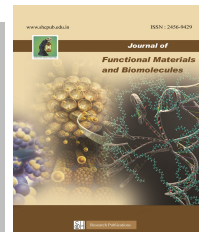




SACRED HEART RESEARCH PUBLICATIONS

Journal of Functional Materials and Biomolecules

Journal homepage: www.shcpub.edu.in



ISSN: 2456-9429

EFFECT OF SHOCK WAVES ON STRUCTURAL AND SPECTROSCOPIC PROPERTIES OF ZINC COBALTITE NANOPARTICLES

Sachin S¹, Swathi S¹, Theophil Anand G¹, S. A. Martin Britto Dhas¹ and S. John Sundaram^{1*},

Received on 15 October 2022, accepted on 24 November 2022,
Published online on December 2022

Abstract

Cubic structured Zinc cobaltite ZnCo_2O_4 nanoparticles were prepared by hydrothermal method. The structure of ZnCo_2O_4 was confirmed by the X-ray diffraction (XRD) technique. The prepared samples were subjected to 100, 150 and 200 shock waves. There is an increase and decrease in intensity in few peaks by the effect of shock waves. SEM analysis results that the ZnCo_2O_4 nanoparticles obtained dense spherical morphology; when the prepared samples exposed to there is a slight change in particle size. UV-Visible analysis reveals the bandgap of ZnCo_2O_4 . The control ZnCo_2O_4 nanoparticles was found to be 3.0 eV, after exposed to 100 shock waves the bandgap decreased to 2.8 eV, at 150 shock waves the bandgap increased to 2.9 eV and at 200 shock waves the bandgap of ZnCo_2O_4 further increased to 3.1 eV. VSM analysis the measurement of magnetic behavior of magnetic materials, it results that the control ZnCo_2O_4 nanoparticles exhibits super paramagnetic behavior. When the prepared samples exposed to 100, 150 and 200 shock the change in magnetic changed into paramagnetic behavior was observed. From the Raman spectroscopy of ZnCo_2O_4 , Zn-o and Co-o vibration only obtained hence the prepared sample was pure and it is noted that for 100 shocks.

Keywords: ZnCo_2O_4 , Shock waves, Nanoparticles, Magnetic behavior, Vibrational energy.

1 Introduction

Super capacitors have created a very good awareness for future generation power storing devices because of their power density and higher energy density. Nano-scale metal oxides had been admired lot of attentiveness in high-capacity anode materials for future generation super capacitors [1]. The 3d transition metal oxides, cobalt oxides had been shown theoretically high capacity and very good cycling performance Cobalt [2]. Co_3O_4 partially eco-friendly and low Comparing other metals. Moreover, it has been observed that phase transition studies and their mechanisms are possible ways to understand the structural properties of material under the low temperature to high pressure and high pressure to high temperature conditions [3] and then it gives another transformation has characteristics features as compare to the pressure compression and temperature-based phase transformation

conditions Hence, so many researchers have been working about the shock wave induced phase transformation on crystalline materials [4]. At recent years, huge number of articles had been published in the field of shock waves impact on crystalline materials and their phase transformation. The nanocrystalline materials had attained a position of good strength that's why they have an excellent role in industrial application (5). These kinds of shock wave impact study and therefore the results obtained may offer clear proof for the pertinency of materials for specific applications like part atomic power plants, thermal protecting systems etc [6,7]. particularly materials having a polymeric nature have the good structure stability and commercial application. On a similar path, in recent years, we have place wide effort toward understanding the part transformation mechanism at wave coated conditions for metal chemical compound nanocrystalline material like Al_2O_3 , ZnO, MnO, TiO_2 , ZrO_2 , CeO₂, CuO, Fe₂O₃, and Co_3O_4 [8]. On the opposite hand Co_3O_4 NPs bear state change against the impact of shock waves. The current work is designed to investigate the impact of shock waves on Zinc cobalt nanoparticles (ZnCo_2O_4) NPs [9]. The sample material was prepared by hydrothermal method and shock wave recovery experiment was done by table high pressure driven shock tube. The shock wave applied sample may undergo structural, morphological and magnetic properties are noticed by various analytical techniques such as powder X-ray Diffractometer (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM).

2 Experimental Sections

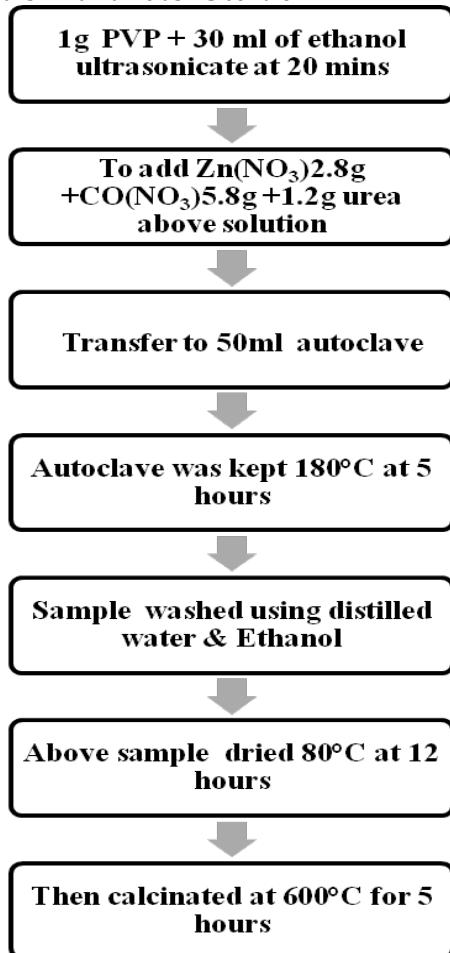
Material synthesis:

All the chemical reagents were of analytical grade and used as received without any purification. 1g of Polyvinylpyrrolidone (PVP) is dissolved in 30 ml of ethanol and the solution was ultrasonicate the solution using digital ultrasonicator for 20 minutes. Then 1mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 7mmol of urea was added to the above solution and stirred until it was completely dissolved. The previously described solution was taken into a 100ml stainless steel autoclave.

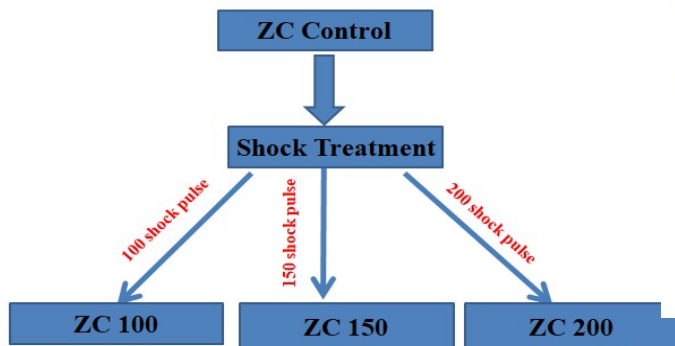
*Corresponding author: e-mail: johnsundaram@shcpt.edu

¹ Department of Physics, Sacred Heart College (Autonomous), Tirupattur - 635 601, Tamilnadu, India,

The autoclave was kept in hot air oven at 180°C for 5 hours, and then cooled to the room temperature. After the reaction time Green color precipitate was obtained. Then the precipitate was washed with deionized water and ethanol for several times. The sample was dried at 80°C for 12 hours. Then the dried powder was annealed at 600°C for 5 hours. And name as ZC control.



Shock wave Treatment :



3 Results and Discussion

X-Ray diffraction has been analyzed by the powder X-ray diffractometer with Cu-K α radiation for the identification of structural properties. The control sample had diffraction at 18.95 $^{\circ}$, 31.09 $^{\circ}$, 36.66 $^{\circ}$, 44.44 $^{\circ}$, 58.98 $^{\circ}$, 64.76 $^{\circ}$ 2 θ values for corresponding (111), (220), (311), (400), (511), (440) hkl values respectively. All the diffraction peaks are belongs to the zinc cobaltite well suited with the JCPDS card number 81-2299 having Cubic crystal structure and lattice parameters Face -Centered and space group Fd3 $_m$ (227) is show in figure [1]. In (111) plane the peak intensity increases by the effect of shock wave due to the degree of crystalline nature increase. The plane 220 peaks for 100 and 150 the peak intensity decreases and at (200) the peak increases Due to the continuous re-orientation of the planes. For (311) and (400) plane the peak does not have any variation in peak, peak intensity changes due to the unit cell compression it plays the role in conductivity of atoms[12]. For (511) plane the peak decrease at 100 shocks, increase at 150mshocks broaden at 200 shocks and the changes are done by the continues arrangement of high strain in crystalline planes. For (440) the peak decrease due to the surface termination of atomic planes. Due to the atomic planes arrangement of grain boundaries the crystalline sizes are varied. The size of the crystalline size is 25nm. The crystalline sizes are calculated using debyes scherrer formula.

$$D = K\lambda / \beta \cos \theta.$$

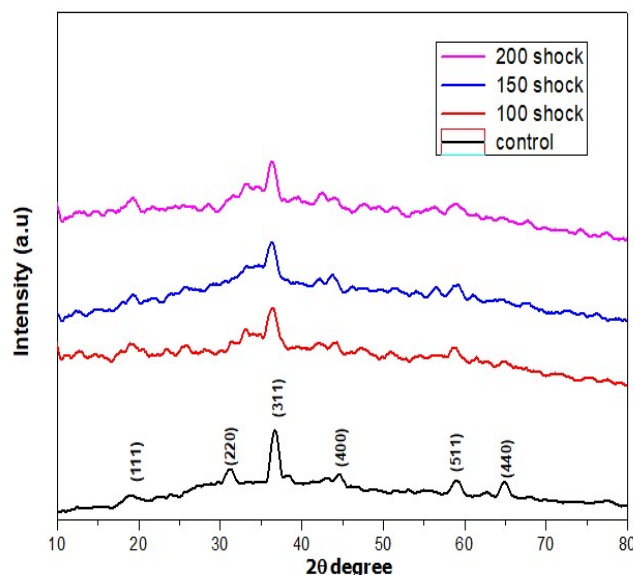
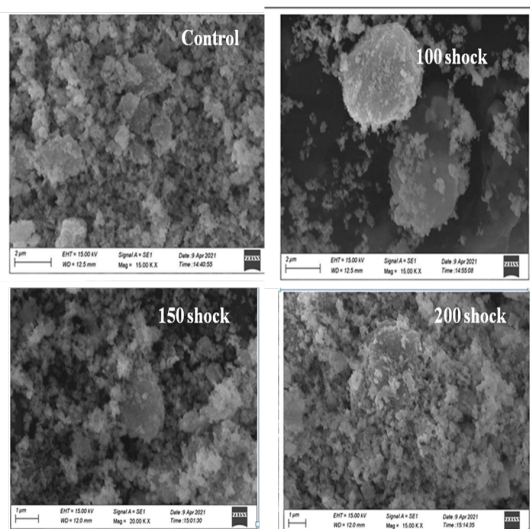


Fig 1 X-Ray diffraction pattern of ZnCo $_2$ O $_4$ under different shock wave conditions

3.1 Morphological analysis:

The scanning electron microscopy (SEM) analysis of control and shock wave loaded zinc cobaltite NPs are shown in the below figure. The control obtained zinc cobaltite NPs reveals dense spherical morphology with the average particle size 32nm. When we apply the shock wave the particle size was found to be varied for 100,150, and 200 shocks respectively. From the above statement we confirm that the zinc cobaltite morphology under shock wave pulses there is a slight change in each size of the SEM images.



3.2 UV-visible analysis:

UV – visible spectrum of ZnCo₂O₄ is shown below. The UV-visible absorption spectra are mainly described for the nanoparticles formation analysis the material stabilization. Fig (2) shows the UV-visible absorption analysis of prepared ZnCo₂O₄ NPs using hydrothermal method.

The band gap of the ZnCo₂O₄ nanoparticles can be calculated by Tauc's formula,

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

E_g – band gap energy
 α - absorption coefficient
 hν- photo energy
 c- constant

Sample	Band gap (eV)
ZnCo ₂ O ₄ control	3.0
ZnCo ₂ O ₄ 100 shock	2.8
ZnCo ₂ O ₄ 150 shock	2.9
ZnCo ₂ O ₄ 200 shock	3.1

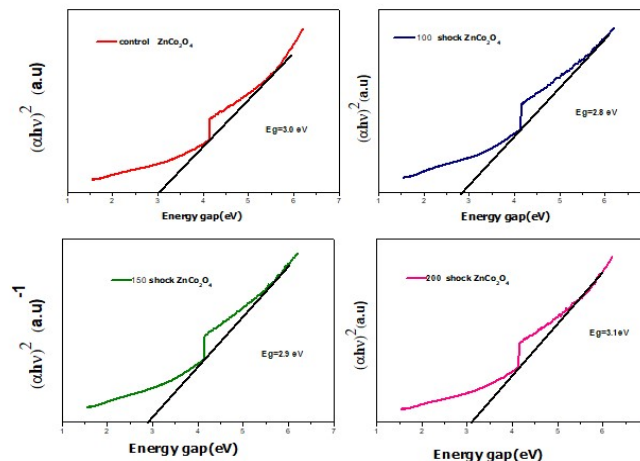
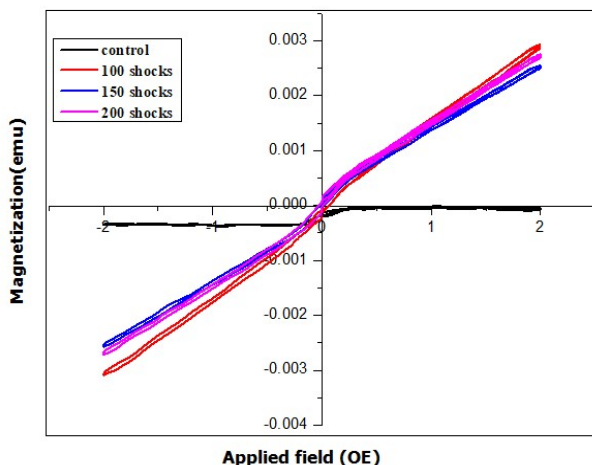


Fig 2 optical absorption spectra of ZnCo₂O₄ under different shock wave conditions

3.3 VSM Analysis

The VSM technique is highly adopted to understand magnetic behaviour of the cobaltite sample with respect to various pressures. The hysteresis loop of the control and shock wave loaded sample is shown in the below figure. The control sample exhibits the superparamagnetic behavior having no retentivity, because the magnetic loop passes through the origin co-ordinates with minimum coercivity. When the shock wave is loaded both magnetic saturation and coercivity increases. The shock wave loaded sample changes from superparamagnetic to paramagnetic behavior. The magnetization (×10⁻³emu), coercivity (Oe), retentivity (×10⁻⁶ emu) values of control and the shock wave loaded sample is represented in the below table. Hence, we conclude that the zinc cobaltite nanoparticles have magnetic phase transition on increasing the shock wave loaded conditions. Thus the zinc cobaltite have minimum stability at different shock waves.

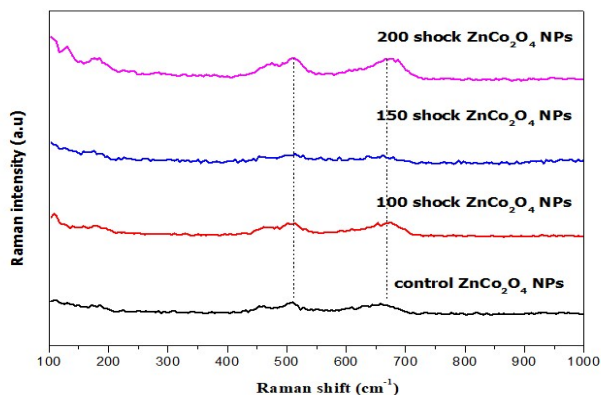
Experimental condition	magnetization(×10 ⁻³ emu)	coercivity (Oe)	retentivity (×10 ⁻⁶ emu)
Control Znco ₂ O ₄ NPs	-3.94481	0.00274	-
100 shocks Znco ₂ O ₄ NPs	0.002939	-7.09765	0.0029
150 shocks Znco ₂ O ₄ NPs	0.002566	1.42287	- 0.0119 0
200 shocks Znco ₂ O ₄ NPs	0.00274	6.81475	- 0.0253 0



3.4 Raman spectrum

The Raman spectroscopy was used to analyze the vibration modes, defect and the crystallographic phases as well as phase purity. The below figure, shows the Raman spectrum of control ZnCo_2O_4 NPs, figure b,c,d, represent the Raman spectra of zinc cobaltite after the shock loaded experiment of 100,150, and 200 shocks respectively. The spectra has three Raman bands located at 476, 516, 682 cm^{-1} and they correspond to E_g , F_2g and A_{1g} modes. Based on the Raman vibration modes, the test sample belongs to the cubic structure.

The bond between co-O vibration contributes to A_{1g} Raman mode. The F_2g mode is due to the Zn-o stretching in ZnCo_2O_4 . E_g Raman modes is mainly due to the oxygen vibration, A_{1g} and E_g are active Raman bands. From the Raman spectroscopy of ZnCo_2O_4 , Zn-O and Co-O vibration only obtained hence the prepared sample was pure and it is noted that for 100 shocks the intensity of the peaks are increased. For 150 shocks there is widening of the peak again the intensity of the peaks are increased in the case of 200 shocks. These changes may be due to the surface defects and particle size effect which are caused by the effect of shock wave. On comparison with the control and shocked ZnCo_2O_4 , no major notable peak shift occurred in the Raman bands.



4 Conclusions

ZnCo_2O_4 nanoparticles were successfully prepared by hydrothermal method. The synthesized Zinc cobaltite nanoparticles were subjected to different shock wave conditions (100, 150 and 200 shocks). Its structural changes and the properties were analyzed by X-ray diffractational study. The SEM studies show that the ZnCo_2O_4 are dense sphere-like particles. The change of phase occurred in Zinc cobaltite nanoparticles under different shock wave conditions. Further, ZnCo_2O_4 NPs were characterized by means of UV analyses, which shows that the synthesized nanoparticles are pure and changes in bandgap under shocked condition. From VSM analysis the effect of shock waves can be seen in magnetization after 100 shock pulse. From the Raman spectroscopy of ZnCo_2O_4 , Zn-O and Co- vibration obtained hence the prepared sample was pure.

Acknowledgements

This work was partially supported by Management of 'Sacred Heart College (Autonomous), Tirupattur Tirupattur District, Tamil Nadu India, through Don Bosco Research Grant.

REFERENCES

- [1] J. Cherusseri, K.K. Kar, Hierarchically mesoporous carbon nanopetal based electrodes for flexible supercapacitor with super long cyclic stability, *J. Mater. Chem. A* 3(43)(2015) 21586-215998.
- [2] Gueddouh, A.: Magnetic moment collapse induced by high-pressure in semiborides *Phys.* 56, 944-957 (2018)
- [3] Gueddouh, A.: The effects of magnetic moment collapse under high pressure, on physical properties in mono-borides *Trans.* 338, 1-17 (2017)
- [4] Bandaru, N., Kumar, R.S., Sneed, D., Tschauer, O., Baker, J., Antonio, D., Luo, S.-N., Hartmann, T., Zhao, Y., Venkat, R.: Effect of Pressure and Temperature on Structural Stability of MoS_2 . *J. Phys. Chem. C* 118, 3230-3235 (2014).
- [5] . Devika, M., Reddy, N.K., Jayaram, V., Reddy, K.P.J.: Sustainability of aligned ZnO nanorods under dynamic shock-waves. *Adv. Mater. Lett.* 8, 398-403 (2017)
- [6] . Kalaiarasi, S., Sivakumar, A., Martin Britto Dhas, S.A., Jose, M.: shock wave induced anatase to rutile TiO_2 phase transition using pressure driven shock tube. *Mater. Lett.* 219, 72-75 (2018)

- [7] H. Liu, J.Wang, One-pot synthesis of ZnCo_2O_4 nanorod anodes for high power Lithium ions batteries *Electrochim Acta* 92 (2013) 371-375.
- [8] Haq, S.: Fabrication and characterization of AgO , SnO_2 and TiO_2 nanoparticles for multiple applications. *Mansehra*. 1, 1–130 (2017).
- [9] Sivakumar, A., Victor, C., Nayak, M.M., Dhas, S.A.M.B.: Structural, optical, and morphological stability of ZnO nano rods under shock wave loading conditions. *Mater. Res. Express* 6, 045031(2019).
- [10] Sivakumar, A., Suresh, S., AntoPredeep, J., Balachandar, S., Martin Britto Dhas, S.A.: Effect of shock waves on dielectric properties of KDP crystal. *J. Eletron. Mater.* 47, 4831–4839 (2018)
- [11] Rita, A., Sivakumar, A., Jose, M., Dhas, S.A.M.B.: Shock wave recovery studies on structural and magnetic properties of $\alpha\text{-Fe}_2\text{O}_3$ NPs. *Mater. Res. Exp.* 6, 095035 (2019).
- [12] Rita, A., Sivakumar, A., Dhas, S.A.M.B.: Investigation of structural and magnetic phase behaviour of nickel oxide nanoparticles under shock wave recovery experiment. *J. Superconduct. Novel Magnet.* 1, 3–8 (2020).
- [13] Sivakumar, A., Soundarya, S., Jude Dhas, S.S., Bharathi, K.K., Dhas, S.A.M.B.: Shock wave driven solid state phase transformation of Co_3O_4 to CoO nanoparticles. *J. Phys. Chem. C* 124, 10755–10763 (2020)