Preparation of CuO$_{1-x}$-Mn$_x$ ($x=0.03, 0.05, 0.07$) and MATLAB modelling for sustainable energy harvesting applications

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Abstract. A different Mn$_x$(x=0.03, 0.05, 0.07) doped on CuO$_{1-x}$ has been successfully synthesised by a co-precipitation method by maintaining a pH-12. The nature of Mn doped CuO nanoparticles has been characterized with the help of X-Ray Diffraction (XRD). The Mn in the lattice sites of CuO gives the monoclinic crystal structure with C2/c space group which has been confirmed through JCPDS card no: 05-0661. The morphology variations with Mn doping have been examined with the help of field emission scanning electron microscope (FE-SEM) and Energy Dispersive X-Ray Spectroscopy (EDS). Additionally, band properties have also been noticed via Ultraviolet-Visible (UV) Spectroscopy. The band gap of material has been calculated as 2.39 eV, 1.96 eV and 2.25 eV for energy harvesting modelling through MATLAB with temperature difference behaviour of material. The thermodynamic modelling has been used for energy harvesting application with the help of MATLAB and the Seebeck coefficient has been calculated for thermoelectric modelling of CuO-Mn$_x$.

Keywords: MATLAB Simlink Programming; Thermoelectric Application; Band Gap Data of Material.

1. Introduction

Nanostructure metal oxides have novel properties that are different from the properties of metal oxides with bulk form because of the size difference in the particles. The reduction of size of the particle deals with the quantum size effect [1]. The band gap energy of particles is very much useful for many modelling techniques with the help of thermo-quantum effects. The material like CuO has a great attractive nature in recent years due to its thermal, electronic conductivity and opto-electronic behaviour in solar panels, compressors, thermalsensors, waste heat recovery and so on [1]. The several techniques such as sol-gel method, hydrothermal method, microwave method and electro-chemical method have been reported for synthesis of CuO nanostructure material. However, the doped materials on copper oxide are more attracted in the recent years. The simplest way to dope the material with metal oxides is led by Co-precipitation technique [2]. The co-precipitation method reduces the
synthesis time and provides small particles and quantum size distribution with high purity, which are considered as advantages of this method. A modelling is a more precious work for good applications; in that way Alberto Ferrari et al. [4] recently developed a new numerical model using MATLAB for temperature dependent iteration to analyse seebeck coefficient, electric resistivity and thermal conductivity for thermoelectric application. Similarly, Abouali Shamshiriet al. [3] generated (Finite element modelling) FEM codes for seebeck coefficient and internal electric resistivity measurement by using MATLAB software. Here, MATLAB R2013a software is used to connect band gap from experimental data and some numerical algorithms are used for thermoelectric modelling. Finally, in this paper authors use co-precipitation method to synthesis CuO$_{1-x}$Mn$_x$ nanostructures and those properties are analysed with the help of X-ray diffraction, UV, PL and FE-SEM. The calculated band gap is very much useful for modelling the same material for thermoelectric applications. The various results show the thermal behaviour that may be considered for sustainable energy harvesting applications.

2. Experiment – Method and Materials

2.1. Materials

The materials used for synthesis nanostructure of CuO$_{1-x}$Mn$_x$ are Copper(II)acetate monohydrate(Cu(CH$_3$COO)$_2$.H$_2$O), Manganese(II)acetate tetrahydrate (Mn(CH$_3$COO)$_2$.4H$_2$O), CTAB and sodium hydroxide from MERCK Pvt ltd.

2.2. Method

The CuO$_{1-x}$-Mn$_x$ was prepared by co-precipitation method with the precursors of copper acetate and manganese acetate in doped range (x= 0.03, 0.05, 0.07). In the synthesis process 0.035 M of copper acetate was poured into 200ml of water in a beaker and it was stirred well. After a few minutes, a combination of sodium hydroxide and CTAB are added in the ratio of 2:1 to reduce copper acetate into copper hydroxide. A blue precipitation was noticed during this process along with pH range 13-14. Then, the manganese acetate was added in the doped range of x and the process of stirring was continued with 600 rpm. In order to get finer particles, it is preferred 600-800rpm. After an hour, the beaker and compounds were maintained at 68°C with pH- 12 while stirring was on. Then, the hydroxide compounds were partially decomposed and then blue precipitation changed into brownish black precipitation. Then, the nanostructure particles were washed well with double distillation water and dried at 110°C for a day. Finally, expected product was obtained and the product was examined with the help of tools like XRD, UV, PL and FE-SEM etc.

3. Results and Discussion

3.1. XRD Analysis

Figure 1 shows the XRD pattern of pure CuO and Mn$_x$ doped CuO with x= 0.03, 0.05, 0.07. The diffracted peaks examined confirm the monoclinic crystal structure with C2/c space group. All the peaks at 2θ= 31.67°, 35.45°, 38.54°, 45.35°, 53.40°, 61.41°, 66.22°, 67.70° and 75.12° are almost matched with JCPDS card no. 05-0661 and corresponding (-110), (002), (111), (-112), (-202), (020), (202), (-113), (-310), (220), and (-222) planes are also matched with JCPDS. Further, a small metallic
natured Mn peak at 30.12° is observed while at (x=0.07) and intensity of the peaks get minor amount of decrease in x=0.03 due to some distortion and increase at x= 0.05 & 0.07 due to crystalline nature. This nature is also noticed on the crystalline grain boundaries in the Figure 2 and the crystalline size are found using Debye scherrer formula is shown in Table 1. The crystalline boundaries variation may increase the band gap energy at x= 0.03 and 0.07 and decrease at x=0.05, which are due to rearranging grain boundaries shown in the FESEM.

**Table 1. Crystalline Size and d value for x=0.03, 0.05, 0.07**

| Dope range (x) | Major Peaks position2θ (deg) | Interplanar distance d (nm) | Average Crystalline Size (nm) |
|----------------|------------------------------|-----------------------------|-----------------------------|
| Pure CuO       | 35.45°, 38.54°               | 2.33174, 2.53224            | 18.65                       |
| 0.03           | 35.47°, 38.56°               | 2.31995, 2.52076            | 19.40                       |
| 0.05           | 35.49°, 38.58°               | 2.31866, 2.52301            | 17.80                       |
| 0.07           | 35.50°, 38.59°               | 2.31658, 2.52363            | 16.75                       |

![Figure 1. XRD pattern of pure CuO and Mn, doped](image)
3.2. **FE-SEM Analysis**

The morphology of surface and elemental composition of prepared samples are shown in the Figure 2 (a, b, c, d). The cluster formation of nanostructured (CuO$_{1-x}$-Mn$_x$) morphology is observed in Figure 2a and the uniform aggregation is also observed on x=0.07 (Figure 2c); it can be compared with XRD peaks representing the highly crystalline nature, which is occurred because of doping Mn$_x$ in CuO$_{1-x}$. For x=0.05, Figure 2b shows the self assembled roasted pattern due to Mn$_x$. The cluster combination of Mn$_x$ dope leads some minor defects with CuO$_{1-x}$ due to interfacial tension for x = 0.03 which is seen from Figure 2a. The topological feature of above surface of the prepared sample CuO$_{1-x}$-Mn$_x$ is observed through EDS spectrum and is shown in Figure 2d. The elements presented in the prepared sample are indicated as copper, manganese and oxygen. Therefore, EDS spectrum helps to know better about the prepared nanostructures by the indication of elements; and they are free from foreign impurities.

![Figure 2. Surface Morphology of a) x= 0.03, b) x=0.05, c) x=0.07, d) EDS Spectrum](image)

3.3. **UV Analysis**

The optical absorption for the prepared nanostructured particles CuO$_{1-x}$Mn$_x$ is analysed with the help of ultraviolet spectroscopy. The absorption range of CuO as 245 -265 nm is shown in Figure 3a. Similarly, the doped Mn$_x$ is mixed well with CuO$_{1-x}$ as examined in XRD and it is also seen by the slight change in UV. Therefore, the Mn$_x$ absorption range is around 415-434 nm. The band gap of the
material is found as 2.39 eV, 1.96 eV and 2.25 eV for x=0.03, x=0.05, and x=0.07, respectively, which are shown in Figures 3b, 3c, and 3d.

Figure 3. a) UV absorption, Band Gap for b) x=0.03, c) x=0.05, d) x=0.07

4. Thermoelectric Modelling

The new approach of Non-linear equilibrium thermodynamic numeric model has been formed with the help of MATLAB algorithm, the material behaviour and properties are compared with many literature reports [5-10] and the band gap is included with thermal positive affinity numeric algorithm for seebeck effect (electric conduction from temperature coefficients), expressed in micro volt per Kelvin ($\mu V/K$) [11, 12]. The positive reaction affinity for sustainable energy harvesting application is

$$A = -RT \mu (\ln Q - \ln Q_0)$$  \hspace{1cm} (1)

where,

R= Atmosphere constant  
T= Temperature expressed in Kelvin  
$\mu$ = Band gap (eV)  
$\ln Q$ = logarithm of observed activity  
$\ln Q_0$ = logarithm of thermal equilibrium states.
The Number $N^+$ indicates the positive reaction affinity for each element (particle).

$$N^+ = \frac{V(1 + 2\mu)}{\alpha(Q_y - Q_x)}$$ (2)

The Seebeck ($\alpha$) is performed for the metal significant difference $Q_p = (Q_y - Q_x)$. Then, the charge transportation $q$ is rewritten with $\alpha$ for band gap energy inclusion.

$$\alpha = \frac{k}{q} \left( \left| Q_p - \mu \right| \right)$$ (3)

In accordance with Mass law of thermal equilibrium, for the equation (1), $Q_0$ for algorithmic modelling is

$$Q_0 = \frac{N_{Cu} N_{Mn} N_o}{N_{Cu} + N_{Mn}^+} \times T$$ (4)

Here, Cu, Mn, O have material properties to positive reaction affinity for energy harvesting application. This work is done with MATLAB R2013a Software in literature reports [5, 7, 8, 12] and modified algorithms. The Seebeck coefficient has been calculated with the help of reported literature numerical model algorithms [3, 4, 12] and the modelling structure of material with respect to temperature (K) is shown in Figure 4.

![Figure 4. Numerical modelling Structure by using algorithms](image-url)
4.1. Seebeck Analysis

The amount of voltage gain with respect to the temperature difference is said to be seebeck. The seebeck coefficient of the material is slightly varied with x=0.03, x=0.05 and x=0.07, as it is shown in Figure 5, the temperature withstand of the material is 530 K for x=0.03 and the required coefficient varies with temperature (530K, 450μV/K). Similarly, for x=0.05 the coefficient varies at two points (510K, 452μV/K), (580K, 490μV/K) and for x=0.07, the coefficient varies at four points (470K, 451μV/K), (520K, 453μV/K), (630K, 540μV/K), (710K, 515μV/K). Here, the increase and decrease of the peak points are due to the material band gap and morphology variations on the prepared material. The uniform morphology with good band gap at x=0.07 gains seebeck at four varied points. Hence, it is a very good material for energy harvesting than other x.

Figure 5. Sustainable energy harvesting seebeck for thermoelectric applications
5. Conclusion

The CuO$_{1-x}$Mn$_x$(x = 0.03, x=0.05 and x=0.07) was successfully prepared by co-precipitation method. The XRD, FE-SEM/ EDS and UV are analyzed with the help of characterization tools. The newly approached algorithms from literature report help to carry out successful modelling. The XRD analysis confirms that CuO$_{1-x}$Mn$_x$(x = 0.03, x=0.05 and x=0.07) have good crystalline nature with average crystalline size of 16-20nm. The EDS spectrum shows that there is no impurity on the material preparation. The morphology difference from FE-SEM and band gap from UV helps to identify the prepared material as a material that is good for sustainable energy harvesting application and is also used at modelling for thermoelectric device by using MATLAB software. The successful simulations undergo for sustainable energy harvesting application with results of seebeck coefficient. From the results, authors suggest x=0.05 and x = 0.07 as good materials for device fabrication than x=0.03.

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