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Synthesis, Morphology, and Optical Properties of CuI Microcrystals

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Abstract—We have studied the effect of synthesis conditions on the luminescence spectra of ultrafine CuI powders. The results demonstrate that synthesis conditions (the reductant of Cu^{2+}, the anion of the copper(II) salt, initial solution concentrations, and the presence of a stabilizer) influence the size and shape of the forming CuI particles and, accordingly, their luminescence spectrum. The highest luminescence intensity near $\lambda_{max} \simeq 720$ nm ($\lambda_{ex} \simeq 370$ nm) is offered by regularly shaped tetrahedral particles 1.1–1.2 μm in average size.

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INTRODUCTION

One important issue in modern optoelectronics is a search for nanosystems capable of efficiently converting UV radiation to the visible range.

CuI-containing films possess interband absorption at $\lambda \le 410$ nm and rather efficient luminescence at $\lambda \simeq 420$ nm. In addition to the "edge" luminescence ($\lambda \simeq 420$ nm), they may exhibit luminescence at $\lambda_{max} \simeq 720$ and 820 nm, due to electron–hole recombination at surface defects of CuI [1, 2], but the efficiency of this luminescence is low.

As shown by Malashkevich et al. [3], the quantum yield of CuI luminescence in sol–gel derived oxide films activated with CuI microcrystals exceeds 80%, and the fraction of photons emitted in the band at $\lambda \simeq$ 720 nm approaches 100% at $\lambda_{ex} = 370$ nm. For this reason, such films can be regarded as potential converters of UV radiation, harmful to silicon solar cells, to the spectral region of their highest sensitivity, which would improve their efficiency. Oxide–CuI xerogels are potentially attractive as luminescent markers for security and authentication applications.

The preparation of copper(I) iodide has been the subject of extensive studies. Most approaches use the reduction of Cu^{2+} to Cu^+ by various agents (sodium sulfite or thiosulfate, sulfurous acid, acetone, sodium borohydride, and others), followed by CuI precipitation with a potassium iodide solution [4–6]. There are also techniques that employ reactions of iodine with ultrafine copper [7–9] and copper(II) sulfate with potassium iodide [10].

The purpose of this work is to study the morphology, dimensions, and luminescence spectra of CuI microcrystals in relation to synthesis conditions, which will subsequently make it possible to assess the influence of these factors on the luminescence spectra of CuI-containing oxide films and xerogels as the most promising materials for practical application.

EXPERIMENTAL

In our experiments, we used synthesized and off-the-shelf (pure grade) CuI. We employed several synthetic procedures based on the reduction of Cu^{2+} to Cu^+ by sodium sulfite (procedure 1); potassium iodide (2); and potassium iodide, with polyethylene glycol (PEG) as a stabilizer (3). In addition, colloidal copper produced by reducing Cu^{2+} with sodium borohydride was oxidized by atmospheric oxygen in the presence of potassium iodide (4).

Procedure 1. CuI was synthesized according to the scheme [4]

$$2CuSO_4 + Na_2SO_3 + 2KI + H_2O$$
$$\rightarrow 2CuI + K_2SO_4 + Na_2SO_4 + H_2SO_4.$$

A Na_2SO_3 solution (0.1 M) was added with vigorous stirring to a $CuSO_4$ solution (0.5 M) in the molar ratio $CuSO_4 : Na_2SO_3 = 1 : 3$. To the resultant green-yellow suspension was added dropwise a KI solution (0.1 M) according to stoichiometry, which led to precipitation of whitish substance. After the completion of the reaction, the precipitate was separated by decantation, washed with a small amount of ethanol and acetone, and dried in air at 90–95°C.

The properties of this sample were studied after storage in air for several months.

Procedure 2. A copper(II) salt was precipitated with potassium iodide:

$$2Cu^{2+} + 4I^- \rightarrow 2CuI\downarrow + I_2.$$

To a potassium iodide solution of predetermined concentration was added dropwise with vigorous stirring a copper(II) salt solution. The resultant precipitate was separated by decantation; washed with a 0.02 M potassium iodide solution, distilled water, and ethanol; and dried at 20°C.

To optimize the CuI synthesis conditions and ensure a high product yield, we prepared a number of samples at different concentrations of the starting reagents, which were varied from 0.005 to 0.015 M for the copper salt and from 0.01 to 0.05 M for potassium iodide. At a $CuSO_4$: KI molar ratio of 1 : 2 and 1 : 10, the product yield was 12–18 and 85%, respectively. An excess of KI relative to stoichiometry facilitated dissolution of precipitating iodine, displacing the reaction equilibrium toward CuI formation.

In this procedure, the divalent copper sources were copper sulfate (pentahydrate) and copper nitrate (trihydrate).

Procedure 3. Direct precipitation was carried out as follows [11]: First, we prepared KI (0.38 g) and $CuCl_2$ (0.18 g) solutions in PEG-400 (26.5 g) with constant stirring. After complete dissolution, the solutions were poured together. The resultant solution was added dropwise to a 0.05 M $NaNO_3$ solution (80 mL) at 20°C with stirring. The precipitate was separated by centrifugation; washed with a 0.01 M KI solution; distilled water, and ethanol; and dried at 20°C.

Procedure 4. Colloidal copper prepared by reducing Cu^{2+} with sodium borohydride was oxidized by atmospheric oxygen in the presence of potassium iodide [6]:

$$Cu^{2+} + 3I^- + BH_4^- + 3H_2O$$
$$\rightarrow CuI\downarrow + H_2BO_3^- + 4H_2\uparrow + I_2\downarrow.$$

The divalent copper sources used were copper sulfate (pentahydrate), copper nitrate (trihydrate), copper acetate, and copper bromide. In our experiments, the highest reaction rate and product yield were achieved at pH 2.8–3.0.

To a Cu^{2+} salt solution was added a potassium iodide solution with constant stirring. Next, argon was bubbled through the solution for 15 min and a freshly prepared sodium borohydride solution was added dropwise. The reaction mixture was then stirred for 2.5–3 h and left to stand for 6–12 h. This led to precipitation of a white or cream white dense substance, which accumulated on the bottom of the reaction vessel. The precipitate was separated by decantation, washed with distilled water and ethanol, and dried at 40–60°C.

The initial solution concentrations were calculated so as to obtain the following final concentrations: 10^{-3} M Cu^{2+}, 10^{-2} M KI, and 6×10^{-2} M $NaBH_4$. The product yield was 67–74%.

The CuI samples were characterized by X-ray diffracting (XRD) on a DRON-2.0 powder diffractometer with CuK_α radiation. The dimensions and shape of particles were determined by scanning electron microscopy (SEM) on a LEO 1420. Luminescence excitation and luminescence spectra were measured in the range 250–850 nm on an SM 2203 spectrofluorimeter.

The average particle size and polydispersity index were evaluated as described in Voyutskii and Panich [12].

RESULTS AND DISCUSSION

XRD characterization showed that the off-the-shelf CuI and all the synthesized CuI samples had a cubic structure [13]. The synthesized samples had identical XRD patterns, so Fig. 1 shows the XRD patterns of the off-the-shelf CuI sample and the sample prepared by procedure 4 using $Cu(NO_3)_2$. The synthesized samples had sharp, narrow diffraction peaks, indicative of good crystallinity.

According to SEM data (Fig. 2), the CuI samples consisted of polyhedral (procedure 1), tetrahedral (procedures 2, 4), or platelike (procedure 3) particles ranging in average size from 0.45 to 1.9 μm. The off-the-shelf CuI consisted of well-faceted, irregularly shaped tetrahedral or polyhedral particles with an average size of 1.8 μm and had a broader particle size distribution in comparison with the synthesized samples.

The CuI sample prepared through direct precipitation, using PEG as a stabilizer (procedure 3), consisted of the smallest particles ($d_{av} \simeq 0.45$ μm) (Fig. 2d).

In the case of direct CuI precipitation, the $CuSO_4$: KI ratio influenced the shape and dimensions of the forming particles (Fig. 3). The CuI particles prepared at a $CuSO_4$: KI molar ratio of 1 : 2 from more dilute solutions (Fig. 3a) had the most regular tetrahedral shape. With increasing initial solution concentrations at a constant $CuSO_4$: KI molar ratio, the particle size varies little and the particle shape slightly distorts but remains almost tetrahedral (Fig. 3c). At a $CuSO_4$: KI molar ratio of 1 : 10, there are large agglomerates consisting of finer, face-sharing tetrahedral particles (Fig. 3b). At $CuSO_4$: KI = 1 : 1, we obtained irregularly shaped, elongated particles ranging in size up to 4.0 μm (Fig. 3d). Using $Cu(NO_3)_2$ instead of $CuSO_4$ in this procedure had no effect on the morphology or size of the forming CuI particles.

The CuI samples prepared by procedure 4 using sodium borohydride consisted largely of tetrahedral particles (Fig. 4), independent of the anion of the copper(II) salt (SO_4^{2-}, NO_3^-, CH_3COO^-, or Br^-), but differed in particle size and polydispersity index (table).

The sample prepared using $CuSO_4$ was the most uniform in shape and dimensions (Fig. 4a, table).

All of the CuI samples had similar luminescence excitation spectra, which differed only in intensity and contained a broad luminescence excitation region, from 250 to 410 nm ($\lambda_{em} = 720$ nm), with two weak features at 340 and 410 nm, due to electron excitation from inner levels and directly from the CuI valence band top, respectively, to the conduction band [11]. Note that the intensity of the excitation band varied little from sample to sample in the above spectral region (Fig. 5a).

The luminescence spectra of the CuI samples ($\lambda_{ex} \simeq 370$ nm) showed two bands: one narrow, at

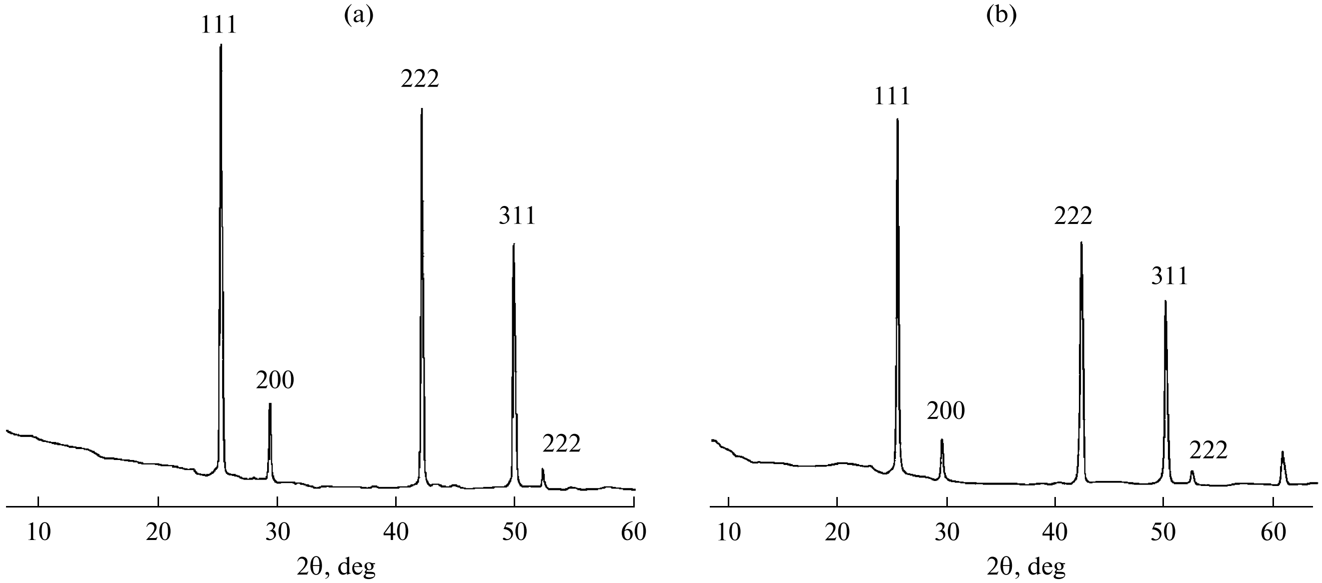

Fig. 1. XRD patterns of CuI samples: (a) procedure 4, (b) off-the-shelf CuI.

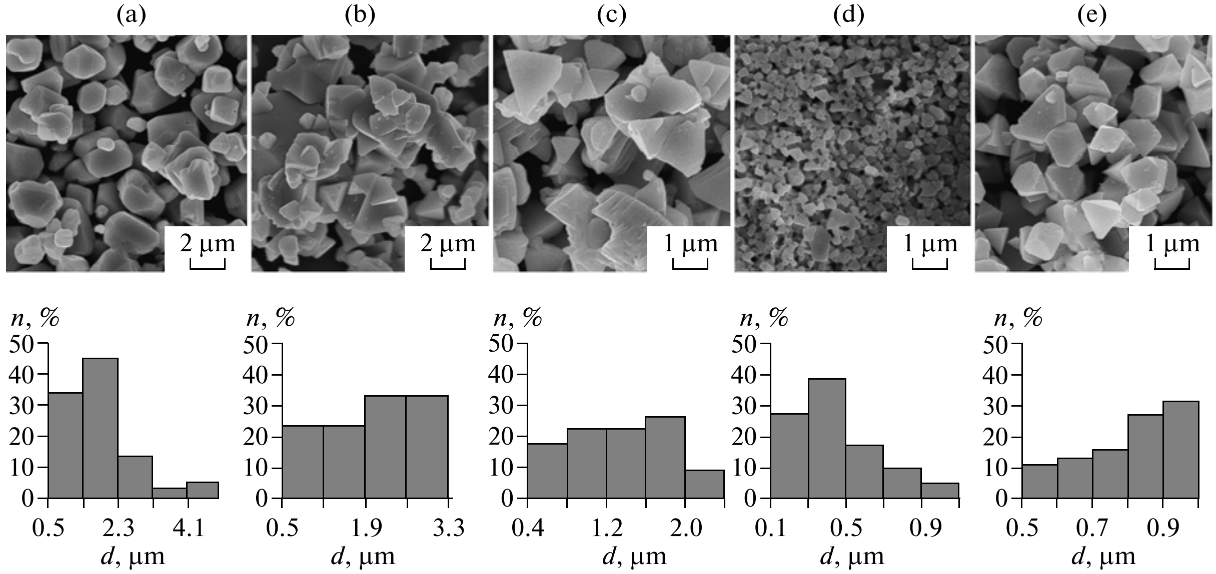

Fig. 2. SEM images and particle size distributions of CuI samples: (a) off-the-shelf CuI, (b) procedure 1, (c) 2, (d) 3, (e) 4.

$\lambda_{max} = 420$ nm, and the other broad, at $\lambda_{max} = 720$ nm (Fig. 5b). The intensity of the luminescence at $\lambda_{max} \simeq 720$ nm correlates with that of the corresponding luminescence excitation spectra, and the intensity of the 420-nm luminescence varies in a more complex manner, which calls for further investigation. It should be emphasized that, in what follows, we consider the effect of synthesis conditions on the luminescence around $\lambda_{max} = 720$ nm.

According to our experimental data, the brightest luminescence at $\lambda \simeq 720$ nm was offered by the CuI samples prepared by procedure 4, independent of the anion of the copper(II) salt used. In those samples, the majority of the particles had a regular tetrahedral shape, with an average size in the range 1.1–1.5 µm. The only exception was the sample prepared from $CuSO_4$, which showed very weak luminescence.

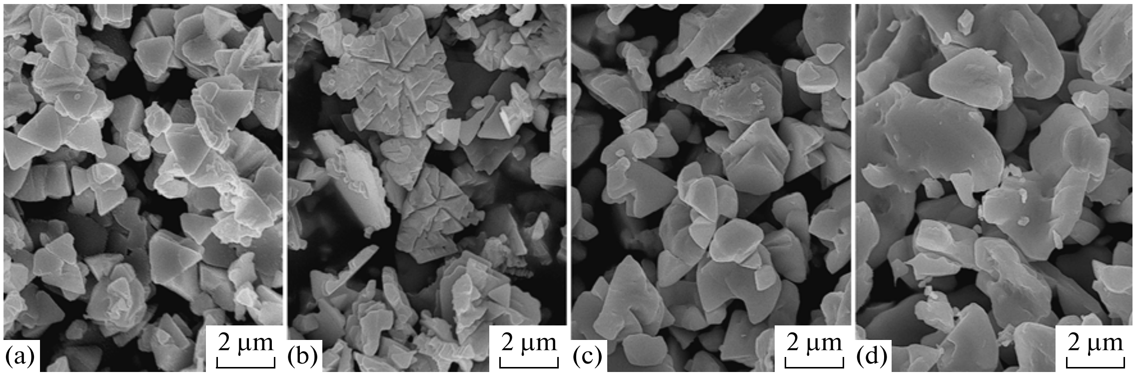

Fig. 3. SEM images of CuI samples (procedure 2) obtained at different $CuSO_4$: KI ratios: (a) 1 : 2 (0.005 M $CuSO_4$, 0.01 M KI), (b) 1 : 2 (0.015 M $CuSO_4$, 0.03 M KI), (c) 1 : 10 (0.005 M $CuSO_4$, 0.05 M KI), (d) 1 : 1 (0.015 M $CuSO_4$, 0.015 M KI).

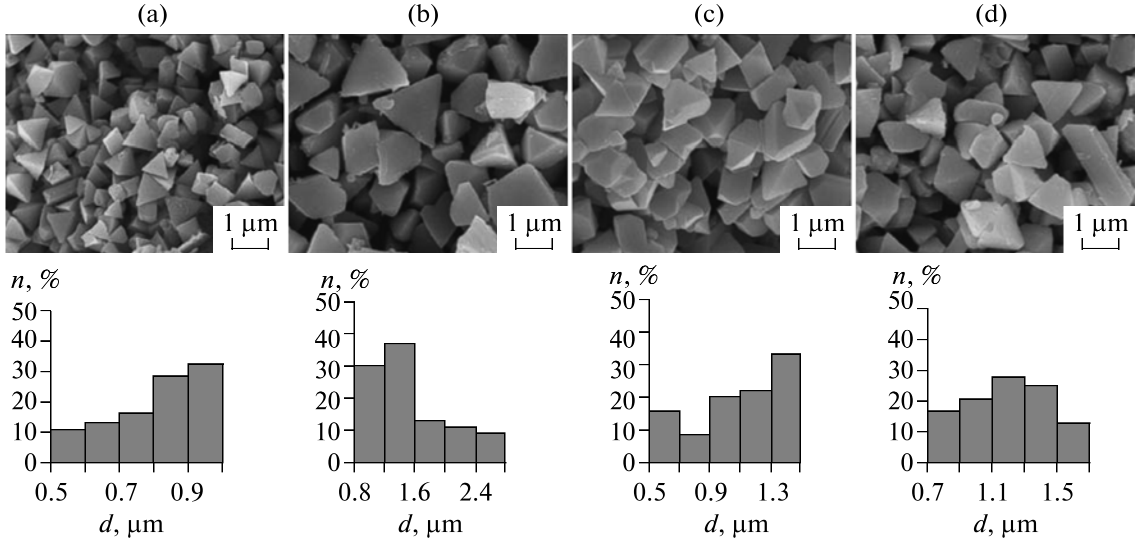

Fig. 4. SEM images and particle size distributions of CuI samples (procedure 4) prepared using different precursors: (a) $CuSO_4$, (b) $Cu(CH_3COO)_2$, (c) $CuBr_2$, (d) $Cu(NO_3)_2$.

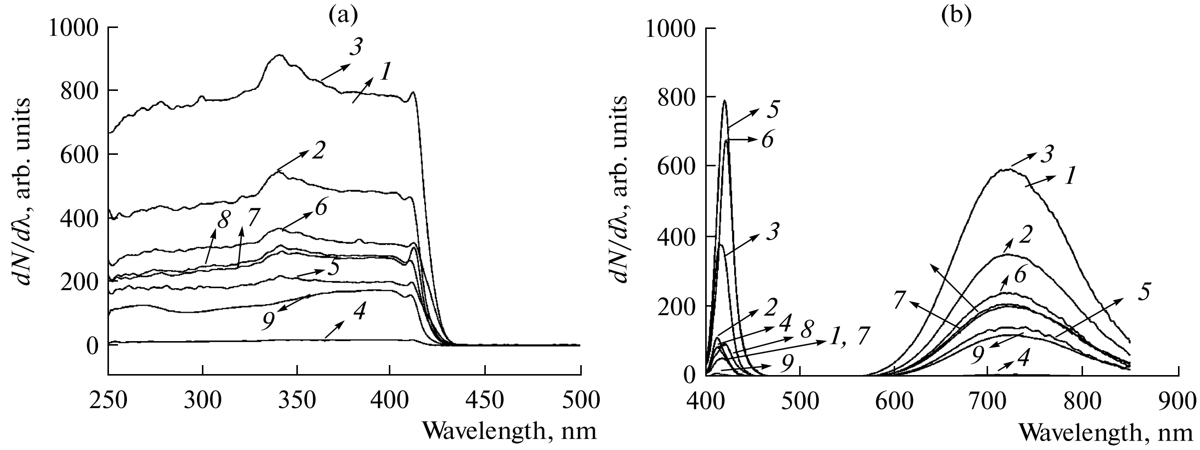

Fig. 5. (a) Luminescence excitation spectra (λ_{em} = 720 nm) and (b) luminescence spectra (λ_{ex}= 370 nm) of CuI samples prepared by (*1*–*4*) procedure 4 using (*1*) copper bromide, (*2*) copper acetate, (*3*) copper nitrate, and (*4*) copper sulfate; (*5*, *6*) by procedure 2 using (*5*) copper sulfate and (*6*) copper nitrate; (*8*) by procedure 1; and (*9*) by procedure *3*; (*7*) off-the-shelf CuI.

Effect of the anion of the copper(II) salt on the average particle size and polydispersity index of CuI samples prepared by procedure 4

Anion	Sulfate	Acetate	Bromide	Nitrate
Average particle diameter, μm	0.8	1.5	1.1	1.2
Polydispersity index	1.1	1.3	1.2	1.4

The off-the-shelf CuI, the samples synthesized using sodium sulfite as a Cu^{2+} reductant (procedure 1), and those prepared by direct precipitation of $CuSO_4$ and $Cu(NO_3)_2$ with potassium iodide (procedure 2), which consisted of large, irregularly shaped particles with an average size of 1.9–2.0 μm, had weaker luminescence (by a factor of ≃3–5).

The sample prepared by procedure 3, using PEG, which consisted of small particles (d_{av}= 0.45 μm) with a nontetragonal shape, showed weak luminescence. The sample synthesized from $CuSO_4$ using sodium borohydride as a reductant had a small particle size (d_{av}= 0.8 μm) and almost zero luminescence intensity.

CONCLUSIONS

We have synthesized CuI by various procedures. Synthesis conditions (the reductant of Cu^{2+}, the anion of the copper(II) salt, initial solution concentrations, and the presence of a stabilizer) have been shown to influence the size and shape of the forming CuI particles.

The smallest CuI particles were produced through direct precipitation, using PEG as a stabilizer (d_{av} = 0.45 μm). The other procedures yielded particles ranging in size from 0.8 to 2.0 μm. The particles differed in morphology:

tetrahedral (colloidal copper prepared by reducing Cu^{2+} with sodium borohydride was oxidized by atmospheric oxygen in the presence of potassium iodide), distorted tetrahedral (Cu^{2+} was reduced to Cu^+ by potassium iodide),

irregular polyhedral (Cu^{2+} was reduced to Cu^+ by sodium sulfite), and

platelike (Cu^{2+} was reduced to Cu^+ by potassium iodide, with PEG as a stabilizer).

The morphology and size of CuI particles influence their luminescence spectra. The optimal size of CuI particles, ensuring the highest luminescence intensity near $\lambda_{max} \simeq 720$ nm, is ≃1.1–1.2 μm. An important point is that, at a given CuI particle size, brighter luminescence is offered by regularly shaped tetrahedral particles.

The present results will be used subsequently to produce oxide films and xerogels based on CuI samples offering the brightest luminescence, with the possibility of using them in silicon solar cells in order to improve their efficiency.

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