MICROWAVE PREPARATION, CHARACTERISATION AND STUDIES OF NANOSIZED COBALT OXIDE

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Abstract

Properties and applications of nano materials depend on the history of the preparative techniques. A simple energy efficient microwave technique is used for the synthesis of materials at nano dimension. Present work reports, the microwave preparation of nanosized Co_3O_4 by thermal decomposition of cobalt oxalate precursor employing polyvinyl alcohol as a fuel. The structure of as synthesised Co_3O_4 is characterised by X-ray diffraction (XRD), bonding by Fourier transfer infrared (FTIR), morphology and particle size by Scanning Electron Microscope (SEM) and Transmission electron microscope (TEM) tools. d c conductivity and magnetic behaviour of the Co_3O_4 is well studied. Crystallite sizes and density measurement of the sample is under taken. The crystallite sizes were calculated using X-ray line broadening and density measurements were under taken by various methods. TEM study shows that, irregular shaped particles are in the nano range. XRD pattern shows the formation of crystalline cubic phase Co_3O_4. The metal –oxygen (Co-O) bond formation was confirmed by FTIR study. The prepared sample shows conducting and magnetic behaviour.

Key words: Microwave, Thermal decomposition, Crystallite size, Density, fuel

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1. Introduction

The synthesis of oxide materials at nano dimention involves considerable synthetic ingenuity. Although one can evolve a rational approach to the synthesis of oxides, there is always an element of serendipity. A verity of oxides have been prepared in the last several years by the traditional ceramic method, which involves mixing and grinding powders of the constituent oxides by heating them at high temperature with intermediate grinding

when necessary. A wide range of conditions often bordering on the extreme, have been employed in materials synthesis; these include high temperatures or precursors, very low oxygen fugacites and rapid quenching. The current trend is to avoid brute force methods in order achieve better control of purity. The so called soft chemistry routes are indeed desirable because they lead to novel products [1-2].

Microwave method finds much importance in the preparation of nanoceramics compared to other synthetic literature methods. Irradiation of microwaves on reaction mixture converts the required product at faster rate and gives the application oriented crystalline product having controlled particle size. The oxide ceramics obtained by microwave synthetic technique shows nanocrystalline nature and also good morphology [3]. Materials based on cobalt oxides have been extensive investigated because of their potential applications in many technological fields. Among the various cobalt oxides Co_3O_4 is an important ceramic oxide used for electrochromic and, magnetic and catalytic applications Electrochromism is characterized as a reversible change of the optical properties of the material by the application of a voltage stimulus and Co_3O_4 represents a promising anodic electrochromic material [4]. Co_3O_4 shows the spinal structure based on a cubic close packing array of oxide ions where one-eighth of tetrahedral holes are occupied by Co(II) ions and one-half of the octahedral holes are occupied by Co(III)ions.

In our earlier studies [5-6], we have successfully prepared the ultrafine gamma ferric oxide nanoparticles from iron oxalate precursor and polymer fuel. Present work reports the synthesis of cobalt oxide nanoparticle using cobalt oxalate precursor employing microwave route. Polyvinyl alcohol (PVA) is used as a fuel for the conversion of cobalt oxalate in to cobalt oxide nanoparticles. Polyvinyl alcohol is a good surfactant and dispersant, hence the precursor will be well dispersed in the molton PVA which is needed for the initiation of combustion process. After partial burning, microwave heat treatment is given for the complete conversion of precursor in to cobalt oxide particles. The prepared sample is well characterised for its structure by X-ray diffraction (XRD), morphology by Transmission Electron Microscope (TEM) and bonding by Fourier Transform Infrared study (FT-IR) techniques. Electrical study of the prepared sample is undertaken. .

2. Experimental

2.1 Materials and methods

Cobalt chloride, oxalic acid and ammonia chemicals are used in the present study were of AR grade. Polyvinyl alcohol of molecular weight 125,000 was obtained commercially is used as fuel. Microwave method is adopted for the synthesis of cobalt oxide nanoparticles

2.2 ***Preparation of cobalt oxalate precursor***

The hydrated cobalt oxalate precursor was prepared by dissolving eqimolar proportions of cobalt chloride and oxalic acid in minimum volume of water and was stirred for about 15 min on a magnetic stirrer. The slight brown coloured precipitate at 5-6 pH and is washed with cold distilled water till it free chloride and excess oxalic acid. Finally, the precipitate is washed repeatedly with dry acetone and then dried under vaccume. [7].

2.3 ***Preparation of Cobalt Oxide***

The prepared cobalt oxalate precursor is mixed with polyvinyl alcohol in the weight ratio 1:5 [8] and ground well using pestle and mortar. The resultant mixture was transferred into a crucible and ignited in an electrical oven. The dispersed phase ignited with the evolution of large volume of gases. Here, PVA reacts with the precursor a partially decomposed product was obtained, after the complete evolution of gases. The temperature of the process does not exceed 300^{o}C at any time. Chemical and physical characterisation of the partially decomposed products did not give any confirmable phases. The possible reason for a partially decomposed product formed may be attributed to the low temperature of the reaction giving rise to the insufficient energy needed for complete conversion. Hence, the sample is treated in a microwave oven to get the desired product. This partially decomposed product was placed in a domestic microwave oven having frequency 2.45GHz for about 20 minutes at 90%. The solid burns by producing carmic red colour light due to the presence of cobalt metal in the precursor and leaving behind a black coloured cobalt oxide sample.

2.4 Density measurement

2.4.1 Density evaluation from X-ray data

The X-ray density of the samples have been computed from the values of lattice parameters using the formula [9-10].

$$d := 8\,\frac{M}{Na^3}$$

Where 8 represents the number of molecules in a unit cell of a spinal lattice

M = Molecular weight of the sample N = Avogardo's number

a = Lattice parameter of the sample

The lattice constant for the cubic was calculated using the equation

$$d = \frac{a}{(h^2+k^2+l^2)^{1/2}}$$

2.4.2 Tap density

The as prepared Co_3O_4 was crushed in agate mortar using a pestle and mortar. A known amount of this powder was filled into a graduated cylinder of 25ml capacity. The cylinder was tapped until the powder level remains unchanged. The volume occupied by the powder was noted. The ratio between the weight of the substance and the volume gave tap density [11].

2.4.3 Powder density

The powder densities were measured using Archimedes principle [12] with a pycnometer and xylene as a liquid medium. The pycnometer of volume 25ml was used. The following weights were taken and used in the density calculation.

$$_{sample} = \frac{(w_2 - w_1)\ _{sol}}{(w_4 - w_3) + (w_2 - w_1)}$$

Weight of the bottle = W_1g, Weight of the bottle + Substance = W_2g, Weight of the bottle + Substance + Xylene = W_3g, Weight of the bottle + Xylene = W_4g, Density of Xylene = $_{sol}$, Density of sample = $_{sample}$

2.4.4 Crystallite size from X-ray data

Detailed knowledge of crystallite size, shape and strain in a finely divided powder often helps to correlate many physical properties of a system undergoing transformation in a solid-state reaction. X-ray line broadening analysis provides a method of finding bulk average size of coherently diffracting domains and r.m.s strain. The average crystallite size (D) from X-ray line broadening has been calculated using the Scherrer equation [13-14]. The instrumental broading was corrected using quartz as a internal standard.

$$D = \frac{0.9\lambda}{\beta_{1/2}\text{Cos}\theta}$$

Where λ is the wavelength of the X-ray beam, $\beta_{1/2}$ is the angular width at the half-maximum intensity and θ is the Bragg angular

2.5 *Characterisation*

The X-ray diffraction patterns were obtained employing a Geol JDX-8p spectrometer using CuKα radiation. The X-rays generator was operated at 30kV and 20mA. The scanning range, $2\theta/\theta$ were selected. The scanning speed $=1^0$ min^{-1} were employed for precise lattice parameter determination. High purity silicon powder was used as an internal standard. The shape, size and distribution of the powder, as prepared tin oxide sample, microstructure of the sample have examined using a Leica-440 Cambridge Stereoscan, scanning electron microscope image. The TEM images were obtained by Technia-20 Philips transmission electron microscope operated at 190KeV. The infrared spectra of the oxide sample were recorded on a Perkin –Elmer FTIR spectrophotometer [Model 1000] in the range 300 cm^{-1} to 4000cm^{-1}. The Co_3O_4 is pressed in the form of circular

pellets of 1cm diameter and 1cm thickness. The dc conductivity measurements of cobalt oxide is made using the conducting silver paste as electrodes on both sides and is carried out by Keithly 2010 electrometer using two probe method. The magnetic study of the sample was done using two probe Vibrating Sample magnetometer (VSM).

3.0. Results and discussion

3.1. X-ray diffraction

Figure1 (a) shows XRD pattern of cobalt oxalate and fuel mixture after igniting in an electrical oven. The observation of the pattern indicates no Bragg's reflections in the pattern due to the amorphous nature and is also indicating the formation of crystalline nature for the compound at higher temperature. Figure1 (b) shows indexed XRD pattern of microwave derived cobalt oxide. The pattern shows large number of peaks confirms the formation of cubic phase Co_3O_4 sample. The d-spacing values of the sample matches well with standard 42-1467 JCPDS file. Unit cell parameters ware obtained by least–square refinement of the powder XRD data. This study reveals that the sample is monophasic $Co_3O_4$with cubic (Fd3m) structure having nanosized particles. The values in the parenthesis indicate miller indices.

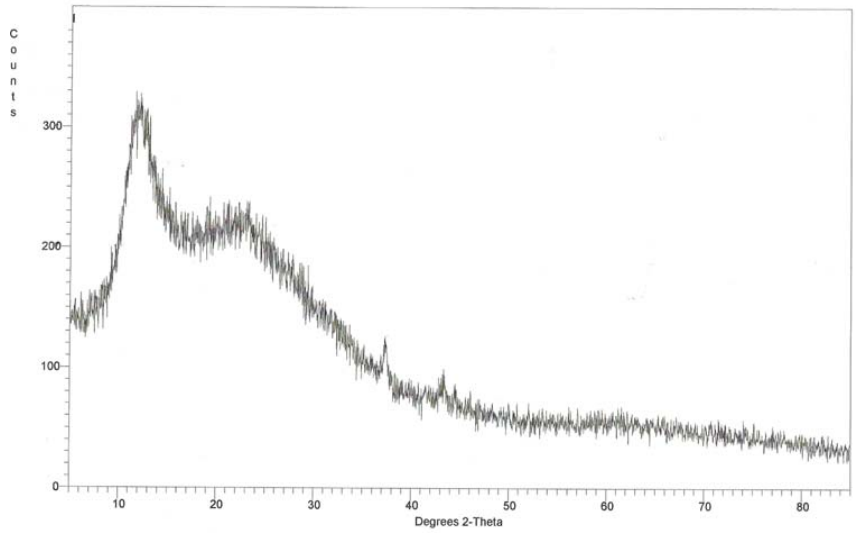

Figure1 (a): XRD pattern of cobalt oxalate and fuel mixture after igniting in an electrical oven.

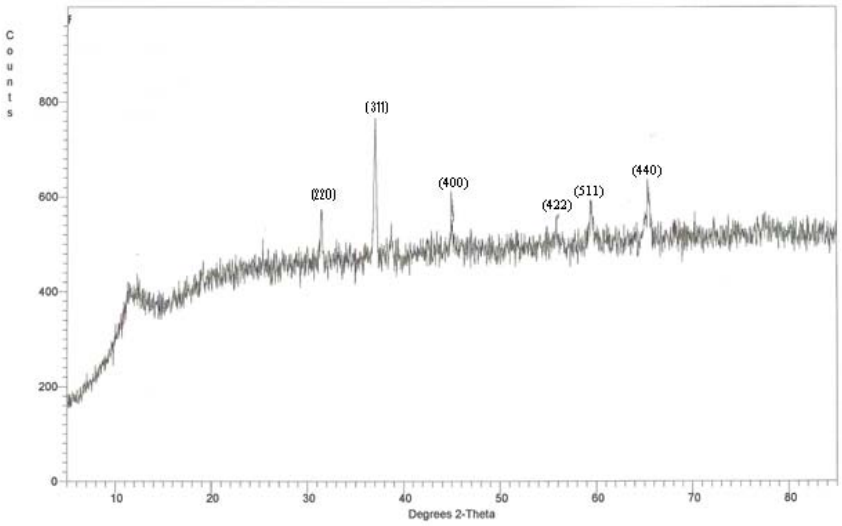

Figure1 (b): Indexed XRD pattern of microwave derived cobalt oxide

3.2. Crystallite size and density

The crystallite size of the co sample is calculated from XRD data is 50 nm. The size obtained is dependent on solid-state transformation reaction, which generally adopts the habit of its precursor. Thus, the conversion of cobalt oxalate precursor into Co_3O_4 is considered being topotactic in nature, indicating that the synthesis of precursor with very small particle sizes would be required for obtaining nanosized cobalt oxide sample. The densities of the sample calculated from XRD data, tap density and powder density is 4886 kg/m^3, 5179 kg/m^3 and 3620 kg/m^3 respectively. The sample shows approximately same density may be attributed to their average shape which might have similar surface area.

3.3. Scanning Electron Microscopy

The morphology of as prepared cobalt oxide was studied by Scanning Electron Microscope tool. Figure 2 shows SEM image of microwave derived Co_3O_4 sample. This shows that particles are irregular shape and some places as spherical agglomerated. A uniform morphology and chemical homogeneity is also observed in the image.

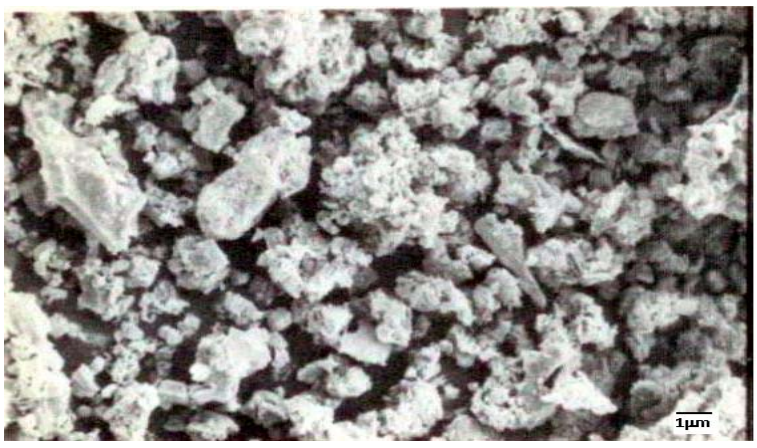

Figure-2: SEM image of cobalt Oxide

3.4. Transmission electron microscopy (TEM)

The nanocrystalline nature of the microwave derived Co_3O_4 sample was further confirmed by Transmission electron microscope image. Figure 3 shows, the bright field TEM micrograph of the prepared cobalt oxide sample. This image represents the crystalline morphology with mostly irregular particle shape and particles are in nano range. The particles seems to be closely joined together to form fine nano spheres.

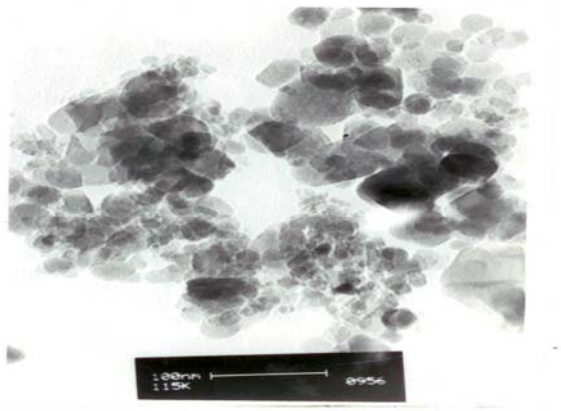

Figure 3: Bright field TEM micrograph image of Cobalt Oxide

3.5. Infrared studies

The bonding nature of the prepared cobalt oxide sample was studied by Fourier transform infra red tool. Figure 4 shows FTIR spectrum of as prepared Co_3O_4 sample. The sample shows the absorption in the region 3350, 1100, 560 and 455 cm-1. The peak 3350cm-1 corresponds to water of absorption and the peak at 1100 cm-1 due to the presence of some overtones. The peaks at 560 and 455 cm-1 corresponds to metal-oxygen (Co-O) vibrational modes of the spinal compound. (Metal oxides generally give absorption bands below 1000cm^{-1} arising from inter-atomic vibrations [15].This conform the formation of Co_3O_4 sample.

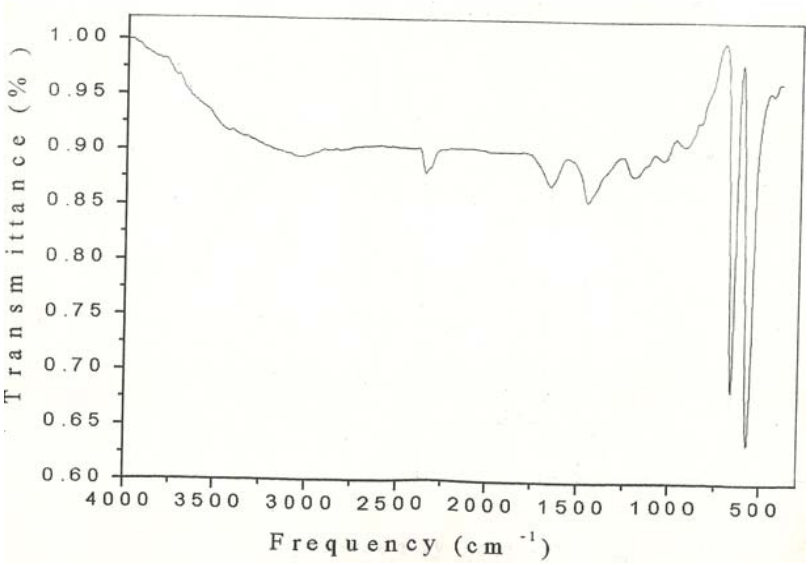

Figure 4: FTIR spectrum of as prepared Co_3O_4 sample

3.6. Electrical conductivity

Figure-5 shows the variation of dc conductivity as a function of temperature for the prepared Co_3O_4 sample. The conductivity increases with increase in temperature up to 110^{o}C followed with exponential increase of conductivity up to 150^{o}C.Then it shows very slow increase in conductivity. The rapid increase in conductivity at 190^{o}C shows the loss of hydroxyl groups from the cobalt oxide.

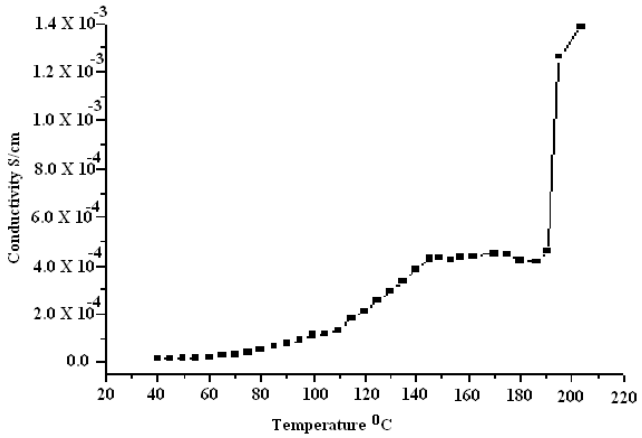

Figure 5: Variation of d.c conductivity of as prepared Co_3O_4 sample

3.7. Magnetic Study

Magnetic study was under taken for as prepared cobalt oxide nanoparticles with the use of magnetic hysteresis trace. Figure 6 shows the M-H loop of Co_3O_4 nanoparticle sample at room temperature with maximum applied field up to 163KOe. The saturation magnetization (Ms) was found to be 65.40Gauss and remanent magnetisation(Mr) was 35.27 Gauss. The obtained hysteresis loop is very narrow but not rounded shape with

coercivity (265.35Oe) indicating formation of magnetic material. The internal area of hysteresis loop represents the capability of magnetic energy storage of material.

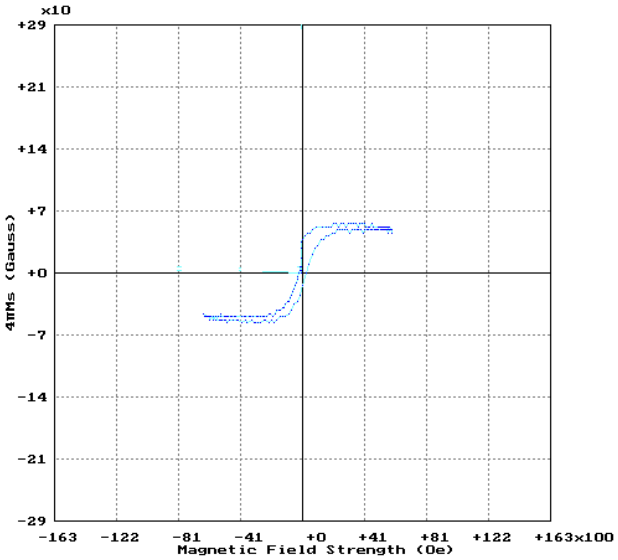

Figure 6: Magnetic hysteresis loop of as prepared Co_3O_4 sample

4. Conclusions

Microwave irradiation is used for complete conversion of cobalt oxalate precursor in to cobalt oxide nanomaterial. Polyvinyl alcohol is used as an efficient fuel in microwave ignition. This preparative technique is very simple and energy efficient to obtain materials at nano dimension. Hence, this method can adopt for the synthesis of other metal oxides at nano dimensions not only for laboratory preparation, this procedure may be extended for large-scale synthesis of metal oxide nanoparticle. The TEM image confirms the nanocrystalline nature of the prepared cobalt oxide. The electrical study of the prepared sample shows semiconductor behavior

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