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**Large  $\gamma$ -CuI semiconductor single crystal growth by temperature reduction method  
from  $\text{NH}_4\text{I}$  aqueous solution**

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**Abstract:**  $\text{NH}_4\text{I}$  has been proved to be a promising cosolvent for cuprous iodide (CuI) single crystal growth from aqueous solutions by the temperature reduction method. In our work, as compared with  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{I}$  offers more advantages for the single crystal growth, such as remarkably increasing the solubility and growth rate of CuI crystal, effectively reducing the impurity concentration, enhancing the crystal quality and crystallinity. Regular centimeter-level size optical quality single crystal was successfully obtained using  $\text{NH}_4\text{I}$  as a cosolvent. Electronic and optical properties of the as-grown crystal were characterized by Hall-effect measurements, optical transmission and photoluminescence spectra, respectively. The results demonstrated the CuI crystal was conductive (high p-type mobility as  $12.81 \text{ cm}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1}$ ) and transparent (great transmittance over 80%).

### Introduction

Cuprous iodide (CuI) is an important functional material with three crystalline structures: the cubic below  $369 \text{ }^\circ\text{C}$  as  $\gamma$  phase, above  $407 \text{ }^\circ\text{C}$  as  $\alpha$  phase, and the hexagon as  $\beta$  phase the between.<sup>1</sup> Within the high temperature phases range, it exhibits a large ionicity employed for applications as  $\text{Cu}^+$  ion conductor.<sup>2</sup> The low-temperature  $\gamma$ -phase belongs to space group

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F-43m and its unit cell contains four molecules.<sup>3</sup>  $\gamma$ -CuI is known as the fastest inorganic scintillation crystal with a short decay time about 90 ps at room temperature, generating a great potential application in ultra-fast scintillators.<sup>4-6</sup> Besides, it is one of the few p-type semiconductor materials with a wide direct fundamental band gap of 3.1 eV and has received much attention in recent years as a hole conductor of fully solid-state dye-sensitized solar cells.<sup>7-10</sup> Such a compound may play an important role in new optoelectronic applications once the large high-quality single crystal is obtained. To meet the great demand, a variety of routes, such as sublimation technique, flux method, hydrothermal route, sol-gel method and evaporation method, have been proposed to grow this crystal.<sup>11-17</sup> However, sublimation technique and flux method require special set-up and high growth temperature, which resulted in  $\gamma$ -CuI crystals with poor quality. Hydrothermal route is performed in a sealed system with high temperature and high pressure, therefore the growth of crystals can not to be observed. Although sol-gel method can be carried out at room temperature, it is unsuited for growing large  $\gamma$ -CuI crystals due to the uncontrollable spontaneous nucleus during the growth procedure. For evaporation method, the crystallization process is very difficult to control. In conclusion, restricted by the various conditions, most of  $\gamma$ -CuI crystals obtained using the above approaches were below centimeter-size and the quality hardly satisfied the request of practical application.

Commonly, the size and quality of crystal are closely related to the process of crystal growth. When large dimensions single crystal materials of high quality are needed for certain applications, solution growth methods may offer an advantage of easier scaling-up process. Temperature reduction method, a low-temperature solution growth method, is the most simple and the low-cost method that has been widely applied to grow large single crystals of water-soluble substances, examples of which include triglycine sulphate (TGS), L-arginine phosphate monohydrate (LAP) and potassium dihydrogenphosphate (KDP).<sup>18-21</sup> This method,

which benefits from the good fluidity of solvent, large diffusion coefficient of solute, the absence of spontaneous nucleation, mild conditions and easily controlled growth parameters, can produce large crystals with low defect density and high crystallinity. But it is uncommon to produce water-insoluble crystals from low temperature aqueous solution.

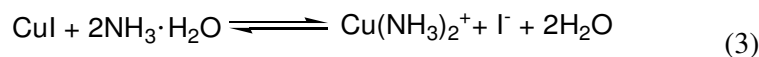
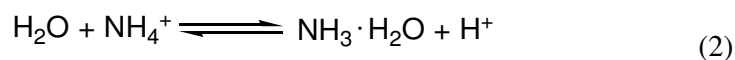
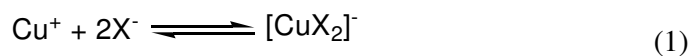
Herein, with the aid of cosolvents  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  or  $\text{NH}_4\text{I}$ , we have realized single crystal growth of  $\text{CuI}$  by the temperature reduction method from aqueous solution for the first time and comparatively analyzed the performance of three members of ammonium halide family.  $\text{NH}_4\text{I}$  behaved distinctively different from its  $\text{Cl}$  and  $\text{Br}$  counterparts, providing some advantages that could address the problems currently encountered in  $\text{CuI}$  crystal growth. In this context, we further investigated electronic and optical properties of the bulk single crystal grown using  $\text{NH}_4\text{I}$  as a cosolvent. In addition to practical purposes of obtaining large  $\text{CuI}$  single crystal suitable for optoelectronic devices, this work provides useful clues for aqueous solution growth of other large water-insoluble wide band-gap semiconductor single crystals, such as  $\text{PbI}_2$ ,  $\text{HgI}_2$ ,<sup>6</sup> and more some of the iodide family which currently is of great interest in different research fields: organometallic halide perovskites and topological insulators.<sup>22-25</sup>

## Experimental

### Design

Since  $\text{CuI}$  is a water insoluble solid ( $\text{p}K_{\text{sp}}=11.96$ ) at normal atmosphere, it is impossible to grow the crystal through the conventional aqueous solution method. Based on this, our efforts should be focused on choosing suitable cosolvents to effectively increase the solubility of  $\text{CuI}$ . In the previous study,  $\text{NH}_4\text{I}$  has been used as mineralizer for the crystal growth of  $\text{GaN}$  and  $\text{CuI}$  by the ammonothermal and hydrothermal method, respectively.<sup>14, 26</sup>  $\text{Cu}^+$  ion of  $d^{10}$  electron configuration possesses outer layer the s- and p-type empty electronic orbits, so that it can form the  $[\text{CuX}_2]^-$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) or  $[\text{Cu}(\text{NH}_3)_2]^+$  complex ions which are combined by the sp-orbital hybrid bonding of the ligands ( $\text{X}^-$ ,  $\text{NH}_3$ ) to  $\text{Cu}^+$  ions. As shown in eqs 1-3, the

solubility of CuI is increased and the metastable zone is broadened by producing the intermediate complexes. With cooling the mixed solution at a relatively low speed, the complexes slowly dissociate and the cuprous halides (CuX) precipitate out. In comparison with CuCl ( $pK_{sp}=5.92$ ) or CuBr ( $pK_{sp}=8.28$ ), it is easier to obtain CuI from the solution thanks to the lower solubility of CuI in water. In this decomplexation reaction condition, growth units can be afford for the self-nucleated seeds and bulk growth of CuI crystals will be realized. Based on the above analyses, we selected the solution containing  $X^-$  or  $NH_4^+$  ions, that is, ammonium halide ( $NH_4X$ ) cosolvent solutions, to grow CuI crystals.



### Solubility

All raw materials used were commercially available in analytical-reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (P.R. China). Deionized water was used as the solvents in our work. To achieve the optimal conditions for single crystal growing, the solubility of CuI in  $6 \text{ mol} \cdot \text{L}^{-1}$   $NH_4X$  solutions, from 30 to 60 °C, was measured by the spectrophotometric method.<sup>27</sup> Firstly, we weighed accurately 6 mol  $NH_4X$  solids, added deionized water until the volume of 1 L of aqueous solutions was achieved. Then, CuI saturated solutions was prepared at certain temperature by dissolving CuI powder in  $6 \text{ mol} \cdot \text{L}^{-1}$   $NH_4X$  aqueous solutions and the mixtures were continuously stirred for 24 hours to ensure saturation. Finally, cuprous ions in a set amount of the supernatants were oxidized into copper ions and followed by determining their concentrations with a PE-lambda 900 spectrometer. The solubility curves of CuI in different solutions were shown in Fig. 1(a) and they can be expressed respectively as

$$S_a = -0.379 + 0.016T \quad (\text{NH}_4\text{Cl solution})$$

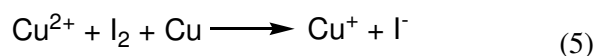
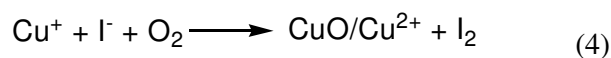
$$S_b = 1.594 + 0.029T \quad (\text{NH}_4\text{Br solution})$$

$$S_c = 10.117 + 0.196T \quad (\text{NH}_4\text{I solution})$$

where  $S$  is the solubility of CuI and  $T$  is the temperature. All of the solubilities increased gradually with increasing temperature and the CuI crystals can be obtained by the temperature reduction method using the above solutions. In addition, the solubility of CuI in  $\text{NH}_4\text{I}$  solution is evidently higher than that in  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{Br}$  solution at the same temperature. In the aqueous solution growth technique, the size of a crystal depends on the amount of material available in the solution, which in turn is decided by the solubility of the material in the solvent. According to this,  $\text{NH}_4\text{I}$  cosolvent could offer certain advantages for the single crystal growth of CuI compared to  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ .

### Crystal growth

The side reaction as eqs (4), ascribed to the existence of oxygen, would reduce the solution stability and has serious effect on the quality of crystal as well as the size. To prevent the oxidation, copper as reductants (eqs 5) and a thick layer of liquid paraffin (1-3 cm height) placed over the solution surface were used.



The experimental apparatus illustrated in Fig. 1(b) was applied to bulk crystal growth of CuI from the self-nucleated seeds in respective solutions. Standard glass crystallizers (2500 mL) with the mixed solutions were surrounded by an external thermostatic water bath with temperature controlled at accuracy of  $\pm 0.01$  °C. All solutions with saturation temperature of 55 °C were prepared by dissolving 12.1, 63.8 and 417.8g of CuI powder in 2 L 6 mol·L<sup>-1</sup>  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$  aqueous solution, respectively. The saturated solutions were filtered through filter film with pore size of 0.15  $\mu\text{m}$  at 65 °C to remove extraneous solids and

colloidal particles. After overheating for 24 h, the temperature of the solutions was reduced to the point of 5 °C higher than the saturation point and the seeds up to  $1.2 \times 1.1 \times 0.9 \text{ mm}^3$  in size mounted on a circular platform holding a reversible rotation rate of about 40 rpm were put into the solutions. For the sake of controlling the number of crystal nuclei during the growth procedure, the temperature of the system was reduced to a critical value of supercooling of 1 °C and then was decreased ranging from 0.1 to 0.5 °C per day to allow seed crystals to grow upwards. In order to maintain the sustained growth of the CuI crystals, the temperature gradient was increased over an interval of three days. The detail growth procedure and experimental parameters were described clearly in Fig. 2. By carefully adjusting the crystal growth parameters and the cooling speed of the solutions, spontaneous nucleation could be suppressed. After 14 days, bulk CuI crystals with different sizes and quality (Fig. 3b) were successfully obtained from  $\text{NH}_4\text{X}$  solutions, respectively.

## Results and discussion

### Analysis of crystal growth

The powder X-ray diffraction (XRD) measurements performed on a Rigaku DMAX 2500 powder diffractometer with a graphite-monochromatized Cu  $K_\alpha$  radiation were used to confirm the phase content of samples generated from different conditions. As shown in Fig. 3(a), all the diffraction peaks in XRD patterns of as-grown crystals are well indexed to  $\gamma$  phase CuI (JCPDS No. 06-0246, space group: F43m) and no other phases were detected. The bulk crystals grown in the presence of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$  were respectively presented in Fig. 3(b). These results clearly demonstrated the achievement of the seed growth of CuI crystal by temperature reduction method with  $\text{NH}_4\text{X}$  as the cosolvent. This was the first example of CuI single crystal growth under low-temperature aqueous solution conditions, in which  $\text{NH}_4\text{X}$  played a crucial role.

As far as the size of crystal was concerned, it was markedly dependent on experimental

cosolvents. Under the growth period of 14 days, millimeter-scaled irregular crystals (Fig. 3b) were gained from  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  solutions respectively while the crystal was easily grown the larger size with a regular shape (Fig. 3b) in  $\text{NH}_4\text{I}$  solution. This disparity might be assigned to the greater solubility of  $\text{CuI}$  in the case of  $\text{NH}_4\text{I}$  that remarkably increased the crystal growth velocity and readily achieved high crystallinity.

In order to verify the elemental composition of the  $\text{CuI}$  crystals grown using different cosolvents, the energy-dispersive X-ray (EDX) spectra (Fig. 3c) were determined by a computer controlled field emission scanning electron microscope SEM (JSM-6700F), which was equipped with an EDX spectrometer. The semi-quantification of elements content within the crystals from the spectra was summarized in table 1. As can be seen, the crystals grown using  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  contained trace halide ion ( $\text{Cl}^-$  or  $\text{Br}^-$ ) impurities, respectively. The EDX spectrum of the crystal generated from  $\text{NH}_4\text{I}$  solution didn't show any signal stemmed from other elements except Cu and I, confirming that the product was consistent with the pure  $\text{CuI}$  crystal and no other foreign impurities. From table 1, it can be calculated that the elemental ratio of the Cu/I was about 0.96:1, which was close to the standard stoichiometric composition. Compared to  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ , the high quality crystals were gained more easily when  $\text{NH}_4\text{I}$  was used as cosolvent and no extra impurities were introduced into the crystal lattice. Furthermore, the trace amount of iodine, which was produced in  $\text{NH}_4\text{I}$  solution by the oxidation shown in eqs 4, acted as the dopant that induced p-type conductivity to  $\text{CuI}$ <sup>9</sup> (i.e., iodine atoms in the bulk crystal accept electrons from the valence band to form I<sup>-</sup> and create hole within the valence band).

In summary, three different cosolvents ( $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$ ) were tested to grow  $\text{CuI}$  single crystal and  $\text{NH}_4\text{I}$  was proved to be a better cosolvent which led to larger size crystals with higher quality. With the aid of  $\text{NH}_4\text{I}$ , the previous procedure for the seed growth was carried on again for 24 days and a light yellow transparent triangular single crystal with side



length over 15 mm and thickness of about 5 mm was obtained (Fig. 4a). The well formed crystal displayed a slightly darker color compared with the CuI crystal as given in Fig. 3(b) and this consequence was associated with different iodine ( $I_2$ ) concentration of crystal in solutions.<sup>16</sup> The maximum cross-sectional photograph of the as-grown crystal shown in Fig. 4(b) combined with the XRD pattern of the crystal plate was depicted in Fig. 4(c). A strong diffraction peak of the (111) plane and the coexistence of the (222) and (333) facets indicated that the CuI crystal growth in  $NH_4I$  solution was preferably oriented along the [111] direction.

### **Characteristics of CuI Crystals grown with $NH_4I$ cosolvent**

CuI crystals have been found with widespread applications in electronics and optoelectronics due to their remarkable properties, thus we further performed optical transmission, Hall-effect measurements and photoluminescence spectrum on the CuI single crystals grown in the presence of  $NH_4I$ . The Z-cut crystal plates of about  $10 \times 8 \times 1 \text{ mm}^3$  in size were polished at face (111) for analyses. Optical transmission spectrum was recorded on a PE-lambda 900 spectrometer with performing wavelength ranging from 200 to 900 nm as depicted in Fig. 5(a). The CuI single crystal had a transparent window with high optical transmission efficiency reached 80% in the range of visible light, demonstrating that the crystal exhibited high quality. In ultraviolet region, it is observed that the sharp absorption edge was centered at 411 nm (about 3.01 eV), which was the characteristic for direct inter-band transitions and close to the value reported in the literature.<sup>6</sup>

The electronic properties of the CuI crystal were investigated on a USA KEITHLEY 2400 employing the standard four-probe method at room temperature. Conductive silver pastes were coated on each corner of the crystal platelet as four electrodes to provide the Ohmic contacts. An AC magnetic field, which was applied perpendicular to the surface of the platelet, was used for the measurement to obtain a Hall voltage with a high signal-to-noise ratio. As a result, the positive Hall coefficient  $R_H = 143.7 \text{ cm}^3 \cdot \text{C}^{-1}$  identified that the crystal had p-type

conduction. As revealed in table 2, the carrier concentration determined from the Hall-effect measurements was  $4.08 \times 10^{16} \text{ cm}^{-3}$  and the hole mobility was  $12.81 \text{ cm}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1}$ , which was on par with that of the current p-type wide band-gap semiconductor materials (table 2). These results indicated that  $\text{NH}_4\text{I}$  cosolvent was appropriate for growing CuI crystals with not only large high-quality but also high mobility.

Fig. 5(b) showed the photoluminescence spectrum of the single crystal ranging from 370 to 500 nm, as measured on an Edinburgh FLS980 fluorescence spectrometer and irradiated with 350 nm excitation light at room temperature. There was an intensive emission viewed at around 429 nm accompanied by a secondary feature presented at about 410 nm, which is different from the single emission peak at 421 nm observed in the spectrum of CuI powder. The sharp band-edge emission at 410 nm was reasonably ascribed to inter-band excitonic transition and provided an evidence for good crystallinity,<sup>14</sup> while the broad luminescent band peaked at 429 nm was associated with the presence of traps level near the valence band maximum which probably arisen from defects. Based on the measured carrier concentration and mobility data, we speculated that the defect probably was built from excess iodine or Cu vacancies instead<sup>9</sup> and it was confirmed by the EDX results.

## Conclusion

Bulk single crystals of  $\gamma$ -CuI had been successfully obtained from the cosolvent solutions ( $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$ ) by the temperature reduction method at the range of 45~55 °C.  $\text{NH}_4\text{I}$  was approved to be a promising cosolvent for the single crystal growth due to its ability to afford a strong solubility of CuI, high growth velocity, well-developed external facets and high crystal quality. The well formed triangular CuI crystal of side length over 15 mm was bred on the self-nucleated seeds in  $6 \text{ mol} \cdot \text{L}^{-1}$   $\text{NH}_4\text{I}$  solution. It exhibited good p-type conduction (hole mobility equaled to  $12.81 \text{ cm}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1}$ ), high transmittance (over 80%), and a sharp band-edge emission located at around 410 nm. In view of its relatively high

transparency and p-type conduction, the crystal could be used as a transparent semiconductor. The present study also provided meaningful references for growing other water-insoluble crystals of relatively large size and high quality as well from aqueous solution.

### Acknowledgment

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### Figure Captions

**Fig. 1** (a) Solubility curves of CuI in  $6 \text{ mol}\cdot\text{L}^{-1}$   $\text{NH}_4\text{X}$  solutions; (b) Experimental apparatus of crystal growth by the temperature reduction method: (1) thermostatic water bath; (2) submerged pump; (3) Cu sheet; (4) glass crystallizer; (5) water seal; (6) motor; (7) heating device; (8) temperature sensor; (9) liquid paraffin; (10) a circular platform made of organic glass; (11) a seed crystal; (12) holder.

**Fig. 2** Schematic drawing of the detail growth procedure (a) and experimental parameters (b) of CuI crystals from  $\text{NH}_4\text{X}$  solution by the temperature reduction method.

**Fig. 3** (a) Powder XRD patterns of CuI crystals grown using different cosolvents and  $\gamma$ -CuI standard (JCPDS card No. 06-0246); (b) Bulk CuI crystals grown from the seeds using different cosolvents under the period of 14 days; (c) EDX spectra of as-grown CuI crystals.

**Fig. 4** (a) Light yellow and transparent CuI crystal grown for 24 days using  $\text{NH}_4\text{I}$  as a cosolvent; (b) Maximum cross-sectional photograph of the crystal; (c) XRD pattern of the crystal plate.

**Fig. 5** Optical transmission spectrum (a) and photoluminescence spectrum (b) of the CuI crystal grown using  $\text{NH}_4\text{I}$  as a cosolvent.

**Table Captions**

Table 1 Concentrations of various elements in the CuI crystals, Values were in weight%.

Table 2 Electronic properties of the CuI crystal and some current semiconductor materials.

**Table 1** Concentrations of various elements in the CuI crystals, Values were in weight%.

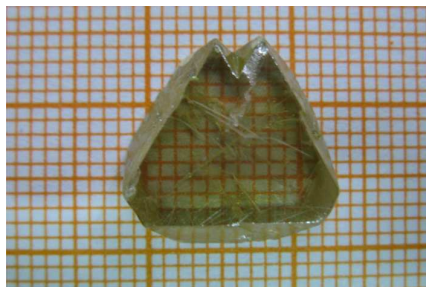
material	form	Cu	I	Cl	Br
CuI <sup>a</sup>	Bulk crystal	34.0	65.5	0.5	
CuI <sup>b</sup>	Bulk crystal	32.6	65.5		1.9
CuI <sup>c</sup>	Bulk crystal	32.5	67.5		

<sup>a, b, c</sup> The CuI crystal of this work grown in solutions: (a) NH<sub>4</sub>Cl solution; (b) NH<sub>4</sub>Br solution; (c) NH<sub>4</sub>I solution.

**Table 2** Electronic properties of the CuI crystal and some current semiconductor materials.

material	form	$R_H(\text{cm}^3 \cdot \text{C}^{-1})$	$n(\text{cm}^{-3})$	$\rho(\Omega \cdot \text{cm})$	$\mu(\text{cm}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1})$
CuI <sup>(1)</sup>	Bulk crystal	143.7	$4.08 \times 10^{16}$	11.97	12.81
Mg-doped GaN <sup>(2)</sup>	film		$1.8 \times 10^{18}$	1.5	11.5
CuAlO <sub>2</sub> <sup>(3)</sup>	film	48.6	$1.3 \times 10^{17}$	1.05	10.4
As-doped ZnO <sup>(4)</sup>	film		$9.92 \times 10^{16}$	10.35	6.08

<sup>(1)</sup> The CuI crystal of this work grown using NH<sub>4</sub>I as a cosolvent. <sup>(2)</sup> Reference 28. <sup>(3)</sup> Reference 29. <sup>(4)</sup> Reference 30.

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Transparent, centimeter-scaled  $\gamma$ -CuI single crystals with p-type conduction were successfully obtained from  $\text{NH}_4\text{I}$  aqueous solutions by temperature reduction method.