

PHASE TRANSITIONS IN MECHANOCHEMICALLY SYNTHESIZED CuI NANOCRYSTALS

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Abstract. CuI nanocrystals were formed by attrition of Cu and I at ambient temperature. They were characterized by XRD to be zincblende, γ -CuI with an average particle size of 20 – 40 nm. The crystallographic phase transitions from zincblende (γ -phase)-to-distorted wurtzite (β -phase)-to-disordered zincblende (α -phase) were also investigated through non-isothermal DSC. Transition temperatures, enthalpies and entropies of these two-phase transitions as well as their “activation energies” were obtained, treating the phase transitions as “reactions”. It is inferred that attrition imparts a partial cation disorder into CuI, unlike a wet chemical reaction. Attrition essentially prepares the fcc Cu lattice for accommodation of I ions in a weakly covalent arrangement.

1. INTRODUCTION

CuI is an important member of the I-VII large gap semiconductors with zincblende crystal structure and tetrahedral Cu-I bonding. It is important as a non-linear optical material and also as an electrochemical sensor material besides being an optoelectronic quantum dot based device material. CuI undergoes a sequence of structural phase transitions [1] from zincblende to pseudo-hexagonal to a more disordered zincblende phase at 642K and 689K respectively.

We have recently found that CuI can be synthesized at ambient temperature in a facile manner in the form of nanoparticles [2], by manual attrition in a mechanochemical reaction (MCR). MCR – triggered by the application of mechanical energy – is characterized by a large negative fractional energy change and is thermodynamically feasible at ambient temperature itself. The entire reaction process can be controlled/increased by the mechanical generation of clean/fresh surfaces due to fracturing, increased defect density and the reduction in particle size [3]. It is important to do this because the usual methods of wet chemical synthesis yield only micrometer-sized particles.

To determine the stability of nanocrystalline CuI for possible device applications, it is necessary to evaluate its thermal stability. This process of making nanocrystalline CuI by MCR may also be viewed as a mechanochemical transformation of Cu with fcc structure to CuI with zincblende structure. An earlier study [4] of such a “transformation” is the γ -FeOOH to α -Fe₂O₃. Advantages of MCR over other methods of synthesis include (a) controlled introduction of cation disorder, (b) convenient manipulation of particle size and (c) requirement of only mild thermodynamic parameters namely ambient temperature and “muscular” pressure.

The aim of our present work is to study an oxidation type “soft” MCR [5] i.e. iodination of copper, by application of mechanical energy. This solid state reaction involves the formation and growth of the product phase at the interface of the reactants, with the latter acting on the diffusion energy barrier. In the present paper, we report on the structural and phase transitional aspects of CuI obtained by mechanical attrition.

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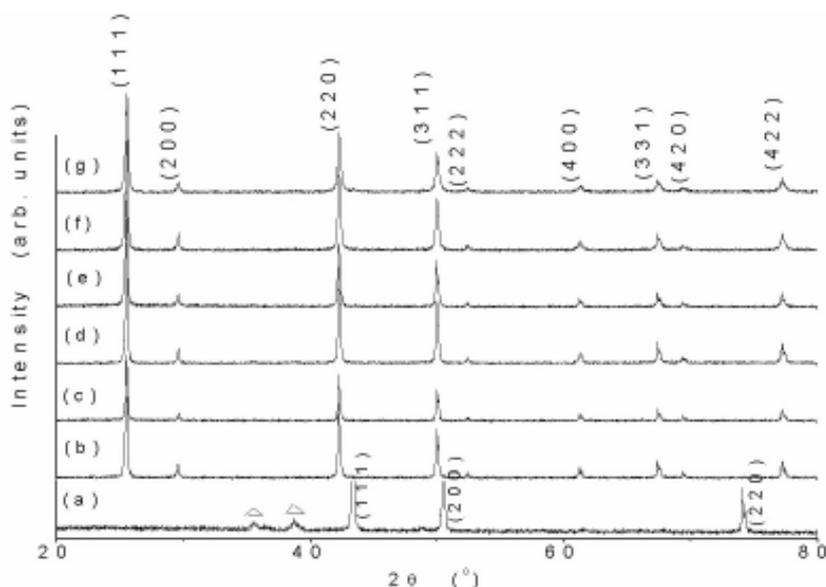


Fig. 1. XRD patterns of the progressive evolution of nanocrystalline CuI with grinding time. (a) Commercial Cu-powder, (b) 2 min., (c) 5 min., (d) 20 min., (e) 30 min., (f) 45 min. and (g) 60 min. grinding with I_2 . The triangle marks in (a) corresponds to CuO.

2. EXPERIMENTAL

CuI was synthesized by taking a 5 gm. batch of stoichiometric mixture of 99.5% pure copper metal powder (SD, India) and purified iodine flakes (LOBA, India). The charge was then transferred to an agate mortar and manually ground in the dark for periods ranging from 5 minutes to over an hour and examined subsequently by XRD at each stage. The samples confirmed by XRD as completely formed CuI were examined for phase stability and phase transitions using a Perkin Elmer (DSC-4) instrument.

3. RESULTS AND DISCUSSION

Surface oxidation of the Cu powders does not seem to retard the formation of CuI as clearly revealed in Fig. 1. It is significant that even 5 minutes grinding is sufficient for almost complete conversion of Cu and I into CuI, which suggests a fast reaction for the present mechanochemical process. As the grinding proceeds, the intensity of the major (111) Bragg peak (Fig. 1) increases to a maximum and decreases thereafter accompanied by an increase in the FWHM. In fact, 60 minutes of grinding produces an XRD pattern with very broad peaks, characterizing the nanoparticle formation. Debye-Scherrer equation based analysis of the X-ray line widths puts the particle size as 40 ± 5 nm. Table 1 summarizes the powder XRD results.

The thermal stability of this mechanically ground CuI has been investigated using DSC in the non-isothermal mode as shown in Fig. 2. On heating the sample at the rate of 10 K/minute, two endot-

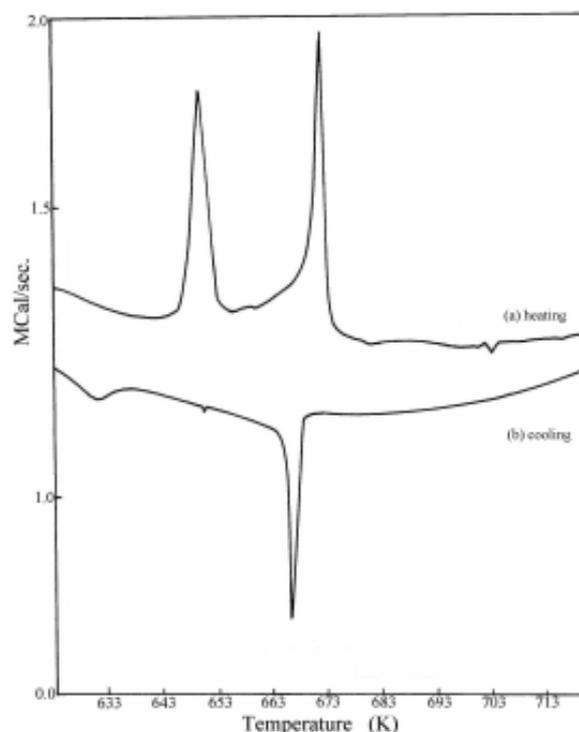


Fig. 2. Non-isothermal DSC (a) heating and (b) cooling curves showing the phase transitions of CuI. Note the hysteresis in the cooling curve.

Table 1. XRD parameters of the mechanically ground samples.

Sample	Lattice Constant (nm)	Unit cell Volume (10^{-24} cm ³)	density (g/cm ³)
Commercial CuI	0.6047	221.12	5.72
2 min.	0.6046	220.10	5.7235
5 min.	0.6044	220.73	5.7301
20 min.	0.6043	220.72	5.7208
30 min.	0.6047	221.09	5.7201
45 min.	0.6044	220.83	5.7257
60 min.	0.6043	220.72	5.7305
JCPDS*	0.6043	220.65	5.7327

(* - Joint Committee on Powder Diffraction Standard data)

Table 2. DSC parameters for the mechanically ground CuI sample. (Commercial sample parameters are given in parentheses for comparison).

Phase transition from	Transition temperature (K)	Hysteresis (K)	Activation energy (kJ/mole)	Entropy (kJ/mole·K)
$\gamma \rightarrow \beta$	650 (649)	19 (13)	3210 (1059)	2.05 (3.18)
$\beta \rightarrow \alpha$	672 (671)	5 (4)	2440 (497)	1.84 (3.52)

hermic peaks, one at 650K corresponding to the $\gamma \rightarrow \beta$ phase transition and the other at 672K that represents the $\beta \rightarrow \alpha$ phase transition of CuI appears [2]. Hysteresis effects are seen in the cooling cycle (Fig. 2, Table 2).

The changes in thermodynamic parameters – enthalpy (ΔH) and entropy (ΔS) – at the phase transitions are given by,

$$\Delta H = kA/m, \quad (1)$$

where k is the calibration constant, A is the area under the endothermic peak and m is the mass of the sample,

$$\Delta S = \Delta H/T_r, \quad (2)$$

where T_r is the transition temperature.

The two structural phase transitions in CuI are further characterized as “reactions” so that the Kissinger method of analysis [6] could well be applied to the DSC thermograms recorded at several heating rates (ϕ) yielding different peak temperatures T_m . The Kissinger relation is,

$$d(\phi/T_m^2)/d(1/T) = -E/R, \quad (3)$$

where E is the activation energy and R is the universal gas constant.

The Kissinger plots for the $\gamma \rightarrow \beta$ phase transition are shown in Fig. 3. The activation energies, 3210 and 2440 kJ/mole for $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transitions respectively, determine the rate at which the particular phase is formed [2]. Table 2 summarizes the DSC data.

A soft mechanochemical metal oxidation type reaction involves mechanical stirring of a metal powder and an oxidant. This “activation” process causes an inelastic local deformation as the surfaces of metal and the oxidant come into close contact [3]. The metal particles are in a mechanically activated state with considerable amount of defects and in-built disorder. There is also a certain amount of reduction in the particle size, resulting in an optimized, reactive interface between metallic and oxidant surfaces. This favors the formation of the oxide as the product phase on a local scale [5].

The time required for the complete conversion of the reactants into a nanocrystalline product depends on the “height” of the diffusion barrier. This barrier offered by the initially formed localized product phase

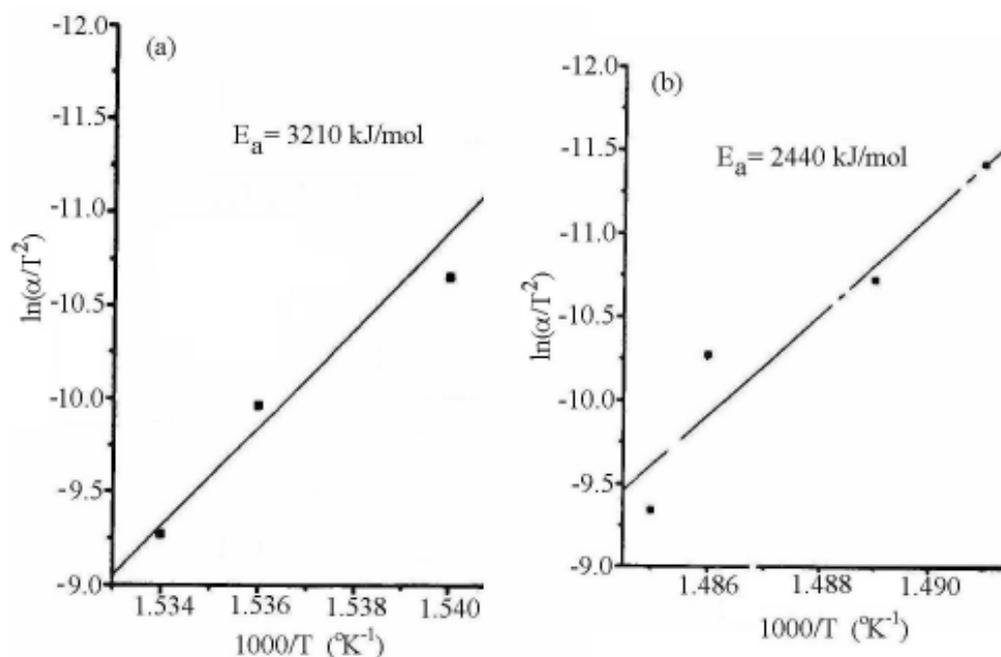


Fig. 3. Kissinger plots for (a) $\gamma \rightarrow \beta$ and (b) $\beta \rightarrow \alpha$ phase transitions.

would be quite high and thus slows down further diffusion processes. As the present MCR takes place at ambient, the concentration of defects and the extent of disorder induced by mechanical deformation would be quite different from that obtained in a wet chemical or in a thermally induced reaction. This in turn associates itself with the incomplete/partial stabilization of the structural disorder in CuI obtained by the present "non-equilibrium" mechanochemical synthesis and accounts for the lower entropy and higher enthalpy values (Table 2) relative to that of the commercial sample [7]. The significantly larger activation energy values obtained for the mechanically ground CuI samples also implies additional "mechanical" barriers to be overcome by the "partially ordered" nanometer-sized particles in which the surface energy component is a significant fraction of the total free energy. This very interesting observation deserves a more detailed theoretical investigation presently underway.

Based on the present XRD and allied measurements, the following steps could be suggested for the formation of AgI [8] and CuI from Ag, Cu and I by mechanical grinding.

1. Shearing of Ag/Cu particles and breaking down of I flakes into small platelets with increased surface area and reactivity,
2. Dissociation of I into I_2 molecules and I atoms,
3. Interfacial reaction involving mechanically activated metal surface and nascent I "cloud" lead-

ing to the formation of active surface Ag/Cu-I groups and

4. Combination of the above groups into "nanocrystals".

These observations help us understand more about mechanically activated solid state reactions as much as they help us optimize conditions for these reactions. This preliminary effort suggests the following future lines of investigations. (1) Characterization of Cu^+ disorder in CuI through careful x-ray and neutron diffraction studies, (2) preparation of solid solutions of the AgI-CuI and CuI-AgI systems and (3) Synthesis of ternary superionic conductors such as Ag_3SI and KAg_4I_5 by this method of mechanical alloying.

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