

Chemical synthesis of nanoparticles of Nickel-cobalt oxide and its conductivity studies

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ABSTRACT

Nano particles of nickel-cobalt oxide are prepared by chemical co-precipitation method by decomposition of their respective metal chlorides, sodium carbonate and EDTA. The average particle size is determined from X-ray line broadening and the diffractogram is compared with JCPDS data and the phase of the particle formed is determined and the shift in the D-value due to the nano nature is also analyzed. The nanoparticles formed have spinel structure. The effect of sintering temperature on the particle size is analyzed. The size of the particles is confirmed by TEM. The surface morphology is revealed by SEM image. EDS confirms the elements present in the sample. The low temperature dc conductivity studies of the sample were carried out and it was seen that the activation energy for the temperature range 100K-250K is 0.37eV and for the range 250K-350K is 0.62eV. The conductivity in the temperature range 275K-350K is much larger than the conductivity in the range 100K-250K. This value is much greater than the value reported for bulk nickel cobalt oxide (0.03 eV). It indicates the enhancement of conductivity in nanosized form of this material.

Key words: Nano particles, arrested precipitation, Calcination temperature
TEM, SEM, EDS, Low temperature conductivity, activation energy.

INTRODUCTION

Nanotechnology involves research and technology development at the 1nm to 100nm range. It creates and uses structures that have novel properties because of small size. It builds on the ability to control and manipulate at the atomic scale. Materials with nano scale microstructure i.e. nanoparticles give rise to some unique properties. Eg:-electrical, magnetic and optical properties. Materials possessing optical transparency and electrical conductivity make up a small class of specialized materials, Transparent conducting oxide. They are categorized most often by their carrier type or by the mechanism of charge transport. Nickel-cobalt oxide is a P-type conducting material that shows promise as an infrared transparent conducting oxide because of its infrared transparency, stability, conduction. 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+ and 3+. Nickel doped cobalt oxide shows P-type semi conducting behavior similar to intrinsic spinel cobalt oxide¹. The interest in Nickel-Cobalt oxide includes uses as electrodes in batteries² in solar cells³ a heterogeneous optical recording media⁴ a super capacitor⁵ an infrared-transparent conducting electrode for flat panel displays, sensors or optical limiters and switches⁶. The spinel oxide of nickel-cobalt has well documented and established applications in electrochemistry.

EXPERIMENTAL

Nano particles of nickel-cobalt oxide were prepared by arrested precipitation from analytical grade cobalt chloride, nickel chloride and sodium carbonate using ethylene diamine tetra acetic acid (EDTA) as the capping agent, the details of which are given elsewhere⁷. The samples were prepared

from 0.5M solution. The choice of selection of 0.5M 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 nano particles. 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 temperature⁸. 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. 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/minute under nitrogen atmosphere. The TGA curve of the carbonate precursor together with the corresponding derivative thermo gravimetry curve is as shown in 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.

Characterization of the sample

The XRD study was carried out by using an 'X'pert pro model X-ray diffractometer employing Cu K α radiation (make PAN analytical, Netherlands) at 40KV and 100mA at a scanning rate of 80minute-1 from $2\theta = 5^\circ$ to 80° . The SEM photographs of the sample were recorded with a Hitachi Model S-3000H scanning electron microscope. The TEM measurements are from national university, Singapore. Pellets of nano particles 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. Using these pellets the low temperature conductivity is measured using a computer controlled TSC apparatus in the temperature range 100K- 350K.

RESULTS AND DISCUSSION

XRD analysis

The nickel-cobalt oxide powders are calcined at temperatures 500°C, 700°C and 900°C

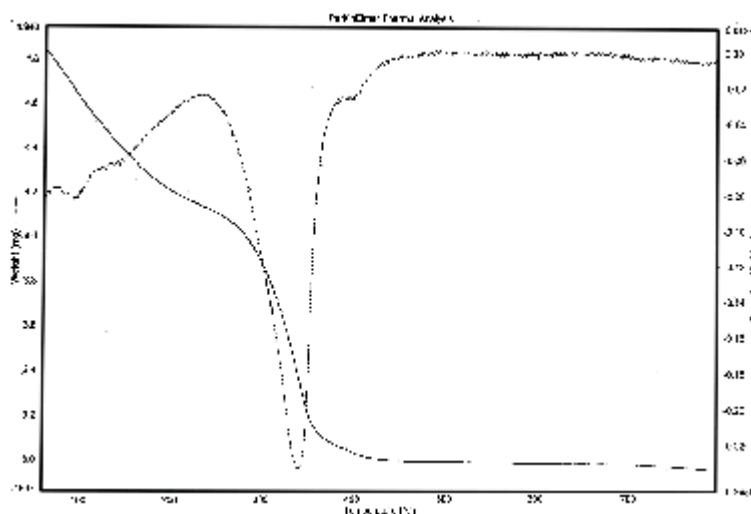


Fig. - 1:TGA/DTA curve of the Carbonate precursor

for 3 hours each. The XRD studies were carried out for the samples prepared from the precursor solutions at concentration of 0.5 M. All the XRD patterns reveal that the nickel-cobalt oxide prepared are crystalline. The XRD patterns of the calcined samples are shown in Fig. - 2.

The XRD studies reveal that the nano particles 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 $d = 0.9\lambda / \beta \cos \theta^\circ$.

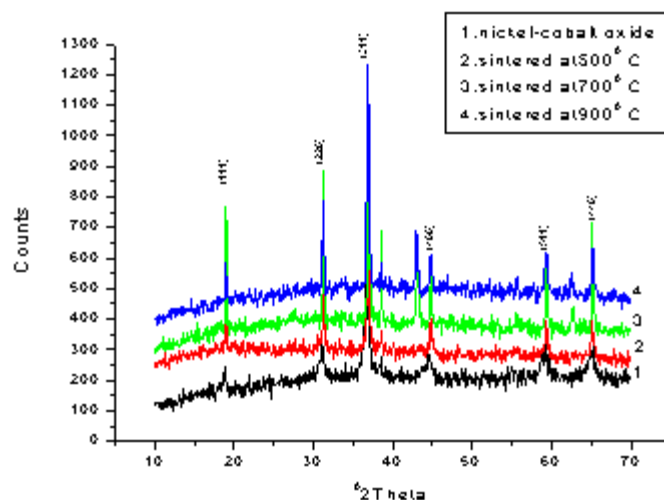


Fig. - 2: X-ray diffraction pattern of nanostructured nickel-cobalt oxide and the samples at different sintering temperature

The particle size for the various calcinations temperature is as shown in Table 1. From the 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 reaction¹⁰.

The XRD analysis when compared with JCPDS (File No 40-1191) reveals the presence of a cubic phase. The lattice parameter is calculated as $a = 8.12 (\pm 0.003) \text{ \AA}$, 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 finger print 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 $2\theta = 36.692890$. Thus the nickel-cobalt oxide nanoparticles have spinel structure.

Table 2 gives the lattice parameter and (hkl) values of the different planes of the as prepared sample of 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 nano sized species of nickel-cobalt oxide¹¹.

Table -1: Variation of particle size of nickel-cobalt oxide and the sintered samples

Sintering temperature	Particle size in nm
Nickel cobalt oxide	15 ± 5
Sintered at 5000 C	24 ± 5
Sintered at 7000 C	34 ± 5
Sintered at 9000 C	35 ± 5

The XRD peaks are broadened due to the nano crystalline nature of the particles. These nano crystals 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, twinning etc. These are believed to be associated with the chemically synthesized nano

Table - 2: Calculated value of lattice parameter from different planes and change in d-values of the sample

2 θ	dobserved	dcal	difference	h, k, l	a ($\text{\AA}$)	Mean a ($\text{\AA}$)
18.82	4.71	4.68	0.03	111	8.16	8.12
31.16	2.87	2.87	0.04	220	8.11	
36.70	2.45	2.45	0.02	311	8.12	
44.60	2.03	2.03	0	400	8.12	
59.06	1.56	1.56	0	511	8.12	
64.98	1.44	1.43	0.01	440	8.11	

crystals 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 crystallite¹².

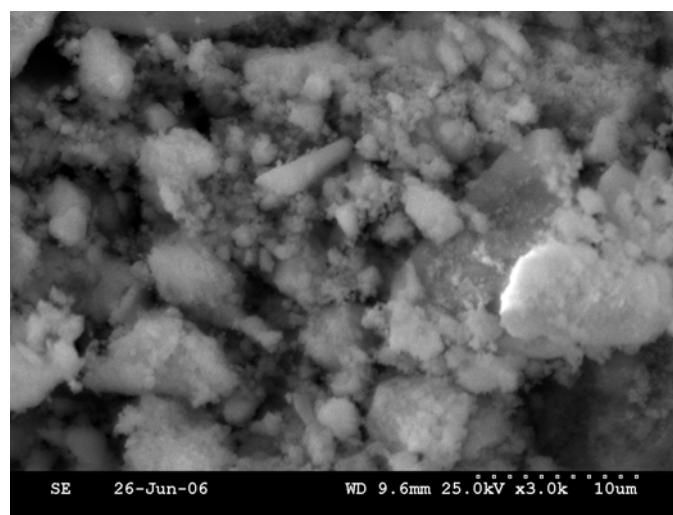
Microstructural studies

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 10-50nm. Fig. 4 shows the TEM image of the nickel-cobalt oxide nanoparticle. It is seen that the nano crystals are more or less cubic

and the particle size is 10nm. The TEM images reveals that there is no agglomeration in the particles of the nano crystal. The selected area diffraction pattern and the energy dispersive spectrum of the sample are shown in the Fig. 4. The pattern can be indexed on cubic, spinel structure of the nanoparticles.

Low temperature DC conductivity studies

The low temperature conductivity studies are carried out in the temperature range 100K-350K. The conductivity at the lowest temperature of measurement (100K) was found to be $9.21 \times 10^{-6} \text{ sm}^{-1}$ which increased to $2.32 \times 10^{-3} \text{ sm}^{-1}$ at 350K. The overall increase of conductivity over the temperature range from 100K-350K was about three order of magnitude. The Arrhenius plots of dc conductivity are shown in Fig. 7. It can be seen from

**Fig. - 3: Scanning Electron micrograph of nickel-cobalt oxide**

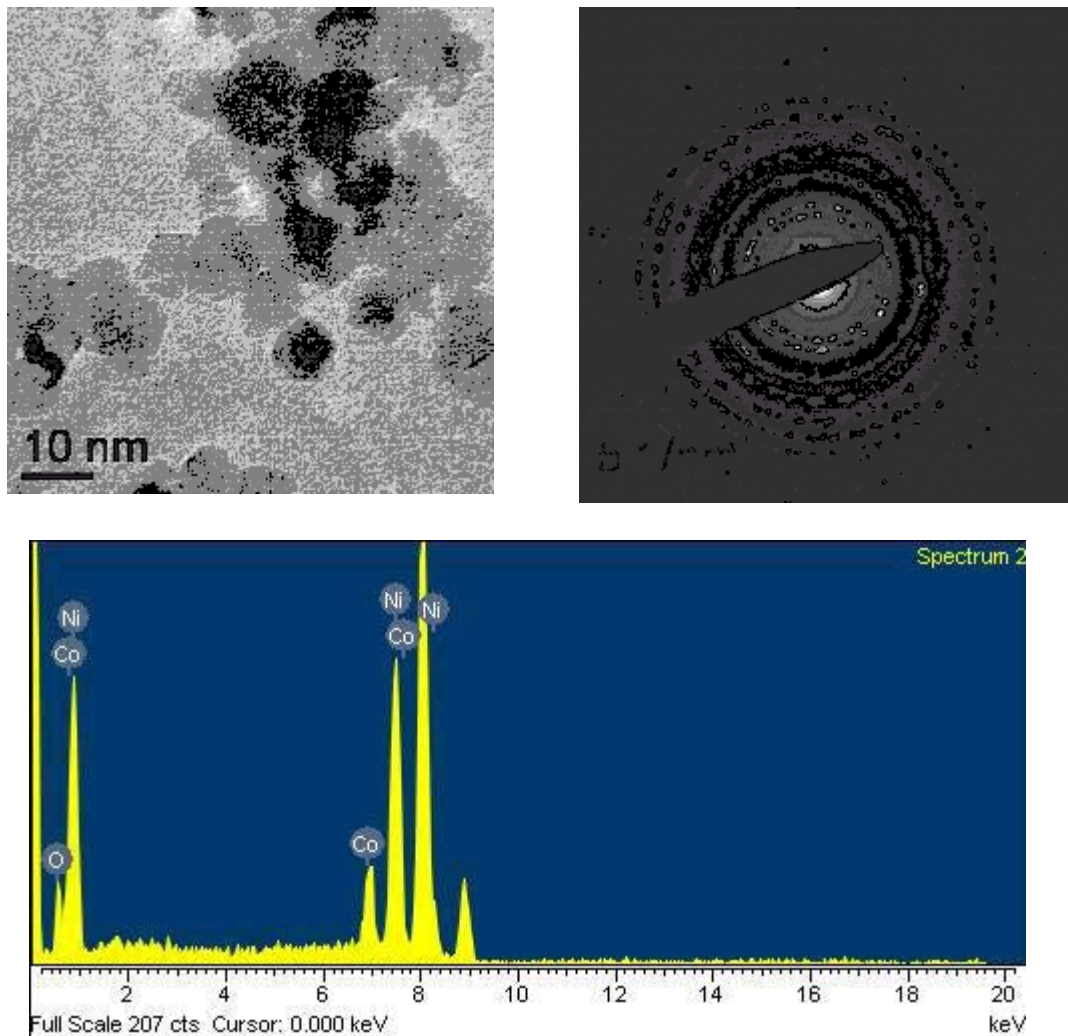


Fig. - 4: TEM, selected area diffraction pattern and EDS picture of nickel-cobalt oxide

the fig.7 that the conductivity increases with increase in temperature and changes by about three orders of magnitude in the temperature range investigated. The rise in conductivity may be due to thermally generated carriers in the sample, and hence Arrhenius type of conduction becomes apparent. A change in the slopes of Arrhenius plot was observed. It is reported that slight change in the slopes is related to transition temperature.¹³ But in our case a phase transition is not found from XRD. The slight changes in slopes may be due to contributions from different regions in the nano composite material (i.e. from grains, grain boundary etc:-) where appearance (disappearance) of space charge polarization takes place accompanied with a change

in activation energy¹⁴. The changes can also be related to change in conduction mechanism. From the literature it is seen that the conductivity in nickel-cobalt spinel oxide is due to polaron hopping¹⁵. The activation energy values are calculated from the slopes of arrhenius plots by fitting the experimental data to the Arrhenius relation $\sigma_{dc} = \sigma_0 \exp(-E/kT)$ where E is the activation energy, k boltzmann's constant, σ_0 a constant and T is the temperature in Kelvin. The values obtained are 0.09030eV in the temperature range from 275K-350K and 0.14552eV from 100K-250K. This value is much greater than the value reported for bulk nickel cobalt oxide (0.03 eV)¹⁶. It indicates the enhancement of conductivity in nanosized form of this material.

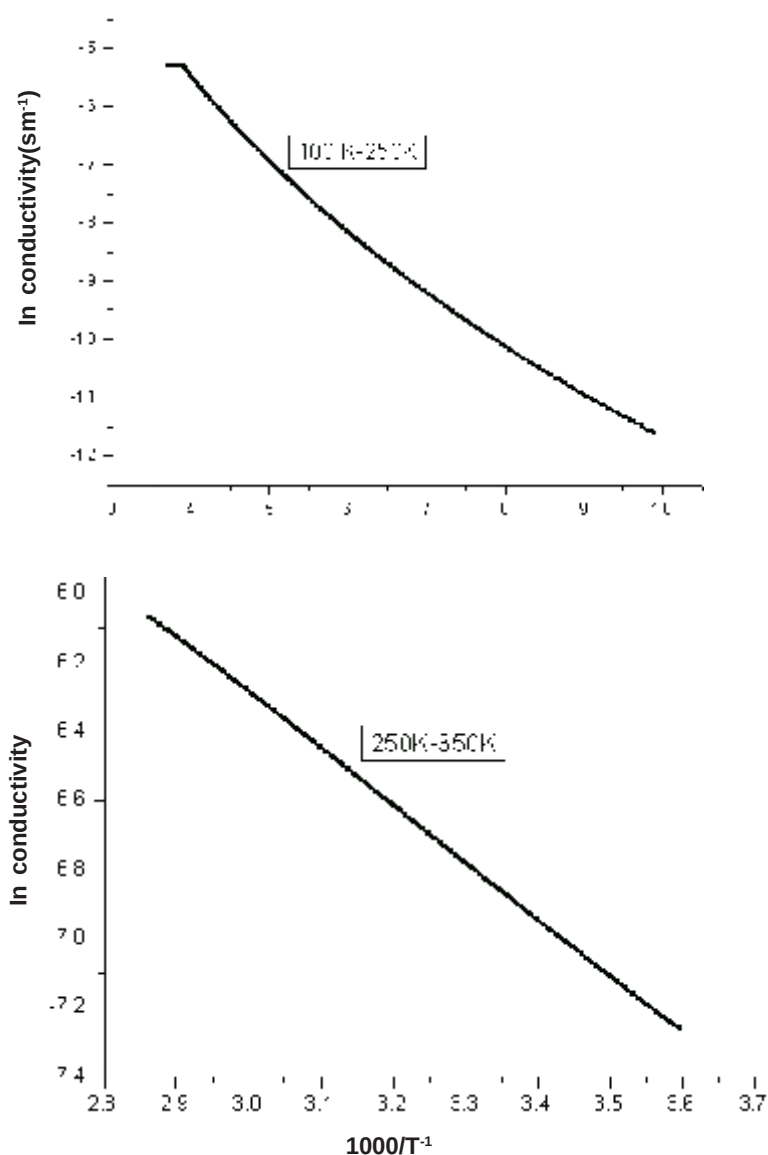


Fig. - 5: Activation energy curve in the temperature range 100K - 250 K and 250 K - 350 K

Conclusion

The experimental results lead to the following conclusions on the properties of nano sized nickel-cobalt spinel oxide. Thermal analysis shows that the decomposition temperature of the carbonate precursor is 350° C. The low temperature (300° C-350° C) exothermic decomposition of the carbonaceous material present in the precursor powder reduces the processing temperature for the

preparation of fine particles of this mixed oxide system. The X-ray diffractogram when compared with JCPDS data confirms a cubic phase with prominent peak at (311). The XRD pattern confirms that the nickel-cobalt oxide formed has a spinel structure. The slight change in d-value can be attributed to the nano sized species of nickel-cobalt oxide. As the sintering temperature increases the particle size also increases. When the annealing temperature

increases the particles have gradually conglomerated to big clusters. The low temperature DC conductivity study revealed that the activation energy in the temperature range 100 K-250 K is 0.09030 eV and that in the temperature range 275 K – 350 K is 0.14552 eV. The slight changes in slopes of the Arrhenius plot may be due to contributions from different regions in the nano composite material (i.e. from grains, grain boundary etc:-) where appearance (disappearance) of space charge polarization takes place accompanied with a change in activation energy. This value is much

greater than the value reported for bulk nickel cobalt oxide (0.03 eV). It indicates the enhancement of conductivity in nanosized form of this material.

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