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Synthesis, characterization and electrical properties of nanocrystalline ZnCo₂O₄ oxide by combustion route

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ABSTRACT

The aim of said study was to obtain nanostructured ZnCo₂O₄ through self combustion synthesis using cobalt nitrate, iron nitrate as precursors and glycine as a fuel, without the subsequent heat treatments after synthesis. The temperature variation with respect to a sample with constant molar ratio was investigated. The crystallinity (phases present and crystallite size: estimated by single-line method) of the product obtained was determined by X-ray diffraction (XRD) measurement, thermogravimetric analysis(TG-DTA), scanning electron microscope(SEM), and high resolution transmission electron microscopy (HRTEM). The synthesis method facilitated the production of spinel ZnCo₂O₄ with crystallite size between 7-37 nm. Electrical properties of the synthesized nanoparticles are studied by AC conductivity measurement. Electrical conductivity of the nanomaterial ZnCo₂O₄ was increased with the temperature.

Keywords: ZnCo₂O₄ nanostructure, XRD, TG/DTA, EDX, SEM, TEM.

INTRODUCTION

In recent years Nanocrystalline zinc cobaltite spinel (ZnCo₂O₄) [1] have been extensively studied owing to their potential uses in many application such as solar energy cells as photoelectric energy conversion materials [2-3]., Photo catalyst [4-5].The basis and more significant application of ferromagnetic semiconductors have raised tremendous scope for study of these spinals for application such as in spintronics [6]. Among many semiconductors materials ZnCo₂O₄ is one potential materials is solar energy conversion and photo catalytic field die to its photo chemicals properties similar to TiO₂ [7-8]. A large number of metal oxides [9],

mixed oxides and Ferrites has shows sensitivity to certain gas species spinal compounds with a general formula AB_2O_4 , have also been proved as important oxides in gas sensors and have been investigate for the detection of both oxidizing and reducing gases $NiFe_2O_4$, $MnFe_2O_4$ and $ZnFe_2O_4$ spinal ferrites have been extensively studied for various oxidizing gas sensing applications [10-11]. We have therefore adopted the combustion synthesis route to obtain nanosized $ZnCo_2O_4$ suitable for gas sensing application. Semiconductors gas sensors present the property of changing the conductivity of the sensing material when this is exposed to different atmospheric gas. The gas sensing mechanism usually depends on the operating temperature. The optimum working temperature of the semiconductor sensors depends on the gas atmosphere and on the properties of the sensors materials selected in every case [12-13].

Conventional semiconducting oxides can be prepared by a variety of methods such as Czochralski method [14], Conventional solid state methods [15], sol gel route [16], Co-precipitation [17] and the hydrothermal reaction over an extensive period [18]. Recently combustion synthesis [19] has emerged as attractive technique for the synthesis of homogeneous high purity and crystalline oxide powder at significantly lower temperature then the conventional synthesis methods. All these techniques require shorter time periods and using less amounts of external energy [20-21]. Also further it has been observed that, the synthesized powder with combustion process retain their nanocrystalline structure even after sintering which is extremely useful for many device applications [22]. Combustion synthesis technique has been found and developed for number of applications in the chemical and ceramic process [23] compared with the other synthesis method has the different advantages of shorting the reaction time, giving small particle size products with narrow particle size distribution, high-purity and development which make possible to obtain spinal oxides in the form of ultrafine or nanoparticles [24-25].

The present research, analyze the synthesis of an n-type spinal $ZnCo_2O_4$ by the combustion method with an average crystalline size of 7-37 nm. Electrical conductivity of the nanomaterial $ZnCo_2O_4$ was increased with the temperature.

EXPERIMENTAL SECTION

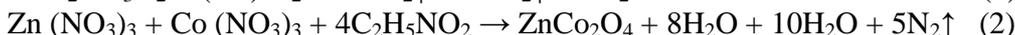
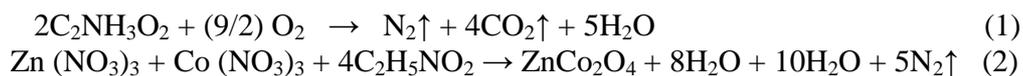
Powder preparation

In present research work synthesized $ZnCo_2O_4$ powder were prepared using combustion synthesis with different molar composition of fuel subsequently the molar composition was maintained constant and process carried out under varying synthesis temperatures.[26-27]

Zinc cobalt oxide ($ZnCo_2O_4$) was synthesized using the modified solution combustion technique starting from solution of $Zn(NO_3)_2 \cdot 6H_2O$ (7.43g), $(Co(NO_3)_2 \cdot 6H_2O)$ (7.27g) and glycine (6.05g). glycine possess ability of high heat of combustion. It is an organic fuel and provides a platform for redox reactions during the course of combustion. Initially the Zinc nitrates, Cobalt nitrates and glycine are taken in the proportion of 1:1:4 in stoichiometric amount and dissolved in a 250 ml beaker to made homogenous paste. Formed paste was evaporated on hot plate in temperature range $70^{\circ}C$ to $80^{\circ}C$ gives thick gel. The gel was kept on a hot plate for auto combustion and heated in the temperature range $170^{\circ}C$ to $180^{\circ}C$. The nanocrystalline $ZnCo_2O_4$ powder was formed within 40-50 minute which sintered at about 300, 500, 800 and $1000^{\circ}C$ for about 4 hours then get black color shining powder of $ZnCo_2O_4$ in nanocrystalline form.

The as-prepared samples were characterized by TG/DTA thermal analyzer (SDT Q600 V 20.9 Build 20), XRD Philips Analytic X-ray B.V. (PW-3710 Based Model diffraction analysis using Cu-K α radiation), scanning electron microscope (SEM, JEOL JED 2300) coupled with an energy dispersive spectrometer (EDS JEOL 6360 LA), A JEOL JEM-200 CX transmission electron microscope operating at 200 kV analysis.

RESULTS AND DISCUSSION



TG-DTA analysis was performed at a heating rate of 10 $^{\circ}\text{K min}^{-1}$ to investigate the thermal properties of ZnCo_2O_4 . The TG spectrum and its 1st derivative represented in Figure 1 show the thermal decomposition of ZnCo_2O_4 , the curve indicates that the slight weight loss of about 13.2% at temperature up to 140 $^{\circ}\text{C}$ in ZnCo_2O_4 powder due to little loss of moisture, carbon dioxide and nitrogen gas. The DTA curve of ZnCo_2O_4 recorded in static air shown in Figure 1 the curve shows that ZnCo_2O_4 did not decompose but weight loss was due to dehydrogenation, decarboxylation and denitration. Further weight loss of about 28% between the temperature range 300 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ and continuous loss in weight about 48% up to 600 $^{\circ}\text{C}$ is attributed to loss of organic materials and yield final product at 650 $^{\circ}\text{C}$. Weight loss and weight gained was very negligible. These indicating that the synthesized powder was almost remain stable from the begging. The formed temperature in the present research work was found to be comparatively similar than that reported corresponding solid state reaction route [28].

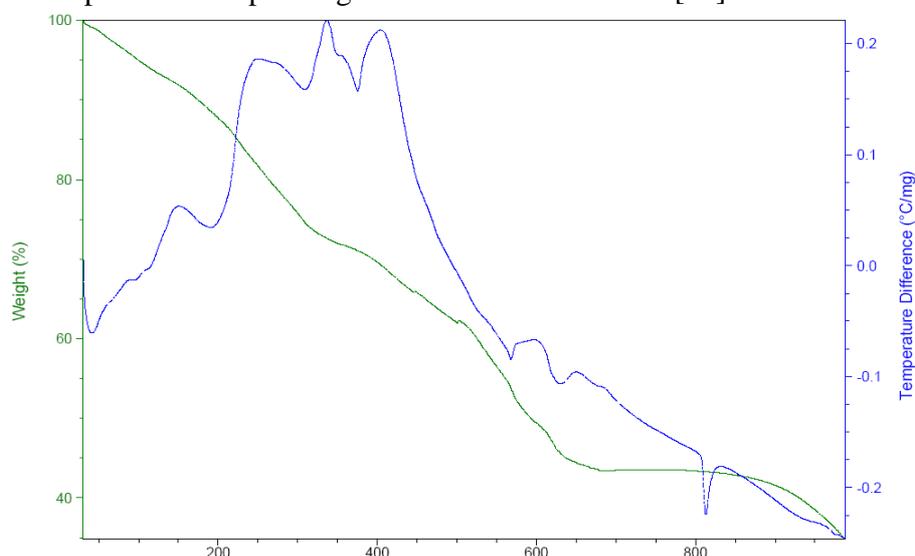


Fig 1. TG-DTA curve of mixed precursor.

XRD studies

The X-ray diffraction patterns of each sample were studied at different temperatures and were shown in Figure 2. The observed d values compared with standard d values and was observed in agreement with standard d value i.e. JCPDS data. (Card number 82-1042). The cubic structure possesses the may be attributed to the different preparation method which may yield different structural defects. The crystalline size was determined from full width of half maximum

(FWHM) with the most intense peak obtained which shown scanning of X-ray diffraction pattern. The crystallite size was calculated by using represented Scherer equation [29-30]

$$d = 0.9\lambda / \beta \cos \theta.$$

Where d is the crystalline size, λ is the X-ray wavelength of the Cu K_{α} source ($\lambda=1.54056 \text{ \AA}$), β is the FWHM of the most predominant peak at 100 % intensity, θ is the Bragg's angle at which peak is recorded. In order to obtain pure nanocrystalline ZnCo_2O_4 particles and understand the thermal characterizations as prepared ZnCo_2O_4 powder is further calcinated at 180, 300, 500, 800 and 1000°C respectively (the calcinated temperature assigned as T_c). Figure 2 present XRD patterns for ZnCo_2O_4 oxide nanoparticles. The effects of the calcinations temperature on the crystallite size of ZnCo_2O_4 particles can be demonstrated. Traces of ZnCo_2O_4 crystallites phases (111), (220), (311), (222), (400),(311), (422) and (511) are detected in the XRD pattern for all calcinated temperatures and then their intensities increase abruptly when the T_c above 1000°C . In general, the sharpness of the XRD peak (i.e. high crystallinity) is increased as the T_c increases. According to the (222) diffraction pattern of ZnCo_2O_4 crystalline, the particle size of ZnCo_2O_4 can be calculated from the full width at half-maximum using the Scherrer equation. Obviously, the particle size of ZnCo_2O_4 changes as the T_c controlled fewer than 180, 300, 500, 800 and 1000°C , the order is 7, 8, 9, 12 and 37 nm respectively. These indicate that the crystallinity of ZnCo_2O_4 is accelerated as the T_c above 500°C illustrates the relationship between the annealing temperature and the average crystal size of the ZnCo_2O_4 nanoparticles. It is obvious that the ZnCo_2O_4 nanoparticle grows slowly at range $300\text{-}500^{\circ}\text{C}$ and $800\text{-}1000^{\circ}\text{C}$, respectively and it was shown that nanoparticle grow rapidly at 800°C .

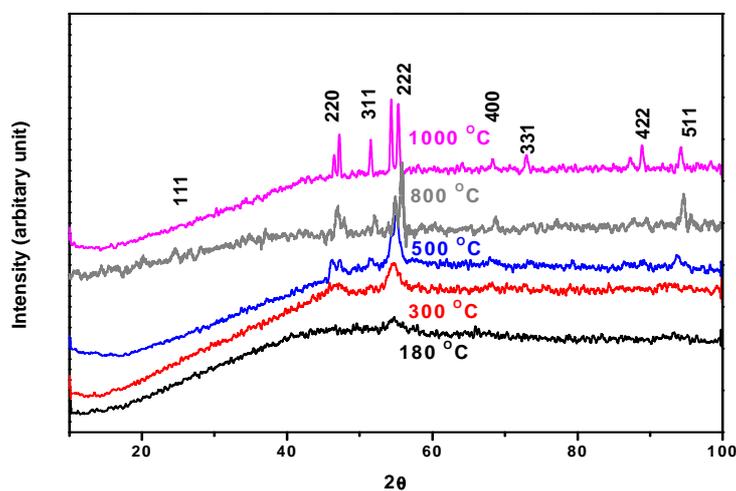


Fig 2. XRD patterns of calcined mixed precursor at 180,300,500,800 and 1000°C .for4h.

Particle size distribution studies

Fig. 3 has been carried out by using dynamic light scattering techniques. (DLS *via* Laser input energy of 632 nm) It was observed that zinc cobalt oxide nanoparticles have narrow size distribute within the range of about 25-30 nm. Which are well match with calculated value and was calculated it from Debye-Scherrer equation.

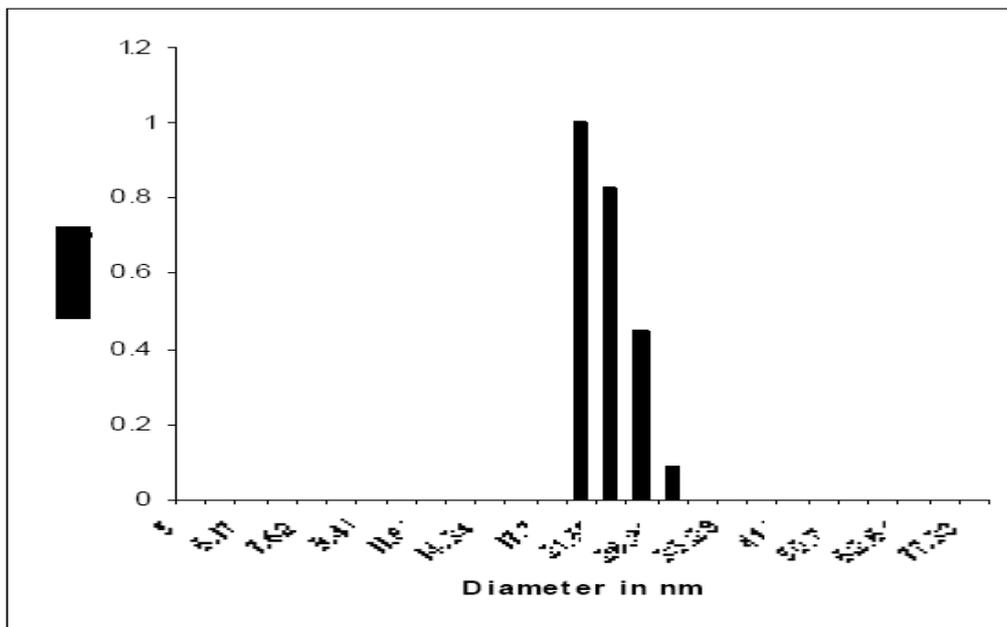


Fig3. Particle size Distribution of as prepared ZnCo_2O_4 powder

SEM studies

The microstructure of the 800°C sintered samples can be visualized from scanning electron microscope (SEM) tool. Fig. 4 depicts SEM images of ZnCo_2O_4 powder it shown the particle morphology of high resolution the particle are most irregular in shape with a nanosize range of 100-200 nm some particles are found as agglomerations containing very fine particles. It can be observed that ZnCo_2O_4 have uniformed size of about $5\mu\text{m}$. It seems that surfaces are smooth, spongy and pores are seen in the micrograph.

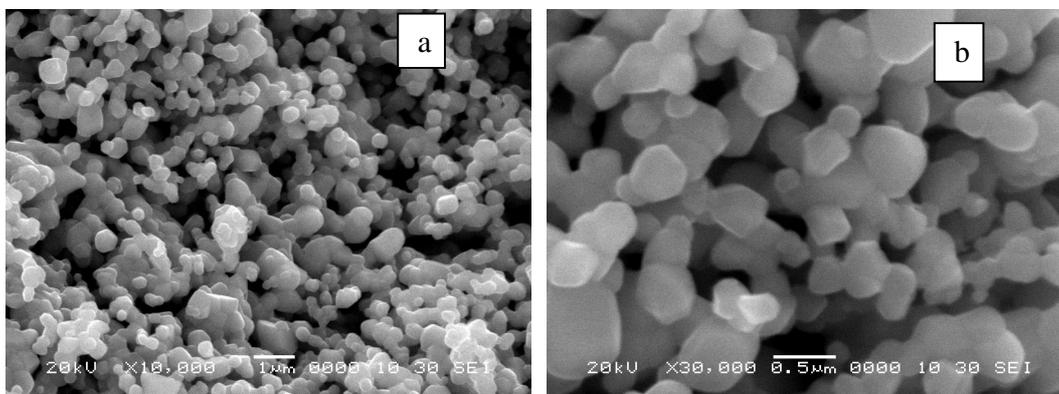


Fig4. SEM images of the self combustion product the powder annealed at 800°C at (a) low resolution (b) high resolution.

EDX studies

The energy dispersive X-ray microanalysis was carried out to know the presence of zinc, cobalt and oxygen peaks confirms in the materials. There was no unidentified peak observed in EDX. This confirms the purity and the composition of the ZnFe_2O_4 nanomaterial. in Fig. 4

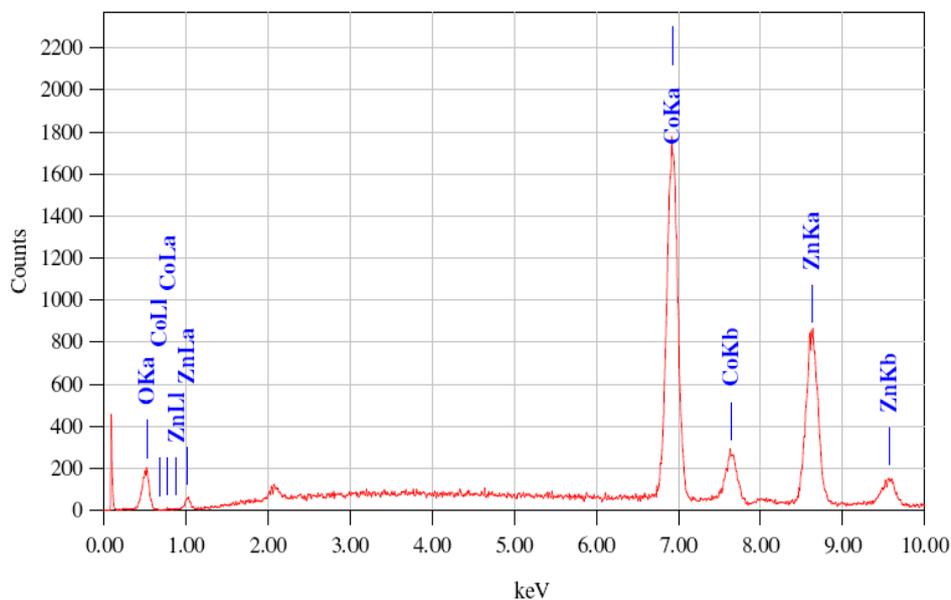


Fig 5. EDX pattern of mixed precursor.

TEM studies

The TEM image of the mixed precursor calcined at 800°C for 4h are shown in Fig. 6. It indicates the presence of ZnCo_2O_4 nanoparticles with size 30-40 nm which form beed type of oriental aggregation throughout the region. The selected area electron diffraction (SAED) pattern shown in Fig. 6 (a) which shows that spot type pattern is indicates the presence of single crystalline particles. No evidence was found for more than one pattern, suggesting the single phase nature of the material.

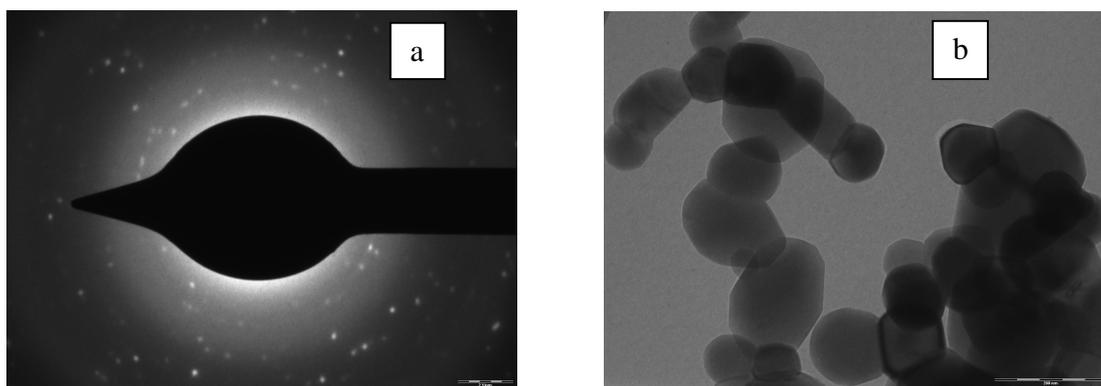


Fig.6. TEM (a) images of nanostructured ZnCo_2O_4 (b) SAED pattern.

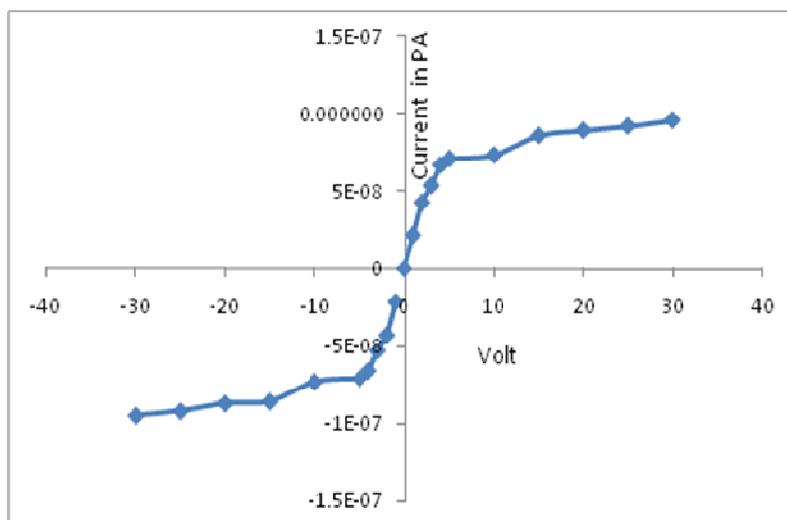


Fig.7. I-V characteristics of the ZnCo₂O₄ sensor

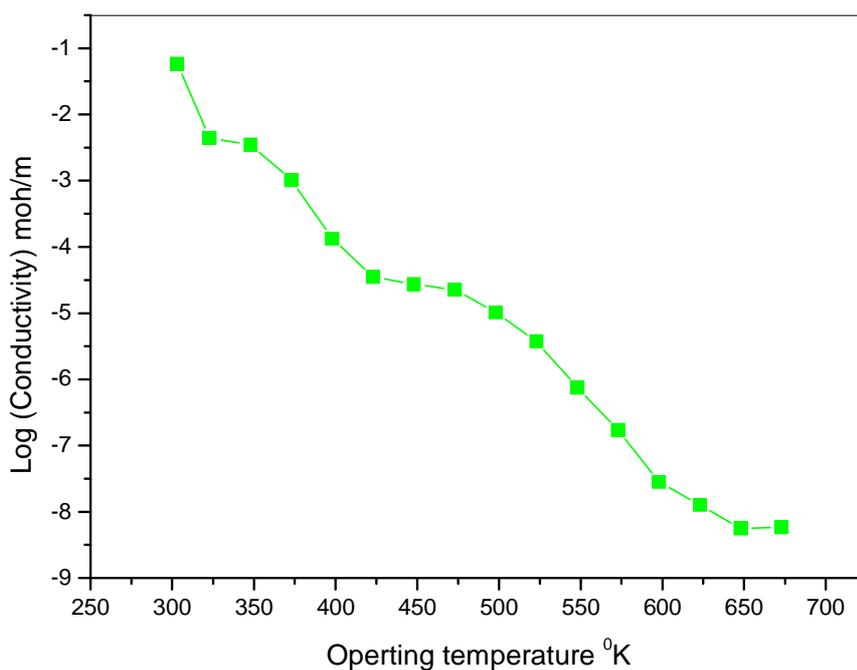


Fig.8 Variation log (conductivity) with reciprocal operating temperature

Electrical Properties

I-V characteristics

Fig.7. depicts I-V characteristics of ZnCo₂O₄ films. It is clear from the symmetrical I-V characteristics that the silver contacts on the films were ohmic in nature.

Electrical conductivity

Fig.8 shows the variation of log (conductivity) with temperature. The conductivity values of sample increase with operating temperature. The increase in conductivity with increasing temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of ZnCo₂O₄. It is observed from fig. 8 that the electrical conductivities of the ZnCo₂O₄ films are nearly linear in the temperature range from 50- 400⁰C in air ambient.

CONCLUSION

Nanocrystalline ZnCo₂O₄ has been successfully synthesized by self combustion route. TG-DTA analysis indicates the phase formation was carried out at 650⁰C. The route may be used for the synthesis of other metal oxide. XRD technique was shown the average crystal size of the ZnCo₂O₄ nanoparticles ranges from about 7-37 nm at 180-1000⁰C respectively. Elemental analysis confirmed by using EDX. SEM micrographs show the material is porous in nature. TEM image shows grain size of the material was 30 nm. These nanoparticles with shows good I-V characteristics with ideal semiconducting nature at room temperature. Electrical conductivity of the nanomaterial ZnCo₂O₄ was increased with the temperature.

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