate structure decomposed and the band at 1440 and 850cm$^{-1}$ peak intensity decreases. After calcinations at 800°C, the bands appear at 690 cm$^{-1}$ and 520 cm$^{-1}$ 440 cm$^{-1}$due to the vibration of Ca-O and Co-O groups.
Fig. 2.27. XRD pattern of precursor and product - Ca$_3$Co$_4$O$_9$
Fig. 2.28. FTIR pattern of precursor and product - Ca$_3$Co$_4$O
2.4.5.7 Estimation of oxygen content by iodometry

A weighed sample ($m_1$) 50 mg was placed in 100ml Erlenmeyer flask with 10ml of 3N HCl are added dissolved in 1 g of KI and stirred with a magnetic stirrer for 10 minutes. After the sample is dissolved completely, an appropriate amount of buffer solution (mixture of 3N Ammonium acetate + 3N Acetic acid) is added to maintain the pH is 3.5. Liberated Iodine was titrated with $Na_2S_2O_3$ solution using 2 ml of 1% starch as the indicator and then 5 ml of 20% KSCN are added and continuously titrate to the disappearance of blue color is end-point. The total added volume of 0.01N $Na_2S_2O_3$ is recorded as $V_1$ (ml). This procedure was repeated for two or three times for concordant values. The oxygen content was determined by iodometric titrations using equation (2.22) for the case of copper. The redox reaction of this iodometry as follows.

$$Co^{4+} + 2I^- \rightarrow Co^{2+} + I_2$$

$$Co^{3+} + I^- \rightarrow Co^{2+} + \frac{1}{2}I_2$$

$$P = \left(\frac{mC \frac{V_1}{M_1}}{m} \right) - 1$$ (2.22)

Where $P$ is the excess oxidation state of cobalt ($Co^{2+P}$), $m$ (g/mol), $M_1$ (g) respectively, the molecular weight and mass of the sample $C$ (mol/l) and $V_1$ (ml) are the concentration and the used volume of sodium thiosulphate. Using iodometric titration formula weight and TGA raw data can be converted into oxygen content value by the following equation (2.23) The weight changes with temperature change caused by in and out of oxygen [M. Karppinen et al (2002); Eun-Seok Lee et al (2008)].

$$9 - \delta = FW \left(1 + \frac{\Delta m}{m} \times 1000\right) - W$$ (2.23)

where $FW$: formula weight of sample determined by iodometry, $\Delta m$: weight change in mg, $m$: initial weight in mg, and $W$: formula weight of sample except $O_{9-\delta}$ part. The oxygen content can be obtained from thermal analysis and iodometric method both proves as ($\delta= 0.05$) $Ca_3Co_4O_{8.95}$. 

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Fig. 2.29. High and low magnification of SEM image of \( \text{Ca}_3\text{Co}_4\text{O}_{9.5} \).
2.4.5.8 SEM Micrograph analysis

Fig. 2.29. (a) & (b) Shows the SEM image of calcium cobalt carbonate precursor and Ca$_3$Co$_4$O$_{9.5}$ particles prepared by the carbonate precursor method. The figures represent several magnifications. In order to investigate the morphology evolution of the precursor samples, the material shows a micro porous combined rod like morphology and the product oxide samples shows a diffused monoclinic like morphology. The figures represent several magnifications. Using the Image J program the diameter values of the spheres were obtained from 160 to 400 nm. In order to investigate micrograph of the material shows a micro porous combined monoclinic like morphology and it was composed of agglomerated grains indicate a good connectivity.

2.4.5.9 EDX analysis

Fig. 2.30. shows the energy dispersive X-ray spectroscopy (EDX) used to quantify the elements exist in the prepared sample by taking a selective portion of SEM image in the form peaks. The EDX pattern confirms the findings of XRD pattern and shows the combination of Ca$_3$Co$_4$O$_{9.5}$. The elemental compositions are listed in the Table-2.4.
Table 2.4. EDX elemental composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>OK</td>
<td>20.00</td>
</tr>
<tr>
<td>CaK</td>
<td>23.77</td>
</tr>
<tr>
<td>CoK</td>
<td>56.23</td>
</tr>
</tbody>
</table>

Fig 2.30. EDX analysis of Ca$_3$Co$_4$O$_9$
2.4.5.10 Diffuse Reflectance spectroscopy studies

Fig.2.31. shows the UV-Visible absorbance spectra for calcium cobalt carbonate precursor contains major peaks at wavelengths of 245, 400nm corresponds to calcite carbonate mineral. The Ca$_3$Co$_4$O$_{9.5}$ oxide product contains major peaks at wavelengths of 509nm due to the presence of Ca-O, Co-O metal oxygen bonds. The relationship between the absorption coefficients $\alpha$ is an incident photon energy $h\nu$. In order to calculate the optical band gap of sample by using Tauc’s relation in equation (2.24)

$$(\alpha h\nu)^n = A(h\nu-E_g) \quad (2.24)$$

Where $\alpha$ denotes the absorption coefficient, $A$ is constant, $E_g$ is band gap and exponent $n$ depends on the type of transition. The optical band gap calculated by using Tauc relation by plotting $(\alpha h\nu)^2$ against $h\nu$ where $\alpha$ and $h\nu$ denote the absorption coefficient and photon energy respectively and by extrapolating the curve to photon energy axis. The band-gap energy ($E_g$) values evaluated using Tauc’s plot as shown Fig.2.32. Optical band gap properties of carbonate precursor and Ca$_3$Co$_4$O$_{9.5}$ oxide product studied by UV-Visible DRS absorption spectra. The optical absorption plot of carbonate precursor shows wide energy band gap as 4eV due to the ligand to metal charge transfer (LMCT) takes place from O$^{2-}$ to octahedral Co$^{2+}$, it reveals the insulating property. The optical absorption band gap of oxide product at 2eV due to ligand to metal charge transfer (LMCT) takes place from O$^{2-}$ to mixed oxidation state of cobalt as (Co$^{2+}$&Co$^{3+}$). Hence d-d charge transfer takes place in the calcium cobalt oxide system it shows a semiconducting behavior. The following Eq. (2.25), (2.26) and (2.27) can explain the mechanism as follows [Kohei obata et al., (2013)].

$$\text{Co}^{4+} \rightarrow \text{Co}^{3+} + h^* \quad (2.25)$$

$$\text{Co}^{3+} \rightarrow \text{Co}^{2+} + h^* \quad (2.26)$$

$$\frac{1}{2}\text{O}_2 + V^{2+} \rightarrow \text{O}^{2-} \quad (2.27)$$
Fig. 2.31. UV-Absorbance spectra of Ca$_3$Co$_4$O$_9$. 

Fig. 2.32. DRS optical band gap for Ca$_3$Co$_4$O$_9$. 

Calcium cobalt carbonate
For the sample under investigation, the semi conducting process can be attributed to the presence of two types of charge carriers, that is, p type, as a hole exchange between Co\(^{4+}\), Co\(^{3+}\) and Co\(^{2+}\) and transfer of O\(^{2−}\) between filled side with vacant oxygen side.

The band gap of these samples was estimated from the fundamental absorption edge at 295nm. The optical band gap was calculated using Tauc relation by plotting \((\alpha h\nu)^2\) against \(h\nu\) where \(\alpha\) and \(h\nu\) denote the absorption coefficient and photon energy respectively and by extrapolating the curve to photon energy axis. The band-gap energy \((E_g)\) values were evaluated using Tauc’s plot as shown in Figure.2.33. The optical absorption band gap at 2.50eV due to ligand to metal charge transfer (LMCT) takes place from O\(^{2−}\) (2p)to Co\(^{3+}\)(3d). Hence ligand to metal charge transfer takes place in the calcium cobalt oxide system it shows a semiconducting behavior.

2.4.5.11 Four probe Hall effect measurements

Hall effect measurements performed with vander Pauw geometry [L.J. vander Pauw (1958)] using a Four probe measurement setup with a field of 8T and a current of 4A in room temperature. Ca\(_3\)Co\(_4\)O\(_9\) sample pressed into a pellet with a diameter of 12mm and sintered at 800°C for 12 hours. The pellet used as a sample for four probe hall measurement. The contacts between the sample pellet and Au lead wires made by modified analytical grade silver paste. The contact resistance between the sample surface and each probe was less than100 Ω.

The resistance of the material \((R_0)\) measured by using the equation (2.28, 2.29)

\[
R_0 = \left(\frac{\pi}{\ln 2}\right) f \left(\frac{R_1+R_2}{2}\right)
\]

\[
f = 1 - \left[ 2 \left(\frac{\ln 2}{2}\right) \left(\frac{R_1-R_2}{R_1+R_2}\right) \right]
\]

where \(R_1\) is the resistance when voltage is measured across the terminal 3 and 4, then current is passed between terminal 1 and 2. \(R_2\) is the resistance when voltage is measured across the terminal 1 and 2, then current is passed between terminal 3 and 4.
The hall mobility was measured by using equation (2.30)

\[ \mu_H = \frac{\Delta R \times 10^8}{B R_0} \]  

(2.30)

where \( B \) is the applied magnetic field, \( \Delta R \) is the change in resistance; \( R_0 \) is the resistance of the material.

Resistivity \( (\rho) = R_0 T \)  

(2.31)

Conductivity \( (\sigma) = \frac{1}{\rho} \)  

(2.32)

Hall coefficient \( (R_H) = \mu_H \rho \)  

(2.33)

Carrier concentration \( (n) = \frac{1}{e R_H} \)  

(2.34)

Where \( T \) is the thickness of the pellet and \( e=1.6 \times 10^{-19} \) is the charge of an electron. The resistivity of material \( (\rho) \) is \( 0.2 \times 10^{-2} \) \( \Omega \)m, hall mobility \( (\mu_H) \) is \( 4 \times 10^{-3} \) \( m^2/Volt \) Sec, hall coefficient \( (R_H) \) is \( 0.8 \times 10^{-4} \) \( m^2/\)coulomb and carrier concentration \( (n) \) is \( 7.0 \times 10^{26} \) \( m^{-3} \) was obtained by using the above equations (2.31-2.34). The charge carrier concentration values lies near to the reported value and it proves as p-type semiconductor. This observation indicate that the electronic structure of \( Ca_3Co_4O_{9.6} \) material contains donors as intrinsic oxygen vacancy and acceptors of cobalt ion in these oxidation states \( Co^{3+} \) and \( Co^{2+} \) double layer interactions in the ceramics.

2.4.5.12 Room temperature Magnetic studies

Fig.2.33. Shows the room temperature magnetic properties of calcium cobalt carbonate precursor and \( Ca_3Co_4O_{9.6} \) oxide product obtained by using Vibrating Sample Magnetometer (VSM). The graph plotted between the magnetic moment versus applied magnetic field (M-H curves) at room temperature. It reveals that both carbonate precursor and oxide material are paramagnetic [Eirin Sullivan et al., (2011); Lassi Karvonen et al., (2011)]. The carbonate precursor magnetic retentivity does not change but increasing magnetic saturation moment due to change in domain size. The decreasing external field coercivity of strontium cobalt carbonate precursor twice to that of oxide due to the presence of cobalt in single \( Co^{2+} \) oxidation state. The carbonate to oxide materials align.
its moment in one direction of spontaneous magnetization and it shows superparamagnetic behavior in anisotropic region. This magnetic behavior is due to the zener double exchange mechanism is possible in the oxide due to the presence of different valence (Co$^{2+}$, Co$^{3+}$ & Co$^{4+}$) of cobalt ion.

2.4.5.13 Antibacterial activity

Well diffusion method was used for the assessment of antibacterial activity. The antibacterial activity of the sample was identified by the formation of Zone of Inhibition. Zone of inhibition is the area on an agar plate where growth of a control organism is prevented by an antibiotic usually placed on the agar surface [Banwari Lal et al., (2004)]. Each bacterial isolate was suspended in brain heart infusion (BHF) and diluted to approximately 105 colony forming unit (CFU/MI) of bacteria. They were flood-inoculated onto the surface of BHI agar and then dried. The antimicrobial activity of Ca$_3$Co$_4$O$_9$-$\delta$ ceramic against E.Coli, Klebsiella pneumonia was tested in well round bottom plates by agar well diffusion method to study the antimicrobial activity of compounds the plates are shown in Fig.7. The five millimeter diameter wells were cut from the agar using a sterile core-borer and 30μL (5μg of compound in 500μL DMSO) of the sample solution were poured into wells. The plates were incubated for 18 h at 37°C for bacteria. The inhibition zone was calculated as half the difference between the diameter of the inhibition zone and the diameter of the compound filled cavity. The inhibited growth of bacteria as clear rings appeared around the samples inserted into the agar plate. The inhibition of zone for each bacterial strain is shown in the table. DMSO was used as solvent control. Ciprofloxacin was used as reference antibacterial agent. The tests were carried out in triplicates.
Fig. 2.33. Room temperature M-H curve of Ca$_3$Co$_4$O$_9$. 
Fig. 2.34. Comparison of antibacterial activity of Ca$_3$Co$_4$O$_{9.5}$ on (a) Klebsiella pneumonia and (b) Escherichia coli
The inhibition zone for Klebsiella pneumonia was consistently larger than for E.Coli. The carbonate precursor has better antimicrobial activity than oxide product, then important thing was noted intermediate precursor (decomposed precursor as a mixture of cobalt oxide and calcium carbonate) its zone of inhibition greater than oxide and carbonate precursor. The antibacterial activity of Ca$_3$Co$_4$O$_9$ was confirmed by Zone of inhibition as shown in Table- 2.5.

**Table- 2.5 Comparison of antibacterial activity of Ca$_3$Co$_4$O$_9$**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Microorganism</th>
<th>Control</th>
<th>Code-KAC</th>
<th>Code -KAP</th>
<th>Code-C1</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Product-Ca$_3$Co$<em>4$O$</em>{9.5}$</td>
<td>Precursor-Ca$_3$Co$_4$(CO$_3$)$_7$</td>
<td>Intermediate precursor</td>
<td>antibiotic Ciprofloxacin</td>
</tr>
<tr>
<td></td>
<td>Inhibition zone diameter (in mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Klebsiella pneumoniae</td>
<td>-</td>
<td>6</td>
<td>9</td>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>Escherichia coli</td>
<td>-</td>
<td>4</td>
<td>6</td>
<td>9</td>
<td>29</td>
</tr>
</tbody>
</table>

**2.4.5.14. Pigment studies**

Generally cobalt based inorganic oxide are used as metallic oxide pigments like cobalt titanate as (green pigment) and cobalt aluminate as (blue pigment). The important requirement for pigment as reflecting nature. The reflecting property as shown in Fig.2.35. comparison of market available pigments to our prepared compound (Ca$_3$Co$_4$O$_9$). Hence this compound Ca$_3$Co$_4$O$_9$ also 85% reflectance. Further comparing the physical and chemical properties of the prepared compound can be tested in paint industry as in Table- 2.6. The results prove the black pigment nature of Ca$_3$Co$_4$O$_9$ compound.
Table- 2.6. Comparison of physical and chemical properties of cobalt based oxide pigments

<table>
<thead>
<tr>
<th>Physical and chemical properties:</th>
<th>Blue pigment Powder</th>
<th>Green pigment Powder</th>
<th>Black pigment powder (CCO-349)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Appearance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Apparent density (gms/cc)</td>
<td>0.60 to 0.70</td>
<td>0.50 to 0.60</td>
<td>0.70 to 0.80</td>
</tr>
<tr>
<td>3. Moisture content at 105 °c</td>
<td>1.0%</td>
<td>1.0%</td>
<td>0.8%</td>
</tr>
<tr>
<td>4. Water soluble matter</td>
<td>1.0 %</td>
<td>1.0%</td>
<td>0.5%</td>
</tr>
<tr>
<td>5. Oil absorption (% by wt)</td>
<td>32.00 to 35.00</td>
<td>30.00 to 33.00</td>
<td>25.00 to 30.00</td>
</tr>
<tr>
<td>6. Median particle diameter</td>
<td>2.50 Microns Maximum</td>
<td>2.60 Microns Maximum</td>
<td>3.50 Microns Maximum</td>
</tr>
<tr>
<td>7. pH of 1% solution</td>
<td>8.0 – 9.0</td>
<td>8.0-9.0</td>
<td>7.0-8.0</td>
</tr>
</tbody>
</table>
Fig. 2.35. Comparing the reflectance of (a) Ca$_3$Co$_4$O$_9$, (b) cobalt green pigment, (c) cobalt blue pigment
2.4.5.15. Conclusions

Ca$_3$Co$_4$O$_{9.5}$ was synthesized by using co precipitation method and found to be polycrystalline in nature. The phase formation temperature by thermal analysis technique indicates that single phase formation of mixed metal oxide at 800°C. The scanning electron microscopic studies indicate that agglomerated diffuse monoclinic and have average grain size ~160 to 400 nm. The elemental analysis by EDX, oxygen defect analyzed from thermal analysis and iodometric titration was in good agreement with the stoichiometry of the product Ca$_3$Co$_4$O$_{9.5}$. The antibacterial activity of Ca$_3$Co$_4$O$_{9.5}$ was confirmed and it was used as antimicrobial coating applications. The optical absorption band gap at 2.0eV due to ligand to metal charge transfer it behave as a semiconducting material. The magnetic studies reveals the Ca$_3$Co$_4$O$_9$ behave as a ferrimagnetic soft material and its carbonate precursor paramagnetic nature. The results prove the black pigment nature of Ca$_3$Co$_4$O$_9$ compound. The results demonstrate that carbonate precursor represents a useful technique for the preparation of layered cobalt based oxides.