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Ambient synthesis and optoelectronic properties of copper iodide semiconductor nanoparticles

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ABSTRACT

Electrically conducting copper iodide (CuI) nanoparticles have been synthesized at room temperature via a simple single step chemical route, using ethyl alcohol as a solvent. The resulting material was characterized by X-ray diffraction, differential scanning calorimetry, optical absorption, photoluminescence, scanning electron microscopy, energy-dispersive X-ray spectroscopy and high resolution transmission electron microscopy to assess the quality of these semiconductor nanoparticles. Thin film was deposited on copper substrate that was used to investigate temperature dependent electrical conductivity. These investigations confirm that the material is semiconductor having a negative temperature coefficient of resistivity. Thermal analysis and X-ray diffraction studies reveal that it is of low temperature γ phase. Energy-dispersive X-ray spectroscopy measurements confirm the stoichiometry of as prepared material. The shift in optical absorption edge towards lower wavelength region ($E_g \sim 4.77$ eV) as compared to its bulk absorption indicates that a decrease in particle size has a significant effect. Photoluminescence peak observed at 2.90 eV is unique to its material property. These optoelectronic properties of CuI will be helpful in the development of future electronic devices.

1. Introduction

In the past few years, copper halides, especially copper iodide, have attracted immense interest due to their promising applications in high-frequency high power electronics and optoelectronic devices [1–5]. These compounds exhibit many unusual properties, such as large band gap, negative spin orbit splitting, large temperature dependency of resistivity, and analogous diamagnetic behavior [6]. Copper iodide (CuI) is a I–VII compound semiconductor which crystallizes into three different phases at atmospheric pressure; these are α, β, and γ phases [3]. The low temperature γ-phase (below 623 K) is a wide band gap semiconductor whose energy gap is close to $E_g \sim 3.1$ eV and exciton binding energy is reasonably high that is ~62 meV, hence it is potential candidate for optoelectronic applications [1]. The γ phase is also known as a potential ultrafast scintillation material with short decay time 90 picoseconds at room temperature [9].

Copper halides are also known as superionic conductors with zinc blende structure whose ionic conductivities are comparable to those of liquid electrolytes, reaching the values as close as 0.1–1 $(\Omega\,\mathrm{cm})^{-1}$ at elevated temperature [11]. The ionic, thermal and electronic conductivities of these compounds were investigated in detail by several authors [12–14]. From the chemical point of view, these compounds are at the borderline between purely ionic alkali–halides and III–V group covalent semiconductors. The zinc-blende crystalline structure, combined with the monovalent character of copper ions, is believed to favor the motion of cations in sublattices formed by anions. At all temperatures, the halogen anions are closely bound to their lattice sites and cations become increasingly mobile, accounting for the high ionic conductivity of superionic phases. Recent studies indicate that instead of liquid electrolytes, p-CuI as the hole conductor (solid electrolyte) has been used in dye-sensitized solid-state solar cells (DSSSCs) [15–20]. It is because of liquid electrolyte in DSSSC that leads to several technological problems such as dye decomposition under photochemical reaction, solvent evaporation, degradation and sealing imperfection [21–27]. Further, the most interesting nature of this compound is that, it is an inorganic semiconductor, its coordination chemistry lets it to readily couple with many organic ligands. Such materials open up the ways to new applications in optoelectronic devices once their quality is improved. Series of efforts have been made by many authors to grow high purity p-type CuI single crystal by hydrothermal and cycle-evaporation methods [1,9]. Number of other techniques such as sol–gel, sublimation and the flux are used to grow micro/nanosized CuI [1–3,6–8]. But synthesizing a high purity phase p-type CuI semiconductor with simple route is still highly desirable. Recently, Li and Wan have reported that etching of copper in a dilute solution of iodine leads to coating of copper iodide crystallites of different morphology on copper

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substrate [5]. The hydrophobicity of these surfaces can be controlled by changing the size of crystallites. In this paper, we present a facile room temperature chemical route for the preparation of high yield γ-phase CuI semiconductor nanoparticles which possess better crystallinity and hence it can be a potential material for optoelectronics.

2. Experimental procedure

All the chemicals such as iodine, ethyl alcohol and acetone were of AR grade and are supplied by s.d-fine chemicals. Copper plate used in the synthesis was of electrolytic grade (99.999%). All reactions were carried out under open air conditions. Prior to use, copper was well cleaned then rinsed immediately with triple distilled water before inserting in a chemical bath.

Iodine (I_2) solution of 1 M was prepared in 50 ml of ethyl alcohol in a conical flask with constant stirring until clear reddish brown solution is obtained. To this, a piece of well cleaned copper sheet (4 g by weight) was added. Solution was then ultrasonicated continuously for more than 15 h, resulting into clear solution along with tan colored precipitate. This indicates that entire amount of iodine is utilized in the formation of CuI nanoparticles. Reaction was carried out under open air and precipitates were repeatedly washed with triple distilled water to remove the byproducts completely. Finally unreacted copper was separated out and resultant powder was collected by drying. This powder was further used for all the characterization and temperature dependent electrical conductivity measurements. X-ray diffraction (XRD) was recorded for 2θ in the range 15–90° using Philips X'pert powder diffractometer with Cu Kα_1 radiation (λ = 1.54056 Å). X-ray pattern was recorded by spreading powder on a glass plate coated with silicon grease with scan step of 0.01 deg/s. Thermal analysis was carried out by using differential scanning calorimetry (DSC) and thermal gravimetric analyzer (TGA) model DSC Q20 and SDT Q600 respectively (TA instruments). Optical absorption was performed by using Hitachi U3310 spectrophotometer in the range 200–400 nm and photoluminescence (PL) at room temperature by Hitachi F-7000 fluorometer using xenon lamp as the excitation source. JEOL-JSM 6360 instrument was used for scanning electron microscopy (SEM) whereas energy-dispersive X-ray electron spectroscopy (EDS) was done using Ultra 55, field emission scanning electron microscope (Carl Zeiss), with EDAX instrument. Tecnai F-30 S-Twin was used to perform high resolution transmission electron microscopy (HRTEM). The temperature dependent electrical conductivity measurements were carried out using Keithley 617 programmable electrometer interfaced with computer.

3. Results and discussion

The structural characterization of as-prepared CuI powder has been carried out by X-ray diffraction and such pattern is shown in Fig. 1. All diffraction peaks well match with JCPDS card No. 06-0246 for CuI. Three main characteristic peaks for CuI at (2θ = 25.66°, 42.64° and 50.22°) corresponding to Miller indices (1 1 1), (2 2 0) and (3 1 1) were observed, which confirm the fcc crystalline geometry of γ-CuI. Particle size (d) was estimated using Scherrer formula [$d = k\lambda/(\beta\cos(\theta))$]; where k is Scherrer's constant taken as 0.9, λ is wavelength of radiation, β is full width half maxima (fwhm) and θ is Bragg angle. The estimated particle size for as prepared powder is about 22 nm. Since no additional peak in the pattern is observed which indicates the material is of monophase. Further this simple chemical route yields good crystallinity of as prepared material at ambient condition.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) results for powdered CuI are shown in Fig. 2. DSC pattern was recorded with a heating rate of 15 °C/min for heating then it was cooled back to room temperature, subsequently again it was recorded for second time. During both the heating process a sharp endothermic peak at 649.73 K is observed which gives indication of a phase transition of CuI. Since three phases of CuI namely α, β and γ exist; above 665 K, between 665 K to 623 K and below 623 K respectively [3], so here the endothermic peak observed at 649.73 K in case of present material has been accounted for γ to β structural phase change. Such phase transition has been well reported in case of CuI for both single crystal as well as powder sample [9,10]. The shift in the transition temperature towards higher value (from 623 K to 649.73 K of γ-to-β phase) is probably due to particle size and intrinsic vacancies associated with cation/anion in the lattice of CuI. Further, the highly reproducible nature of our endothermic peak for first and second heating cycle clearly indicates that the above structural phase transition is completely reversible. This is further confirmed by our TGA result, from the Fig. 2 it can be seen that below 865 K there is no weight loss of material, whereas major weight loss occurs above this temperature. It is seen from graph that at 1070 K weight loss has become almost complete, which is attributed to fastest decomposition of material and is in consequence with the result reported in literature [9,10]. Recently, the structural phase transition in CuI with temperature has been reported [10]. As prepared material was stoichiometric (Cu to I ratio 1:1) that was heated up to 720 K to study the thermal stability by DSC and TGA measurements. On heating cycle this shows a transition from γ to β-phase at 650 K and on cooling the transition shifts to lower temperature 629 K. It is opined that the material looses iodine on heating up to 720 K and it becomes non-stoichiometric. Hence, a shift in transition temperature is accounted for cation/anion ratio. In the present case, on repeated (first and second) heating (up to 670 K) the transition temperature remains unaffected could be

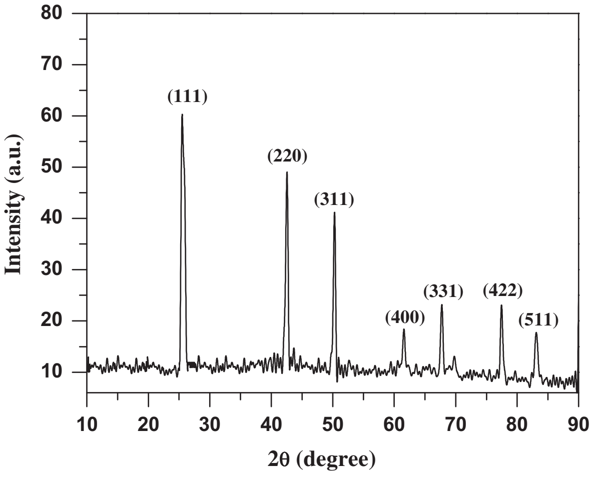

Fig. 1. X-ray diffraction pattern of as prepared CuI powder at room temperature.

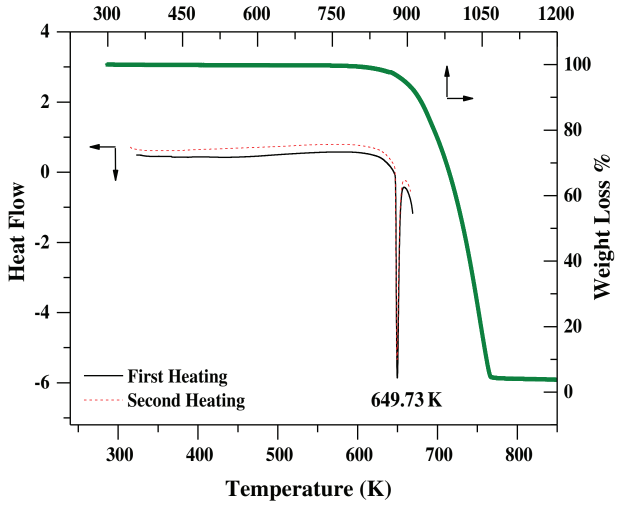

Fig. 2. Combined graph for differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) of as prepared CuI powder. In the figure arrow marks are indicating corresponding axis for DSC and TGA curves. In case of DSC, the solid curve is first time heating of as prepared CuI and dotted curve for second cycle of heating and both the curves were recorded at 15 °C/min heating rate.