EFFECT OF LOW SINTERING TEMPERATURE TOWARDS PHASE TRANSITION AND OPTICAL PROPERTIES OF DELAFOSSITE $CUBO_2$

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ABSTRACT: *Delafossite $CuBO_2$ powder was prepared by solid state reaction for phase transition and sintered at low temperature range of 100-400 ^oC. It was observed that proper and pure phase formation occurs at 400 ^oC. Crystal structure of prepared phase and optical properties were characterized by X-ray diffraction and UV-VIS-NIR spectroscopy. Proper phase was confirmed by previously published reports on this material. XRD particle size was increased upto 300 ^oC but decreased at 400 ^oC as pure phase was obtained at this temperature. UV-VIS-NIR spectroscopy showed that absorption was increased continuously upto 400 ^oC sintering temperature. Bandgap was increased with increase in the sintering temperature. Maximum bandgap of 3.12 eV was achieved in current work which confirmed material's transparency in the visible region of electromagnetic spectrum. As $CuBO_2$ delafossite is a transparent conducting oxide with a wide bandgap and may have potential applications as transparent electrodes and in other opto-electronic devices.*

Key words: Phase transition, Delafossite $CuBO_2$, Solid state reaction method, optical properties, and direct bandgap.

1. INTRODUCTION

In present time, transparent conductor is a flourishing research field of nanotechnology as they have surprizing electrical as well as optical properties. Various n-type TCOs such as ZnO, TiO_2 and In_2O_3 are used in daily life applications due to their high electrical conductivity. p-type TCOs are less in number as compared to the n-type TCOs. At room temperature, p-type TCOs either show high resistance or exhibit less optical bandgap energy. Junctions based electronic devices that are optically transparent such as diodes and transistors demand p-type TCOs with high electrical conductivity and tuneable bandgap [1-4].

Copper based delafossite materials have resolved this problem as these materials have high p-type conductivity and tune-able optical band-gap. Mg doped $CuCrO_2$ is recently reported material with greatest electrical conductivity of 220 S/cm. Snure et al. [1, 5] discovered $CuBO_2$ which is latest p-type TCO having maximum room temperature electrical conductivity among all delafossites without doping

The fabrication and accurate phase development of Cu based delafossite is a problematic task as these materials are multicomponent. Synthesis mechanism reported for $CuBO_2$ like PLD which is very expensive and needs tough experimental arrangement while Sol-gel contains complex chemical steps [5-7]. Herein, $CuBO_2$ is prepared by an easy and simple mechanism of solid state reaction. Effect of low sintering temperature on the structural and optical properties of this novel $CuBO_2$ material have been studied in this report.

2. MATERIALS AND METHODS

Four samples of $CuBO_2$ in powder form was synthesised by taking accurate amounts of H_3BO_3 and $CuCO_3$ precursor powders. These precursor powders were uniformly mixed and grinded for 1 hour. The finely grinded powder for four samples was calcined at 200 ^oC for 2 hours. After re-grinding, this powder was separated into four samples. These samples were sintered at 100 ^oC, 200 ^oC, 300 ^oC and 400 ^oC for 4 hours, cooled in furnace and again grinded the resultant powders.

Powder XRD having Cu Kα radiation with wavelength (λ) of 1.5406 Å was used to analyse these four prepared samples in 2θ range of 20^o – 80^o with step variation of 0.02^o. Optical absorption spectra were taken for $CuBO_2$ powder samples at room temperature using a UV-VIS-NIR spectrophotometer between wavelength range of 300 – 900 nm.

3. RESULTS AND DISCUSSION

3.1 XRD Results

The XRD patterns of all prepared samples at different sintering temperatures are shown in Figure 1. The existence of different peaks in the samples (sintered upto 300 $^\circ$C) such as CuO, B_2O_3 and some minor peaks of actual phase $CuBO_2$ in the XRD patterns specifies that these are polycrystalline structures while the sample sintered at 400 $^\circ$C contains peaks of pure phase $CuBO_2$ only. It can be observed from XRD pattern of sample sintered at 100 $^\circ$C that no peak corresponding to $CuBO_2$ phase exists while only two peaks of B_2O_3 (denoted by ^) are present. At this quite low temperature, reaction does not occur between precursors but H_3BO_3 is converted to B_2O_3 with the evaporation of water. At 200 $^\circ$C sintering temperature, again no peak of $CuBO_2$ phase is found but one peak of CuO (denoted by *****) is appeared as $CuCO_3$ is converted into CuO with the evolution of CO_2 gas. The presence of these peaks show that reaction does not occur upto 200 $^\circ$C sintering temperature. In the next sample sintered at 300 $^\circ$C, some peaks of $CuBO_2$ phase are appeared but with lesser intensity which show that reaction initiated but not occurred completely. The further increase in sintering temperature at 400 $^\circ$C shows the sharp intensity peaks [(100), ((012), (106), (100), (110)] indicating complete formation of proper $CuBO_2$ phase. This sample shows the proper phase formation and good crystalline nature of $CuBO_2$. Peaks of $CuBO_2$ are well matched with previous reports [8]. As reaction is completed between precursors so there is no any characteristic peak of impurities or secondary phase of precursor compounds observed. Thus XRD patterns has confirmed the proper phase of $CuBO_2$ at low temperature.

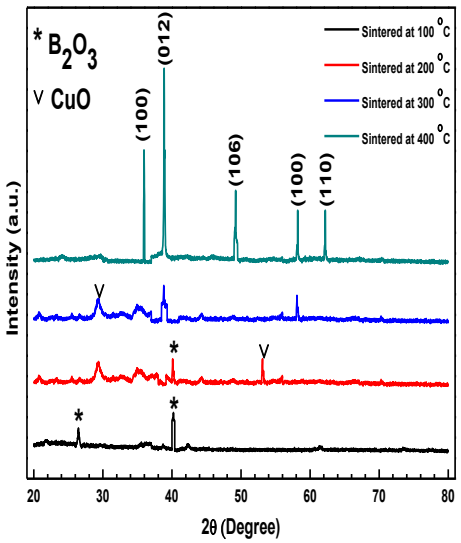

Figure 1. The XRD patterns of the all samples sintered at different temperatures.

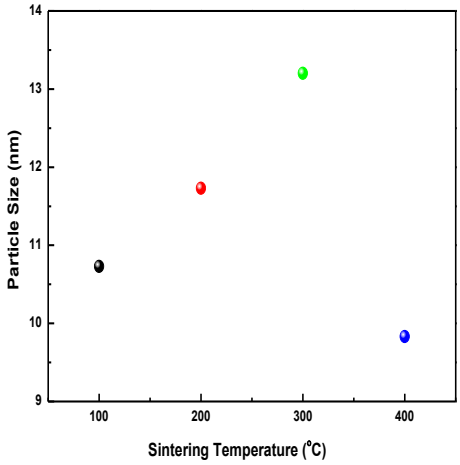

Figure 2. XRD particle size as a function of sintering temperature.

Figure 2 shows the average particle size **(<D>)** found from following Debye Scherer's formula [9], as a function of sintering temperature

$$D = 0.9\lambda/\beta \cos\theta \quad (1)$$

Where λ being X-ray photon wavelength, β denotes the FWHM (full width at half maximum) and θ is angle of diffraction. It is clear from Figure 2 that particle size has been increasing with increase in sintering temperature upto 300 °C. It is believed that particle size increases by increasing sintering temperature. Although particle size is decreasing at 400 °C sintering temperature. The reason behind this decrease in particle size is the formation of pure phase $CuBO_2$.

3.2 Optical Properties

The absorption spectrum of all four prepared samples recorded over the 300–900 nm range with a UV-VIS-NIR spectrometer is shown in Figure 3. The % absorbance is

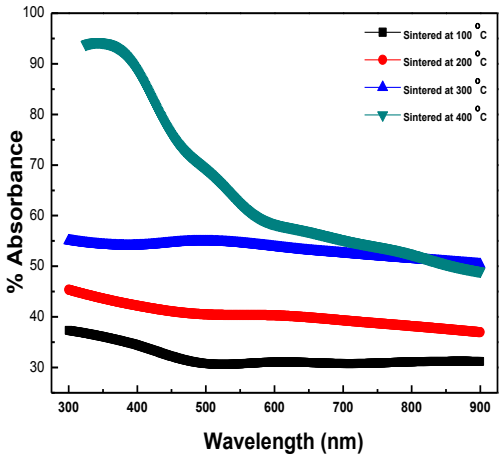

Figure 3. Absorption curves as a function of wavelength for al prepared samples.

increasing with the increase in sintering temperature. As the particle size influences the absorption so due to change in particle size, % absorption is also increased. From Figure 3, flat patterns clearly show that absorption is approximately same for samples sintered upto 300 °C sintering temperature but at 400 °C, there is variation in absorption curve. This sample only contains $CuBO_2$ pure phase so it exhibits high absorption value for wavelengths at 300 nm thus confirming its optical bandgap lying in ultraviolet region.

Over the wavelength range of 350–900 nm, absorption spectrum of $CuBO_2$ powder is continuously decreasing showing its maximum transparency in the visible region.

The absorption coefficient (α) have been calculated using the following relation

$$\alpha = 4\pi k/\lambda \quad (2)$$

Here, k denotes for the extinction co-efficient and λ being incoming photon wavelength.

The direct optical bandgap energy has been found using Tauc's formula [10] and as depicted in Figure 4.

$$(\alpha h\nu)^2 = A\,(h\nu - E_g) \quad (3)$$

Here, hν refers to energy of incoming photon while optical bandgap energy is denoted by E_g whereas A denotes for some arbitrary constant. Figure 5 shows the optical direct bandgap energy as a function of sintering temperature. Like absorption, optical bandgap energy also follows the same trend i.e. optical bandgap energy is increasing with the increase in sintering temperature. Bandgap is also highest (3.12 eV) like absorption for the sample sintered at 400 °C.

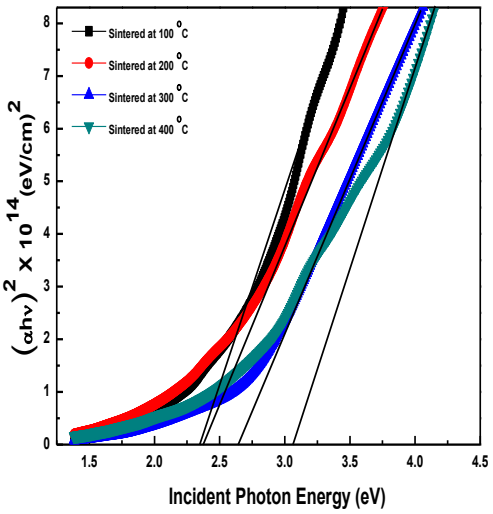

Figure 4. The optical direct bandgap energy of all prepared samples.

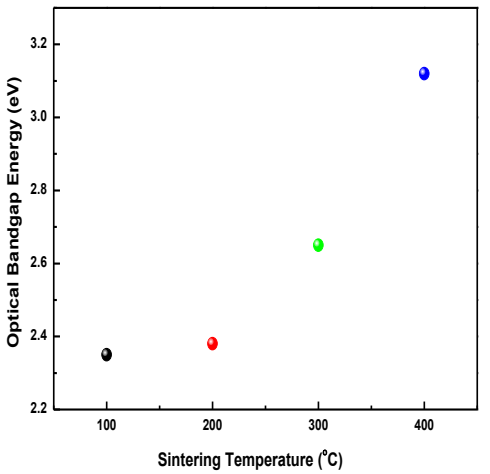

Figure 5. Optical direct bandgap energy as a function of sintering temperature.

Optical bandgap greater than 3.1 eV again confirming that this material is transparent to visible light.

Thus here is a good co-relation between XRD and UV-VIS-NIR spectroscopy results.

4. CONCLUSION

Four samples were prepared via solid state reaction method and effect of low sintering temperature was analysed on phase formation and optical properties of the product delafossite $CuBO_2$. Optical studies showed that bandgap of $CuBO_2$ increases slightly with increasing in particle size. The informal fabrication procedure of $CuBO_2$ described here discovers reasonable method for bulk preparation of this material at low temperature with tuneable optical properties and proper phase.

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