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Influence of temperature on physical properties of copper (I) iodide

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ABSTRACT

Copper (I) iodide (CuI) has been synthesized by wet chemical route at room temperature using freshly prepared copper oxide (CuO) as a precursor. The as-prepared CuI exists in γ - phase and it undergoes two structural phase transition between room temperature and its melting point. Differential scanning calorimetry measurement in both heating and cooling cycles confirms its structural reversible phase transitions from γ to β phase then from β to α phase. In order to understand the underlying physical properties before and after transitions induced by temperature was studied by X-ray diffraction, scanning electron microscopy, fluorescence, fourier transformed infrared spectroscopy and thermal analysis using TGA, DTA and DSC. Copyright © 2011 VBRI press.

Keywords: Transparent p-type semiconductors; phase transition.

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Introduction

Transparent conducting materials are very promising materials because they allow visible light to pass through but absorb ultraviolet radiation. The discovery of p-type transparent conductive materials such as $CuAlO_2$, $SrCu_2O_2$, and $CuInO_2$, and the first demonstration of a UV-light emitting diode using n-ZnO/p-$SrCu_2O_2$ heterojunction have opened a frontier in transparent electronics. Copper (I) iodide is a well-known water insoluble transparent p-type semiconductor material having direct band gap 3.1 eV. It has attracted with steadily growing interest because of its ultrafast scintillation property with a decay time of about 90 ps at room temperature [**1**] and its usage in dye sensitized solar cells as a solid transparent hole transporting electrolyte [**2**]. Recently, CuI is emerged also as an effective reusable catalyst for various organic transformations [**3**]. CuI exists in three polymorphs forms (α, β and γ) between room temperature to its melting point (T_m = 606 °C). The low temperature γ-phase which exists below 370 °C has a zinc blend type structure. The high temperature α-phase exists above 390 °C with cubic structure. An intermediate β-phase also exists between γ and α phases. CuI is well known to exhibit the superionic behaviour in the high temperature, where the mobile Cu ions migrate between the sites in the sub-lattice of immobile iodine ions [**4**]. The conductivity approaches 0.1 Ω^{-1} cm^{-1} in γ-phase is slightly higher in β-phase and in α-phase it reaches higher value 1 Ω^{-1} cm^{-1} but the γ-phase conductivity depends on the presence of iodine in stoichiometric excess. CuI has been prepared by numerous techniques such as reactive sputtering [**5**], pulsed laser deposition [**6**], laser assisted molecular beam deposition (LAMBD) [**7**], polymer assisted reaction [**8**], iodination of thin copper films [**9**] and wet chemical synthesis using CuO suspensions [**10**]. Recently, CuI@SWNT nanocomposites by filling of single-walled carbon nanotubes (SWNTs) having inner diameter 1–1.4 nm by CuI nanocrystals via capillary technique was also reported [**11**]. This method is based on the impregnation of pre-opened SWNTs by molten CuI in vacuum with subsequent slow cooling up to room temperature. When compared with other routes, wet chemical oxide route seems to be easier and cost effective because in this method CuI can be prepared at room temperature itself. Hence we employed this route for the synthesis and investigated its annealing temperature induced effects to understand the underlying changes in structural, thermal, optical and microstructural properties.

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Experimental

Synthesis

The precursor, CuO nanorods are freshly synthesized by co-precipitation method by neutralizing 0.1 mol/l concentration of aqueous $CuCl_2.2H_2O$ with sodium hydroxide solution. It led to the formation of copper hydroxide precipitate along with the by-product sodium chloride. This precipitate was aged for three hour then washed repeatedly with distilled water to remove the by-product. The precipitate was filtered, dried at room temperature and annealed at 100 °C for one hour to get the CuO. In the presence of hydroxylamine hydrochloride ($NH_2OH.HCl$), the oxygen of CuO suspension was replaced by adding aqueous potassium iodide (KI) solution in drop wise. Hydrochloric acid was added in drop wise for maintain the pH value at 5 throughout the reaction period. Then, the precipitate were washed and dried at room temperature overnight then annealed in between 150 to 550°C for 0.5 h using a muffle furnace under nitrogen gas flow to study its annealing temperature induced effects on various properties.

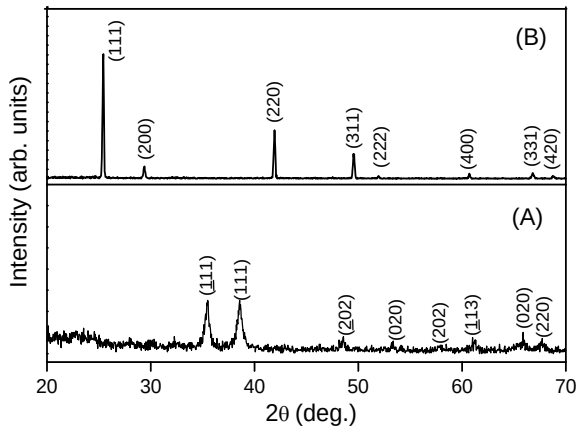

Fig. 1. XRD patterns of (A) precursor CuO (B) as-prepared γ-CuI.

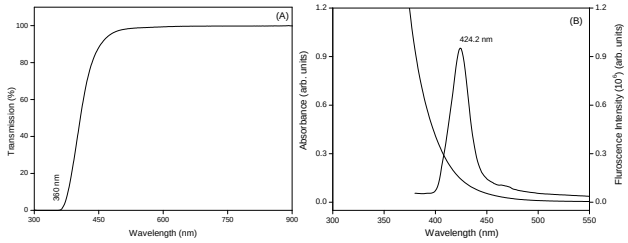

Fig. 2. (A) Optical transparent nature of as-prepared γ-CuI (B) UV absorbance and room temperature fluorescence emission behaviour of γ-CuI.

Characterization techniques

The structural studies were performed using X-ray diffraction (XRD) technique by Seifert diffractometer using Cu-$K_{\alpha 1}$ radiation (λ = 1.5406 Å). Optically transparent nature of the samples in the wavelength range 200 to 1200 nm was investigated using Shimadzu UV-vis spectrophotometer. Fourier transformed infrared spectroscopic analysis was done with Horiba FT-210 spectrometer using KBr. Phase transition were studied using DSC instrument in both heating and cooling with 10 ^oC rate. The Varian carry-5E fluorometer were used to record fluorescent behaviour at room temperature and Philips XL-40 scanning electron microscopy (SEM) was used for study its microstructural properties. Thermal stability of the CuI were studied for both annealed in nitrogen atmosphere at 300 and 450 ^oC for 0.5 h by simultaneously TGA and DTA was studied using NETZSCH-Gerätebau GMBH thermal analyzer instrument in nitrogen atmosphere with heating rate of 20 °C per min.

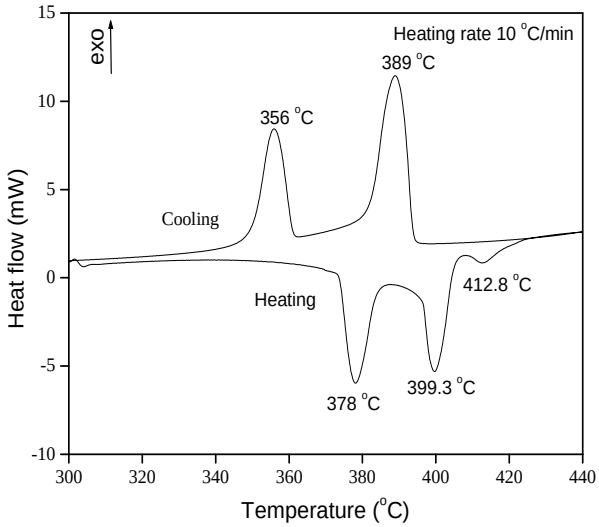

Fig. 3. Thermal behaviour of as-prepared γ-CuI by using Differential scanning calorimetry.

Results and discussion

XRD patterns of the precursor CuO nanorods and the as-prepared CuI are shown in **Fig. 1**. The diffraction patterns are compared with JCPDS files which confirms CuO is in monoclinic (80-1916) phase and CuI is in cubic (83-1137) phase. The average crystallite size of the precursor CuO is determined to be 14 nm from the full width at half maximum of the 100 % peak using Scherer formula [**12**]. The UV-Vis transmission spectrum of the CuI was shown in **Fig. 2 (A)**, for do this measurement 1.46 g of the CuI was dissolved in 50 ml of moisture free acetonitrile. High transmission in the visible region was founded with onset at 360 nm. This onset value agrees with the previously reported results [**13**]. UV absorbance and room temperature fluorescence emission behaviour of as-prepared γ-CuI reveals that this material is wide band gap with direct transition, the respective plots were shown in **Fig. 2(b)**. Temperature induced phase transition in this sample has been studied using differential scanning calorimetry and the spectrum is as shown in **Fig. 3**. Both heating and cooling curves are recorded in the temperature range 300 to 450 °C at the rate of 10 °C per minute under argon atmosphere. During heating three exothermic peaks were observed. One peak at 377.5 °C, which corresponds to γ to β phase transition, the second one at 399.3 °C represents β to α

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phase transition and the third peak at 412.8 °C is related to the crystallization of α-phase. On cooling with the same rate we observe hysteresis type reversible transitions. During the heating, iodine might have released from the samples giving non-stoichiometry and destroys the stability of the transformed phases which led reversible transition.

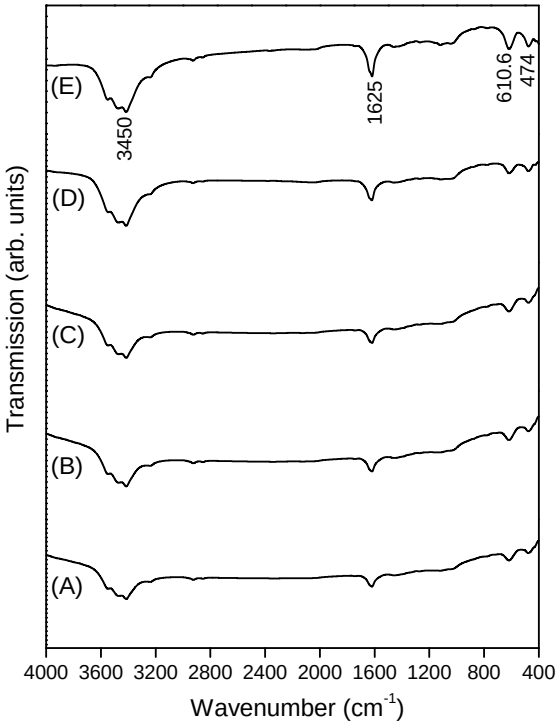

Fig. 4. Structural analysis of γ-CuI annealed at different temperatures for 0.5 h (A) as-prepared, (B) 150 °C, (C) 300 °C, (D) 450 °C and (E) 550 °C.

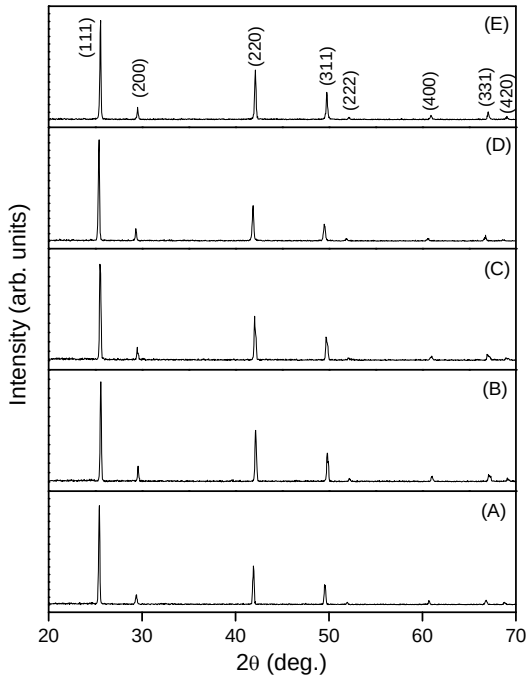

Fig. 5. FTIR spectra of γ-CuI annealed at different temperatures for 0.5 h (A) as-prepared, (B) 150 °C, (C) 300 °C, (D) 450 °C and (E) 550 °C.

Structural analyses of annealed samples are shown in **Fig. 4**. All the heat-treated samples are in γ-phase only. Prolonged heat treatment may release iodine from the sample leading to iodine non-stoichiometry. Such non-stoichiometry induced structural changes are not observed from XRD patterns even though the sample annealed at 550 °C for 0.5 h. FTIR transmission spectra for as-prepared and heat treated samples are shown in **Fig. 5**. For all the samples, a broad peak observed in between 3000 to 3500 cm^{-1} is due to O-H stretching vibration and the peak at 1624 cm^{-1} corresponds to CO adsorbed on the surface. The peaks at 610.6 and 474 cm^{-1} are the two characteristic peaks of CuI sample, both this peaks exists in all the samples. The peak at wave number 474 cm^{-1} is assigned to Cu-I stretching vibrations. The existence of those two peaks even after annealing at different temperatures reveals that the material remains in γ-phase alone. This observation is very consistent with XRD results and both the measurements reveals that this material is undergoing reversible phase transition.

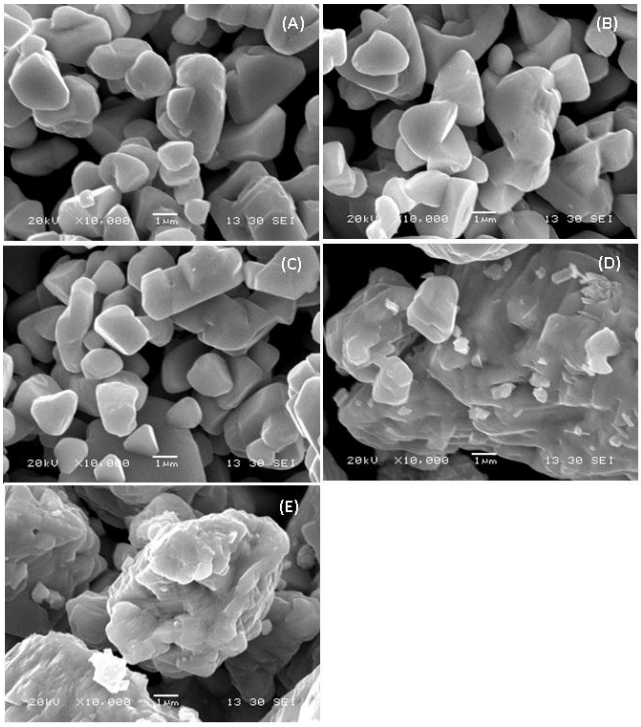

Fig. 6. Scanning electron microscopic images of γ- CuI samples for 0.5 h (A) as-prepared, (B) 150 °C, (C) 300 °C, (D) 450 °C and (E) 550 °C.

The scanning electron microscopic images of CuI samples are shown in **Fig. 6**. All the images confirm that the samples are crystalline in nature. Generally, in wet chemical synthesis process, the primary particles nucleated from solutions are known to grow by molecular addition or aggregation with small subunits. The types of solvents can also affect the particle growth after nucleation, because the particle interaction potential is different in each solvent. In this work during the synthesis, pH value 5 was maintained constantly by addition of hydrochloric acid. Because of acidic atmosphere, particles dimension and the morphology are not controllable. But change in morphology and dimension in 450 °C and 550 °C annealed samples are due

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to γ to β phase transition at 377.5 °C followed by β to α phase transition at 399.3 °C which led to iodine non-stoichiometry in the samples. Under cooling the iodine deficient CuI grains are agglomerates and lose its morphology.

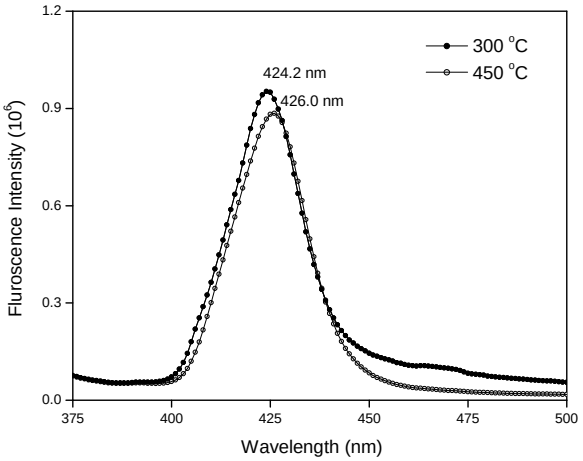

Fig. 7. Fluorescence behaviour of γ-CuI annealed at 300 °C and 450 °C for 0.5 h.

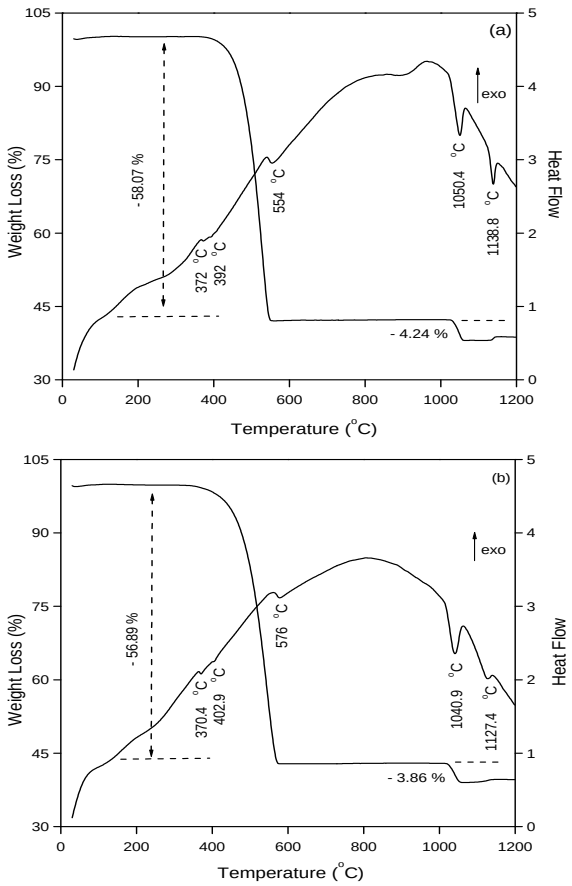

Fig. 8. Thermal analysis of γ-CuI annealed for 0.5 h at (a) 300 °C and (b) 450 °C.

Room temperature fluorescence emission behaviour of γ-CuI annealed at 300 and 450°C was shown in **Fig. 7**. As shown in the figure, 300°C annealed sample exhibits one characteristic emission peak at 424.2 nm while 450°C annealed sample exhibits a shifted emission peak at 426 nm. The emission energy difference 0.015 eV might be due to the creation of a trap below the conduction band. DSC measurement confirms, between 300 to 450°C this material is undergoing two reversible transition and during reversible transition the iodine stoichiometric variations happens which are not evident from structural and FTIR analysis and it induces defect creation which led a trap generation below the conduction band. To support the florescence results, we did the simultaneous TG-DTA measurement in the nitrogen atmosphere for the same 300 and 450 °C for 0.5 h annealed samples. The obtained TG-DTA plots were shown in **Fig. 8** (**a**) and (**b**). There are two zones of weight loss between 420 to 560 °C and 1020 to 1060 °C and a weight gain between 1120 to 1150 °C during annealing process in both the samples. The first zone weight loss due to the liberation of iodine from the sample, the 450 °C annealed sample showing 1.2 percent of weight loss higher than the 300 °C annealed after this zone both the samples are completely loss the iodine and transformed as copper. The second zone weight loss in TGA is happened because of copper melting. DTA also shows the iodine loss by an endothermic peak at 554 °C for 300 °C and 576 °C for 450 °C annealed. Also 'γ to β' and 'β to α' phase transitions by two endothermic peaks between 370 to 400 °C temperature.

Conclusion

Single phase of CuI has been synthesized successfully by wet chemical route at room temperature using freshly prepared copper oxide (CuO) as a precursor. DSC measurement in both heating and cooling cycles confirms the occurrence of structural reversible phase transitions from γ to β phase then from β to α phase in CuI sample. The release of iodine from the sample was observed from the TGA results was confirmed by fluorescence and TG-DTA measurements. This stoichiometric variation creates defects which led a trap formation and the red shift in room temperature fluorescence emission wavelength.

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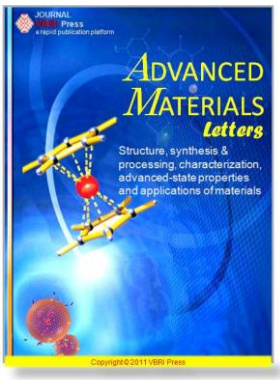

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