Optical, electrical and structural studies of nickel-cobalt oxide nanoparticles

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Nanoparticles of nickel-cobalt oxide are prepared by chemical co-precipitation method. The particle size is determined from X-ray diffraction studies and TEM image. The surface morphology is revealed by SEM image. The effect of sintering on the particle size is analyzed. The FTIR studies have been used to confirm the formation of metal oxide. The characteristic stretching and bending frequencies of the sample are analyzed. An absorption band is observed to occur at 350 nm and another one around 650 nm. From the analysis of absorption spectra, the nickel-cobalt oxide (sintered at 500°C, 700°C and 900°C) are found to have direct band gaps ranging from 1.827 to 1.61 eV. Electrons are highly localized in nanoparticles and interaction between these localized states give rise to the observed band gap. The effect of temperature and frequency on the dielectric behaviour and ac electrical conductivity have been studied for nanosized sample of nickel cobalt spinel oxide prepared by chemical co-precipitation method. The dielectric permittivity of nanosized nickel cobalt spinel oxide sample is evaluated from the observed capacitance values in the frequency range 100 kHz-5 MHz and in the temperature range of 300-403 K. It is seen that with decreasing frequency, the dielectric constant increases more obviously than that of conventional materials. As the temperature increases more and more dipoles are oriented resulting in an increase in the values of dipole moment. Space charge polarization and rotation direction polarization play a crucial role in the dielectric behaviour of this nanosized material. Further from the permittivity studies ac conductivity is evaluated.

Keywords: Nanoparticles, Arrested precipitation, Calcination temperature, Fourier transform infrared spectrum, Absorption spectra, Optical band gap, AC conductivity, Dielectric permittivity

Nanocrystalline materials are solids composed of crystallites with characteristic size (at least on one dimension) of a few nanometers. The discovery of these materials by Gleiter can be viewed as one of the most fascinating ones of the past decades¹. Not only the electronic, magnetic and optical properties but also catalytic and electrical properties of nanostructured materials are much different from those of the bulk form and depend sensitively on size, shape, composition and preparation condition². The enhanced dielectric properties of nanocrystalline materials exhibiting unusual properties play a vital role in the development of new materials³-⁶. Researches in the field of fine grain mixed oxide systems have gained immense importance because of their potential applications in many areas of technology⁷-⁹. Studies on the effect of temperature and frequency on the dielectric behaviour offer valuable information about conduction phenomena in nanostructured material¹⁰. The dielectric properties of oxides depend considerably on the size and shape of the particles. The micro electronic industry has been emphasizing on reduction in size of the device elements such as transistors, resistors and capacitors. However, there are practical difficulties to these achievements including the lack of ultra fine precursors to manufacture these components, poor dissipation of the tremendous heat generated due to faster speeds and poor reliability: Thus there is need to obtain ultra pure materials of nanometer size which have high energy density and better thermal conductivity.

Doping cobalt oxide with nickel produced a significant increase in electrical conductivity while maintaining the spinel structure. Nickel cations are found to reside in octahedral sites with a valence of $2^+\text{and } 3^+$ represented by the equation below¹¹.

$$\text{Co}_{1-y}\text{Co}_3^{3+}\left[\text{Co}_{2-x}\text{Ni}_{y}^{2+}\text{Ni}_{x}^{3+}\right]\text{O}_4$$

Nickel doped cobalt oxide shows P-type semi conducting behaviour similar to intrinsic spinel cobalt oxide¹². The interest in nickel-cobalt oxide includes uses as electrodes in batteries¹³ in solar cells¹⁴ a

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heterogeneous optical recording media\textsuperscript{15} a super capacitor\textsuperscript{16} sensors or optical limiters and switches\textsuperscript{17}.

**Experimental Procedure**

Nanoparticles of nickel-cobalt oxide were prepared by arrested precipitation from analytical grade cobalt chloride, nickel chloride and sodium carbonate using ethylene diamene tetra acetic acid (EDTA) as the capping agent, the details of which are given elsewhere\textsuperscript{18}. The samples were prepared from 0.5 M solution. The choice of selection of 0.5 M is a compromise between quantity and quality. If we go for low molarities the quantity obtained will be very small; on the other hand high molarities will increase the size of the nanoparticles. The metal carbonate precipitate was separated from the reaction mixture and washed several times with alcohol and then with distilled water to remove impurities, including the traces of EDTA and the original reactants if any. The wet precipitate was dried and thoroughly ground using an agate mortar to obtain the metal carbonate precursor in the form of fine powder. On heating to the required temperature the metal carbonate precursor decomposes to form metal oxide. In this process the particle size is governed by the solution concentration, rate of precipitation and calcination temperature\textsuperscript{19}.

The calcination temperature of the carbonate precursor was determined from TGA and DTA analysis. The TGA and DTA of the samples were taken using Perkin-Elmer, diamond TG/DTA apparatus. The precursor on heating decomposes to form nickel-cobalt spinel oxide. Thermo-gravimetric analysis of the carbonate precursor was carried out to determine the decomposition temperature and the rate of decomposition. The TGA analysis was performed in the temperature range from 28°C to 800°C at a heating rate of 15°C/min under nitrogen atmosphere. The TGA curve of the carbonate precursor together with the corresponding derivative thermo gravimetry curve is as shown in the Fig. 1.

The decomposition temperatures are found to lie between 300°C and 350°C. Thus, the heat treatment of the ground precursor powders at their respective decomposition temperature and beyond, results in the evolution of heat from the combustion of the residual carbonaceous material. This facilitates the reaction among the constituent metal ions and the formation of the desired oxide phase at a relatively low external temperature. Here, the carbonate precursor powder is heated at 350°C for three hours to get the mixed oxide nanoparticle.

![Fig. 1—GA/DTA curve of the Carbonate precursor](image-url)
Characterization of the sample

The XRD study was carried out by using an ‘X’ pert pro model X-ray diffractometer employing Cu-K\(_\alpha\) radiation (make PAN analytical, Netherlands) at 40 kV and 100 mA at a scanning rate of 8°min\(^{-1}\) from 2\(\theta\) = 5°-80° from Regional Research Laboratory, Thiruvananthapuram, Kerala, India. FTIR spectra of the sample were recorded in an FTIR spectrophotometer, (Thermo Nicolet, Avatar 370D). The SEM photographs of the sample were recorded with a Hitachi Model S-3000H scanning electron microscope from CECRI, Karaikudi, Tamilnadu, India. The TEM images were from National University, Singapore. The TEM images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Specimen were prepared by spreading a drop of their ethanol suspensions on to copper grids coated with a thin amorphous carbon film and allowed to dry in air. Pellets of nanoparticles of nickel-cobalt oxide of diameter 13 mm and thickness 1-2 mm are made by applying a pressure of 4 tonnes in a hand operated hydraulic press. The dielectric permittivity measurements on the pellets of nickel-cobalt oxide nanoparticles were carried out using a home made dielectric cell and an HP 4285 LCR meter in the frequency range 100 kHz-5 MHz from 300 to 403 K. The principle of parallel plate capacitor was employed for the calculation of permittivity. The LCR meter was interfaced with a PC using a virtual instrumentation package called Lab VIEW. With this provision around 20,000 data points could be acquired in a matter of 4-5 min.

Theory

The dielectric permittivity of the nanosized samples of nickel-cobalt spinel oxide were calculated using the relation

\[
C = \frac{(\varepsilon_0 \varepsilon_r A)}{d}
\]

where \(C\) is the capacitance of the sample, \(A\) is the surface area of the sample, \(\varepsilon_0\) is the permittivity of free space and \(\varepsilon_r\) is the dielectric permittivity of the sample. The ac conductivity of the sample can be evaluated from the values of dielectric permittivity (\(\varepsilon_r\)) and loss factor (\(\tan \delta\)) using the equation

\[
\sigma_{ac} = 2\pi \varepsilon_0 \varepsilon_r f \tan \delta
\]

where \(f\) is the frequency.

Results and Discussion

XRD studies

The nickel-cobalt oxide powders prepared are calcined at temperatures 500°C, 700°C and 900°C for 3 h each. The XRD studies are carried out for the samples prepared at concentration of 0.5 M. All the XRD patterns reveal that the nickel-cobalt oxide prepared are crystalline. The XRD patterns of the nickel-cobalt oxide and the calcined samples are shown in Fig. 2.

The XRD studies reveal that the nanoparticles of mixed oxide formed by chemical method are crystalline. The fine particle nature of the mixed oxide is reflected in the X-ray line broadening. The relative crystalline sizes are determined from the XRD line broadening using the Scherrer equation

\[d = \frac{0.9\lambda}{\beta \cos \theta} \]

The particle size for the prepared nickel-cobalt oxide and the sintered samples are as shown in Table 1. From this table it is clear that as the sintering temperature increases the particle size increases. This indicates that the size of the crystallites can be adjusted by controlling the temperature of the reaction.

<table>
<thead>
<tr>
<th>Sintering temperature</th>
<th>Particle size, nm</th>
<th>Band gap, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel cobalt oxide</td>
<td>17 ± 5</td>
<td>1.827</td>
</tr>
<tr>
<td>Sintered at 500°C</td>
<td>24 ± 5</td>
<td>1.79</td>
</tr>
<tr>
<td>Sintered at 700°C</td>
<td>34 ± 5</td>
<td>1.748</td>
</tr>
<tr>
<td>Sintered at 900°C</td>
<td>35 ± 5</td>
<td>1.61</td>
</tr>
</tbody>
</table>

Fig. 2—X-ray diffraction pattern of nanostructured nickel-cobalt oxide and the samples at different sintering temperature
The XRD analysis when compared with JCPDS (File No 40-1191) reveals the presence of a cubic phase. The lattice parameter is calculated as $a = 8.12 \pm 0.003$ Å, which is found to be in agreement with JCPDS value. In the diffractometer, the angle ($d$-spacing) and intensities of the high angle reflected beams serve as a fingerprint for the crystal structure. The XRD pattern when compared with JCPDS reveals the structure as spinel oxide. The most intense peak (intensity 100) is from the (311) plane which corresponds to an angle of $2\theta = 36.69289^\circ$.

Table 2 gives the lattice parameter and $(hkl)$ values of the different planes of the nickel-cobalt oxide and the change in the $d$-values of the sample. The slight change in the $d$-values can be attributed to the nanosized species of nickel-cobalt oxide.

The XRD peaks are broadened due to the nanocrystalline nature of the particles. These nanocrystals have lesser lattice planes compared to the bulk, which contributes to the broadening of peaks in the diffractogram. This broadening of the peaks could also arise due to the microstraining of the crystal structures arising from defects like dislocations and twinning. These are believed to be associated with the chemically synthesized nanocrystals as they grow spontaneously during chemical reaction. As a result, chemical ligands get negligible time to diffuse to an energetically favorable site. It could also arise due to lack of sufficient energy needed by an atom to move to a proper site in forming the crystallite.

**Microstructural studies**

For microstructural analysis the as synthesized samples are directly transferred to the chamber of the SEM without disturbing the original nature of the products. The SEM images of the sample are shown in Fig. 3. The SEM picture reveals that the particles are more or less spherical in shape. Moreover the particle size can be estimated to lie in the range 10-50 nm.

![Fig. 3—Scanning Electron micrograph of nickel-cobalt oxide.](image)

![Fig. 4—TEM, selected area diffraction pattern and EDS picture of nickel-cobalt oxide](image)

**Table 2**—Calculated value of lattice parameter from different planes and change in $d$-values of the sample.

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>$d_{\text{observed}}$</th>
<th>$d_{\text{cal}}$</th>
<th>difference</th>
<th>$h, k, l$</th>
<th>$a$ (Å)</th>
<th>Mean $a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.82</td>
<td>4.71</td>
<td>4.68</td>
<td>0.03</td>
<td>111</td>
<td>8.16</td>
<td></td>
</tr>
<tr>
<td>31.16</td>
<td>2.87</td>
<td>2.87</td>
<td>0.04</td>
<td>220</td>
<td>8.11</td>
<td></td>
</tr>
<tr>
<td>36.70</td>
<td>2.45</td>
<td>2.45</td>
<td>0.02</td>
<td>311</td>
<td>8.12</td>
<td>8.12</td>
</tr>
<tr>
<td>44.60</td>
<td>2.03</td>
<td>2.03</td>
<td>0</td>
<td>400</td>
<td>8.12</td>
<td></td>
</tr>
<tr>
<td>59.06</td>
<td>1.56</td>
<td>1.56</td>
<td>0</td>
<td>511</td>
<td>8.12</td>
<td></td>
</tr>
<tr>
<td>64.98</td>
<td>1.44</td>
<td>1.43</td>
<td>0.01</td>
<td>440</td>
<td>8.11</td>
<td></td>
</tr>
</tbody>
</table>
**FTIR studies**

Infrared spectroscopic (IR) studies of the nickel-cobalt oxide powders and heat treated samples are done using a Perkin-Elmer FTIR Spectrophotometer between 500 cm\(^{-1}\) and 3000 cm\(^{-1}\). The IR absorption spectra are shown in Fig. 5. The broad absorption band in the region around 3425 cm\(^{-1}\) is due to the presence of co-ordinated/entrapped water, and this absorption decreases as the sintering temperature increases\(^24\). The presence of some carbonaceous material is evident from the IR spectra which depicts strong band at 1634 and 1262 cm\(^{-1}\) corresponding to carboxylate ion\(^25,26\). The band around 650 cm\(^{-1}\) corresponds to bending modes of vibration of cobalt oxide and that around 575 cm\(^{-1}\) corresponds to bending modes of vibration of nickel oxide. The other bands may be due to micro structural formation of the sample\(^27\). This IR spectra are typical for cubic spinels with space group Fd3m, with two bands of high intensity in the range 550-690 cm\(^{-1}\).

Here it is seen that there is a shift in the IR active mode, which is due to due to nano size grains. For a nanosize grain, the atomic arrangements on the boundaries differ greatly from that of bulk crystals, both in co-ordination number and bond lengths, showing some extent of disorder\(^28\). Crystal symmetry is thus degraded in nanosize grains. The degradation in crystal symmetry results in the shifting of IR active mode\(^29\).

**UV/Vis spectral studies**

Energy band of materials is related to absorption coefficient \(\alpha\) by the Tauc relation

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

… (3)

where \(A\) is a constant, \(h \nu\) is the photon energy, \(E_g\) is the band gap and \(n\) is an index which assumes values 1/2, 3/2, 2 or 3 depending on the nature of the electronic transition responsible for the absorption.

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Fig. 5 — FTIR spectra of nickel-cobalt oxide and the samples sintered at 500°C, 700°C and 900°C.
$n=1/2$ is taken for an allowed direct transition. Therefore, by plotting a graph between $(\alpha h\nu)^2$ and $h\nu$ in eV, a straight line is obtained which gives the value of the direct band gap. From the absorption spectra shown in Fig. 6 it can be seen that an absorption band is observed at $\approx 350$ nm for some of the samples. This corresponds to excitation of surface plasmons in the composite nanoparticles. In addition to the absorption band at 350 nm the samples also show the presence of an additional absorption band at wavelengths around 600 nm. This band may be due to coupling of the plasmon modes between neighbouring particles. From Fig. 6 it is observed that absorption decreases with the increase in wavelength. This decrease in the absorption indicates the presence of optical band gap in these metal oxides. Tauc relation as given in Eq. (3) is used for the determination of direct band gap, in the spinel oxide. Variation of $(\alpha h\nu)^2$ with $h\nu$ in eV for nickel-cobalt oxide powders and the samples sintered at different temperatures are plotted in Fig. 7. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ gives the value of the direct band gap of the material. The values so obtained are also given in Table 1. From this table it is seen that as the sintering temperature increases the particle size increases and

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Fig. 6—Absorbance versus Wavelength of nickel-cobalt oxide and samples sintered at 500°C, 700°C and 900°C

Fig. 7—$(\alpha h\nu)^2$ Versus photon energy in eV of nickel-cobalt oxide and samples sintered at 500°C, 700°C and 900°C
the band gap decreases. So the band gap has an inverse dependence on the grain size.

**AC conductivity studies**

The variation of dielectric constant ($\varepsilon$) with frequency of the applied field for temperatures from 300 K to 403 K of the sample is shown in Fig. 8. From the dielectric studies it is seen that with decreasing frequency, the dielectric constant increases much more obviously than that of conventional materials. According to theory, the dielectric behaviour of nanostructured materials is primarily due to different types of polarizations present in the material. Nanocrystalline materials possess enormous number of interfaces, and the large number of defects present in these interfaces can cause a change of positive or negative space charge distribution. When an electric field is applied these space charges move and are trapped by these defects resulting in the formation of dipole moments. This is called space charge polarization. Interfaces in nanostructured materials possess many oxygen ion vacancies, which are equivalent to positive charges giving dipole moments. Exposed to an electric field, these dipoles will rotate, giving a resultant dipole moment in the direction of the applied field. This is called rotation direction polarization. Thus high value of dielectric constant at low frequencies is mainly due to the space charge polarization and rotation direction polarization. As the temperature increases, more and more dipoles will be oriented, resulting in an increase in the value of the dipole moment. This is why the dielectric constant increases with increase in temperature for fixed frequencies. The values are shifted upwards when the temperature increases.

The variation of ac electrical conductivity as a function of frequency and temperature for the sample is shown in Fig. 9. It is seen that as frequency increases the conductivity remains more or less a constant at low temperatures but for higher temperatures as the frequency increases the conductivity also increases. The nature is similar for other temperatures, but the values are shifted upwards as the temperature is raised. Electrical conductivity in nickel cobalt spinel oxide is believed to arise through polaron hopping. Windschietal report that Ni$^{3+}$ has a role in conductivity such that the mechanism of conduction is a charge transfer between resident divalent and trivalent cations suggesting it is possibly assisted by the magnetic nature of the oxide particles. Nickel-cobalt oxide is probably a defect conductor due to adsorption of oxygen similar to nickel oxide where high oxygen partial pressure increases conductivity. Cation vacancies produced from oxygen adsorption create holes in the valance band and therefore classified as an electron defect semiconductor. The nickel cobalt oxide system exhibits conductivity with highly localized carriers bound to the lattice with an accompanying lattice strain, i.e., with polaron conduction.

**Conclusions**

Thermal analysis shows that the decomposition temperature of the carbonate precursor is 350°C. The low temperature (300-350°C) exothermic decomposition of the carbonaceous material present in the precursor powder reduces the processing
Acknowledgement

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References