Structural, morphological and optical properties of Ce doped CuO nanoparticles prepared by co-precipitation method

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Abstract: The Cerium (Ce) doped Cupper oxide (CuO) nanoparticles (NPs) prepared by co-precipitation method. The XRD patterns showed that the synthesized CuO NPs exhibits monoclinic structure. The FESEM image showed that, the synthesized Ce doped CuO NPs were formed nanoflake like structure. The Chemical compositions were identified by EDAX spectra. The Cu-O stretching vibrations were observed by FT-IR spectra located at 531 cm^{-1} for Ce doped CuO NPs respectively. UV-Vis absorption spectra, the absorption edge peak observed at 231 nm for Ce doped CuO NPs samples. The PL spectral measurements revealed that the broad emission bands observed, due to cupper interstitials (Cu_i) and oxygen vacancies (V_O).

Keywords: CuO; Ce; XRD; UV; FTIR; PL;

1 Introduction

In general there are number of metal oxides are available in nature but some of the metal oxides are most useful in accordance with their applications in day to day life in science and technology. In the periodic table transition metals are large in number and have number of applications in different fields. Among the oxides of transition metals, CuO nanoparticles are of special interest because of their efficiency as nanofluid in heat transfer application. For example it has been reported that addition of CuO improves the thermal conductivity of water.

The Nanoparticles research is gaining increasing interest due to their unique properties, such as increased electrical conductivity, toughness and ductility, increased hardness and strength of metals and alloys, luminescent efficiency of semiconductors, formability of ceramics. Some transition metal oxides like ZnO, TiO2, Fe3O4, etc. proved as potential candidates for so many applications. In the same way CuO is also one of the useful metal oxides and which has so many applications in various fields.

The uniqueness of CuO nanoparticles is even though, they are metallic in bulk but they behave like semiconductors when they are in nanosize. Semiconducting materials have been particularly interesting because of their great practical importance in electronic and optoelectronic devices, such as electrochemical cell, gas sensors, magnetic storage devices, field emitters, high-tc super conductors, nanofluid and catalysts, etc. Due to the potentiality of CuO, it acts as a catalyst, whereas all metal oxides are not useful for the catalytic activity. In the fabrication of super capacitors also CuO is very useful and in nanorange it has the wide band gap nearly equal to ZnO. The favourable band gap of CuO around 2.6 eV makes it useful for solar energy conversion and it can be used as solar cell window material. The CuO nanoparticles act as a good catalyst in some of the chemical reactions [1, 2].

In the present investigation, Cerium (Ce) doped Copper oxide (CuO) nanoparticles (NPs) prepared by co-precipitation method. The synthesized Ce doped CuO NPs were characterized by X-ray diffraction studies (XRD), Field Emission Scanning Electron microscope (FESEM), Energy dispersive X-ray spectroscopy (EDAX), Fourier Transform infrared spectroscopy (FE-IR), UV-Vis spectroscopy (UV - Vis), and Photoluminescence spectroscopy (PL) studies carried out.

2 Materials and Method

2.1 Synthesis

Copper (II) nitrate hexahydrate (AR), Cerium (III) hexahydrate and NaOH (AR) were used as precursor materials for the synthesis of Ce doped CuO NPs.

The synthesis of 0.001M of cerium (III) nitrate hexahydrate (AR) was mixed with 0.099M of copper (II) nitrate hexahydrate (AR) solution. 0.8 M amount of NaOH solution was under constant magnetic stirring for 30 min under room temperature followed by heating process for 5 hours at 80 ˚C and obtain the homogenous solution to form black precipitate. The resulting solution is reflexed at room temperature for a day. So obtained residual was washed several times with deionized water and ethanol. The resulted black precipitate was dried at 120 ˚C for 1 hour. The obtained Ce doped CuO samples in powder form were annealed at 700 ˚C in air for 5 hours and used for further studies.

2.2 Characterization techniques

The Ce doped CuO NPs were characterized by X-ray diffractometer (model: X'PERT PRO PANalytical). The diffraction patterns were recorded in the range of 20^o - 80^o for the Ce doped CuO samples where the monochromatic wavelength of 1.54 $\mathring{A}$ was used. The samples were analyzed by Field Emission Scanning Electron Microscopy (Carl Zeiss Ultra 55 FESEM) with EDAX (model: Inca). The FT-IR spectra were recorded using Perkin-Elmer spectrometer. The UV-Vis-NIR spectrum recorded in the wavelength range 200-1100 nm by using Lambda 35. The Photoluminescence spectra were measured using Cary Eclipse spectrometer.

3 Results and discussion

3.1 X-ray diffraction studies

The X-ray diffraction results of the synthesized Ce doped CuO nanoparticles are shown in Figure. 1. The characteristic diffraction peaks are obtained at angles of 28.16, 32.16, 32.1 35.15, 38.35, 47.08, 48.36, 53.13, 55.97, 57.88, 61.16, 65.39, 65.9, 67.71, 72.10, 74.75 and 76.47 corresponding to crystal plane (-110), (002), (111) (-202), (020), (202), (113), (-311), (-113), (311) and (004) respectively. The standard diffraction peaks could be indexed to a monoclinic Ce doped CuO phase (space group $C_{2/c}$) in accordance with the standard (JCPDS card no: 45-0937) [3-5]. Furthermore, the CuO NPs doped with Ce with ionic radii above 1 Å (1.034 Å for Ce^{3+}) have an additional and weak signal corresponding to the (111) diffraction plane of cubic CeO_2 could be observed at 2θ = 28.516 (JCPDS No 34-0394), thus indicating the partial oxidation of Ce^{3+} into Ce^{4+} during the synthesis and the formation of CeO_2.

The lattice constants 'a, b and c' of monoclinic structure can be calculated by using the relation

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

The calculated lattice constant a = 4.565 Å, b = 3.472 Å and c = 5.156 Å for synthesized Ce doped CuO nanoparticles are very closely related to the standard values a = 4.578 Å .b = 3.453 Å, c = 5.16 Å. The average crystallite size of the NPs was calculated after appropriate background corrections from X-ray line broadening of the diffraction peaks using Debye Scherrer's formula [3].

$$\text{Average crystallite size } D = \frac{0.9\,\lambda}{\beta \cos\theta}$$

where λ =1.54060 Å, β is the angular peak width at half maximum in radius and θ is Bragg's diffraction angle. The average crystalline size is estimated as 29 nm for Ce doped CuO NPs

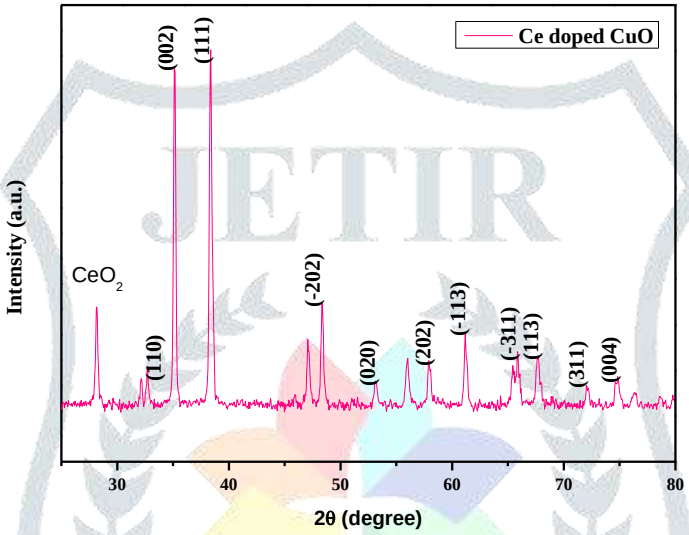

Figure 1 XRD pattern of Ce doped CuO NPs

3.2 FESEM analysis

The FESEM images of the as-synthesized Ce doped CuO nanoparticles are shown in Figure. 2(a-b). The synthesized Ce doped CuO NPs exhibits nanoflake like structure and average thickness is 60-90 nm.

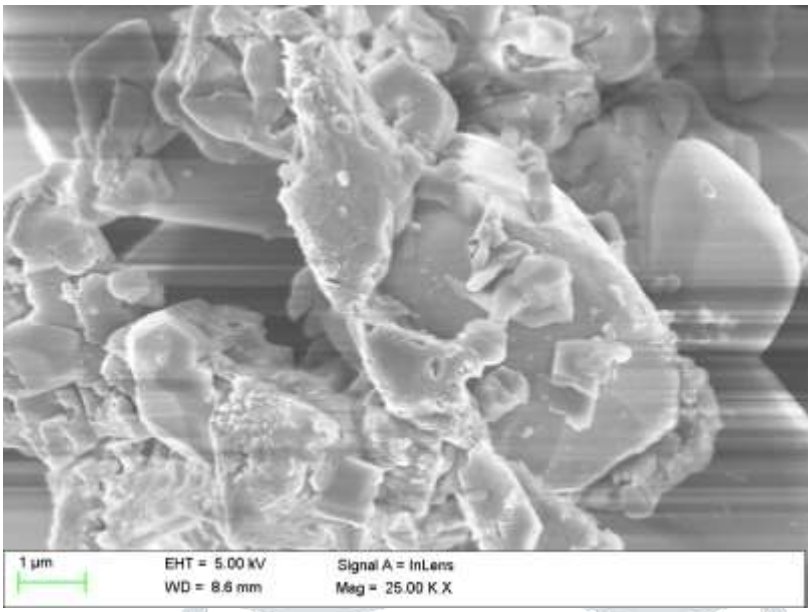

Figure 2a FESEM lower magnification image of Ce doped CuO NPs

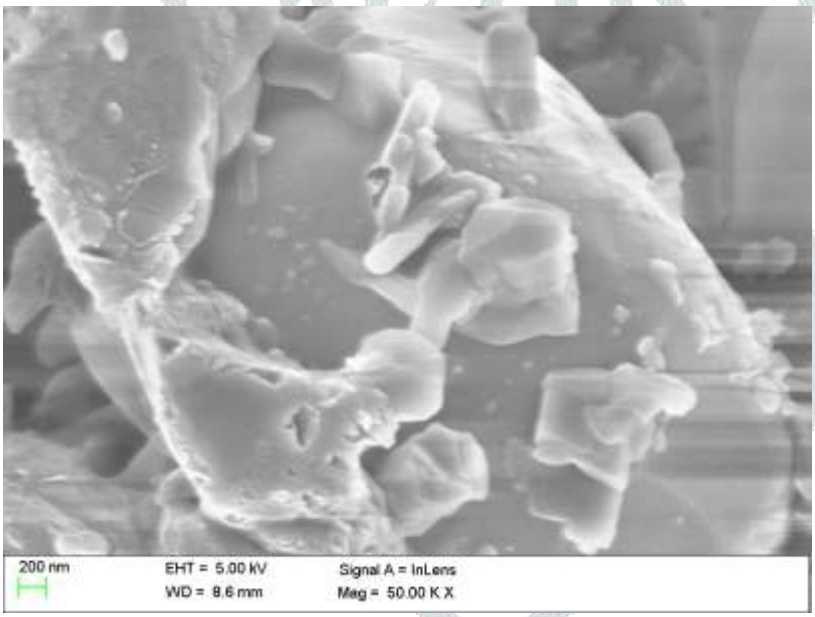

Figure 2b FESEM higher magnification image of Ce doped CuO NPs.

3.3 Energy Dispersive Analysis X-ray (EDAX) Studies

The Elemental composition analysis of the CuO NPs sample is confirmed using EDAX is shown in Figure.3**.** The elemental composition of O, Cu and Ce percentage are given in Table-1. From the Ce doped NiO atomic percentages are 52.43%, 45.53% and 2.04% respectively.

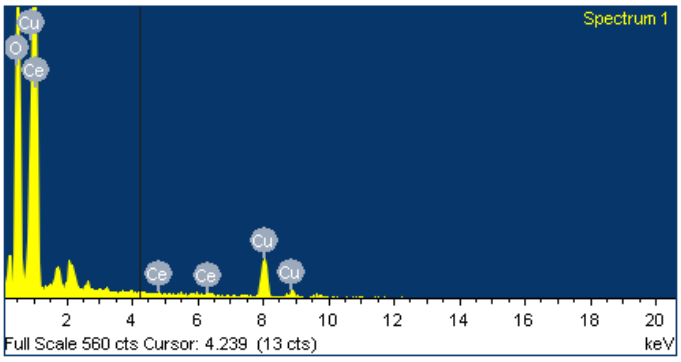

Figure 3 EDAX spectra of Ce doped CuO NPs

Table – 1 Chemical composition of Ce doped CuO NPs

Element	Atomic%
Oxygen	52.43
Cupper	45.53
Cerium	2.04
Total	100

3.4 FTIR spectroscopic studies

Figure 4 shows, FTIR spectra recorded in the range of 400-4000 cm^{-1} for Ce doped CuO NP samples. The peaks in the range of 3020-3650 cm^{-1} correspond to vibrational mode of –OH stretching [6]. The sharp band centered at 3401cm^{-1} for Ce doped CuO, which due to –OH stretching of surface absorbed water molecules. The week C-H symmetric stretching centered at 2820 cm^{-1} for Ce doped CuO NPs. The -OH bending vibration is observed at 1608 cm^{-1} for Ce doped CuO NPs. The absorption peaks in the range of 400-850 $cm^{-1}$are associated with Cu-O, O-Cu-O and Cu-O-Cu lattice vibrations [7]. However, the Cu-O stretching bands are observed at 531 cm^{-1} for Ce doped CuO NPs.

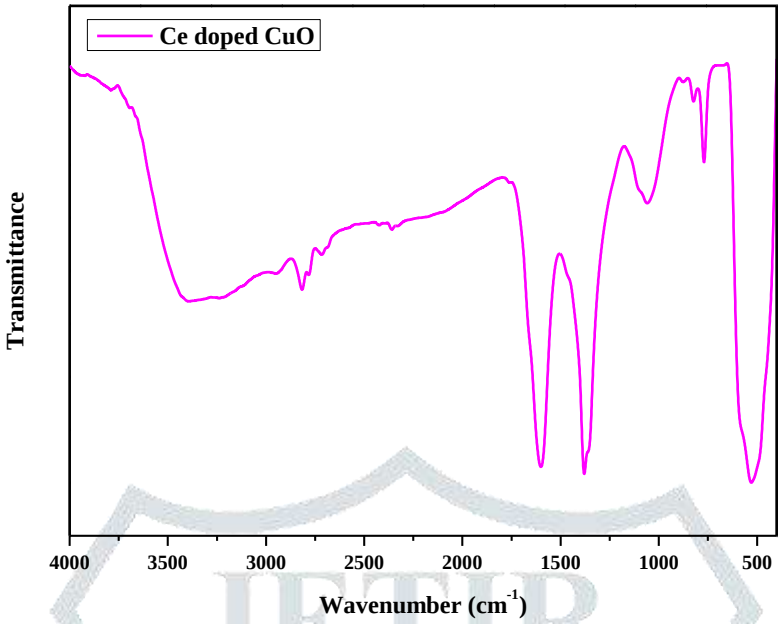

Figure 4 FTIR spectra of Ce doped CuO NPs

3.5 UV-Vis spectroscopic studies

Figure 5 shows, the UV-Vis absorbance spectral analysis of as-prepared Ce doped CuO NPs. The excitonic peaks are observed at 231 nm for Ce doped CuO NPs samples; this can be attributed to the photo excitation of electrons from the valence band to the conduction band.

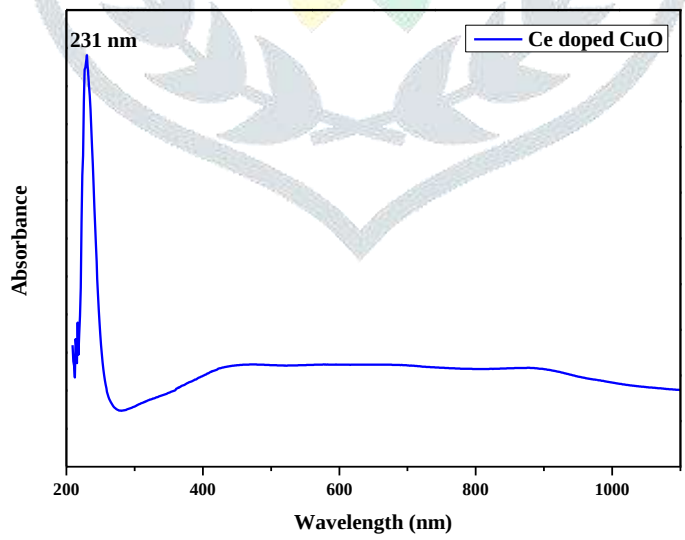

Figure 5 UV-Vis absorbance spectra of Ce doped CuO NPs

3.6 Photoluminescence spectroscopic studies

The photoluminescence spectra of the Ce doped CuO NPs recorded with the excited wavelength of 250 nm as shown in Figure. 6. The emission spectra of the Ce doped CuO NPs sample having six peaks at 302 nm, 338 nm, 375 nm, 400 nm, 440 nm and 453 nm . These bands are three Near Band Edge emission (NBE) and blue emissions respectively. The NBE emissions are 302 nm, 338 and 375 nm attributed to the recombination between electrons in the conduction band holes in the valence band [8]. The violet and blue emission are 400 nm, 440 nm and 453 nm attributed is due to the level emission such as oxygen vacancies and Cu interstitials.

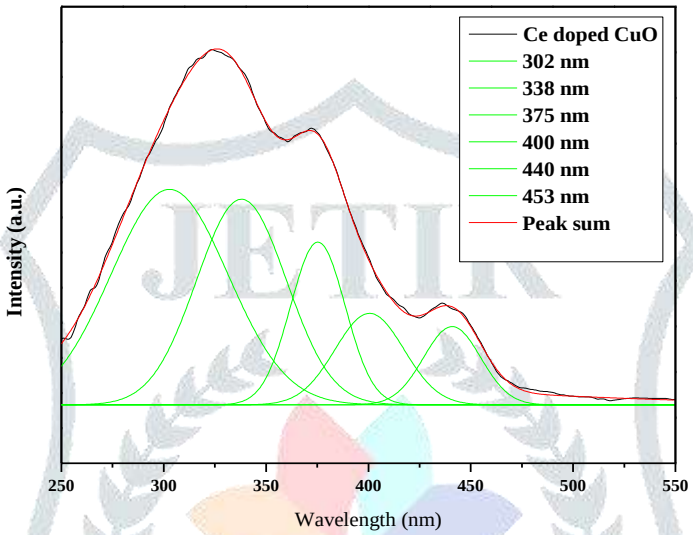

Figure 6 PL spectra of Ce doped CuO NPs

Conclusion

In summary, Ce doped CuO nanoparticles were prepared by co-participation method. The X-ray diffraction pattern synthesized Ce doped CuO NPs exhibits monoclinic structure. The average crystallite sizes are calculated at 29 nm for Ce doped CuO NPs. The FESEM images showed that the Ce doped CuO NPs formed nanoflake like structure. The elemental compositions were obtained from EDAX spectra. The metal characteristics peaks were identified by using FTIR. The UV-Visible absorption edge peak observed at 231 for Ce doped CuO NPs. In the PL spectra, UV and visible luminescence of Ce doped CuO, due to its defects or vacancies, which were generally located on the surface of the NPs.

Author Contributions:

Dr. CB carried out the preparation of the nanoparticles and executes the physical characterization studies and contributed to the main text of the manuscript. Mr. MAR checked the scientific information and flow of the text to maintain a better readability. Further this research work is not funded by any agency.

Compliance with ethical standards:

Conflict of interest: The authors declared that they have no conflict of interest.

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