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Growth habit and optical property of γ -CuI single crystals by temperature difference

method

Yangyang Lv,^a Liwang Ye,^b Zhaojun Zhang,^b Bin-Bin Zhang,^a Zhihuang Xu,^b Xinxin Zhuang,^b

Shuhua Yao^{*a} and Genbo Su^b

^aNational Laboratory of Solid State Microstructures and Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, PR China

^bKey Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

Abstract: High quality γ -CuI single crystals have been grown by a mild temperature difference method with ammonium halide (NH_4X , X=Cl, Br, I) as cosolvents. The growth habit and optical properties of the obtained crystals are systematically examined under different cosolvents. By changing the kinds of cosolvents, the gained crystallites behave octahedron or tetrahedron morphology, respectively. All the as-grown crystals are of high transmittance (over 70%). Simultaneously, the crystals exhibit sharp band-edge emission at around 411 nm, indicating that the interband excitonic transition emission takes dominant position in the spectrum and the intensity of defect emission is dramatically depressed. The possible mechanism of how dose the cosolvents influence the growth habit and luminescence properties of the γ -CuI crystals are discussed. In particular, our results provide valuable clues to improve the luminescence performance of γ -CuI crystals.

Keywords: γ -CuI single crystal; temperature difference method; ammonium halide; growth morphology; luminescence property

1. Introduction

Recently, cubic γ -CuI has attracted steadily growing attention as it is the fastest room temperature inorganic scintillation crystal (ultrafast scintillation decay time of about 90 ps) at present.¹⁻² Besides, it is also p-type direct wide band-gap ($E_g = 3.1$ eV) semiconductor which has potential application

* Corresponding author. *E-mail address:* shyao@nju.edu.cn (S. H. Yao).

in the field of opto-electrical devices.³ However, the low intensity of ultrafast luminescence component at room temperature will be a restriction for its application as ultra-fast scintillator. Therefore, preparation of γ -CuI single crystals with excellent luminescent characteristics, especially ultrafast component luminescence, is of primary importance. In addition, the research on luminescence properties of γ -CuI crystal will also promote its application in opto-electrical devices (e.g. LEDs, detectors). Generally, the optical properties are highly dependent on the crystal quality, which is sensitive to the growth processes. In order to growing high-quality γ -CuI crystal, various approaches have been attempted, such as flux method, sublimation technique, sol-gel method, hydrothermal route and evaporation method.⁴⁻⁹ However, high quality crystals with great optical properties, such as high transmittance and luminescence emission without the defect band, are reported rarely. Therefore, it is still a great challenge for exploring the method to grow γ -CuI single crystal with sufficient size for research and practical applications.

Solution growth method is a versatile one for growing large optical-grade single crystals with low defect density.¹⁰ But γ -CuI is almost insoluble in water ($\text{p}K_{\text{sp}}=11.96$ at 300 K), cosolvent is required for solution growth of γ -CuI. On the basis of our previous studies,¹¹ we concluded that NH_4X ($\text{X}=\text{Cl}$, Br , I) cosolvents could effectively increase solubility of γ -CuI in water and be well suit for crystal growth by low-temperature aqueous solution method. In this work, a home-designed temperature difference method is used for high optical quality γ -CuI crystal growth with NH_4X as cosolvents employing a positive temperature gradient. For solution method growing crystal, the crystal growth habit of inorganic nano/micro-crystals is also of special interest owing to the unique properties and applications for materials of different morphology.¹² So the correlation between the morphology of γ -CuI crystal grains and the cosolvents were investigated. And then optical properties of the crystals grown using different cosolvents were studied. The present results give us an insight on the shape controlled synthesis of γ -CuI nano/micro-crystals and the optimization of luminescence performance of γ -CuI crystals.

2. Experimental

All reagents (A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. (P.R. China). The γ -CuI seed crystals were obtained from spontaneous crystallization experiments by cooling saturated solution. The saturated solutions of 60 °C were prepared by dissolving 1.17, 6.65 and 43.91 g of γ -CuI powder in 200 mL 6 mol L⁻¹ NH₄X aqueous solutions, respectively. Copper sheets and liquid paraffin seal were used to prevent the oxidation reaction of I anions. Several days later, the as-grown γ -CuI crystallites were obtained by slowly cooling the hot-filtered solution. Then the crystallites were washed with ultra-pure water, and dried naturally for further experiment. The crystallites with size nearly 1 mm³ were chosen as seeds mounted on a circular organic glass bar to grow large single crystals from respective NH₄X aqueous solutions, respectively. The crystal growth was performed in a home-designed apparatus. As shown in Fig. 1, the excess polycrystalline γ -CuI nutrient is placed at the bottom of the container (hot zone, 60 °C) to maintain the Cu⁺ and I⁻ ion concentration for a saturated solution and the seed is placed at the upper half (cold zone, 40 °C) surrounded by the supersaturated solution. The temperature difference between the bottom and the upper of the solution induced sufficient convection to transport the growth units to the seeds. Then as γ -CuI powder dissolved at the bottom, the seeds gradually grow into large single crystals. After 30 days, bulk γ -CuI crystals with the size up to 1 cm³ were obtained under different cosolvents. To simplify the subscript, we used the γ -CuI^a, γ -CuI^b and γ -CuI^c to represent the crystals grown from the NH₄Cl, NH₄Br and NH₄I solutions, respectively in the subsequent discussion.

X-ray diffraction (XRD) patterns were recorded on a DMAX 2500 powder diffractometer with a graphite-monochromatized Cu K_α radiation 2θ scans from 5° to 65° using a tube voltage of 40 kV and tube current of 40 mA. X-ray photoelectron spectroscopy spectrum (XPS) was performed on a Thermo Fisher Scientific Co. ESCALAB 250 equipped with monochromatic source Al K_α X-rays radiation (hν = 1486.6eV). In the XPS measurements, the binding energy (BE) scale was calibrated against the BE of C1s at 284.6 eV as an internal standard. Optical transmission spectra were determined by using a SHIMADZU UV-2550 spectrometer with performing wavelength ranging from 200 nm to 700 nm. Photoluminescence studies were carried out on an Edinburgh FLS920

fluorescence spectrometer with wavelength from 350 to 500 nm by an excitation wavelength of 325 nm. All the measurements were performed at room temperature.

3. Results and discussion

3.1 Morphology of the γ -CuI crystallites

As shown in Fig.2, crystallites (Fig.2a-2b) gained from NH_4Cl or NH_4Br solutions appear octahedral, while appear tetrahedral from NH_4I solutions (Fig.2c). The morphology of γ -CuI crystallite mainly depends on the growth rate ratio of different crystal facets. Different facets display different coordination numbers (CNS) of ions exposed on it, and the face with fewer CNS has a faster growth rate.¹³ In our experiment, the exposing ions on $\{001\}$ and $\{111\}$ faces are determined by the employed cosolvents, which decide the state of Cu^+ and I^- ions on the rate-determining interface between the crystal and solution. When NH_4Br or NH_4Cl were used as cosolvents, the concentrations of I^- and Cu^+ in the solutions are nearly equal. Thus, the contribution of Cu^+ and I^- ions to the growth habits of $\{001\}$ and $\{111\}$ faces are equivalent. And the CNS of determining ions (both Cu^+ and I^- ions) at the interface of $\{001\}$, (111) and $(\bar{1}\bar{1}\bar{1})$ faces are 2, 3 and 3, respectively. So the growth rates obey a rule as: $R \{001\} > R (111) = R (\bar{1}\bar{1}\bar{1})$. Consequently, faces $\{001\}$ disappear easily during the crystal growth process. The obtained γ -CuI crystallites often behave a growth habit of octahedron. However, when NH_4I solution was chosen as cosolvent, as concentration of Cu^+ ion was much less than I^- in the solution, thus the growth habits of $\{001\}$ and $\{111\}$ faces are mainly restricted by the interface characteristic of Cu^+ ions. And the effective CNS of Cu^+ ions of $\{001\}$, (111) and $(\bar{1}\bar{1}\bar{1})$ faces are 2, 1 and 3, respectively. Thus, their growth rates obey the rule as: $R (111) > R \{001\} > R (\bar{1}\bar{1}\bar{1})$, and $(\bar{1}\bar{1}\bar{1})$ faces always grow into the dominant exposed surface. Consequently, the obtained γ -CuI crystallites often show tetrahedron morphology.

3.2 Structure and composition characterization of the γ -CuI crystals

As depicted in Fig. 3(a), all the diffraction powder peaks in XRD patterns of the crystals prepared by different cosolvents agree with the standard (JCPDS card No. 06-0246, space group: F43m) of

γ -CuI. No reflections originated from extra phases were observed, indicating that all the as-grown crystals belong to the γ -phase with cubic structure. Then all three as-grown crystal samples were cut along the dominant exposed surface with thickness of about 1 mm and polished for XRD measurements. The XRD patterns only show the reflections from $\{111\}$ faces, confirming that the $\{111\}$ faces easily appear. In XPS experiment, a survey scan was taken to test the elements species in the crystal. XPS Cl 2p core level of γ -CuI^a crystal, and Br 3d core level of γ -CuI^b crystal were revealed in Fig. 3(c)-3(d), respectively. The Cl 2p_{3/2} and Cl 2p_{1/2} core levels appear at the binding energies of about 198.8 and 200.4 eV, respectively. And the binding energies of Br 3d_{5/2} and Br 3d_{3/2} are centered at around 68.9 and 69.8 eV, respectively. The quantification of elements content (at%) of Cl⁻¹ or Br⁻¹ impurity ions within the two crystals from the XPS spectra were 1.23% and 2.19%, respectively. The results demonstrate that γ -CuI^a and γ -CuI^b crystals contained trace Cl⁻¹ and Br⁻¹, respectively. While the XPS of γ -CuI^c crystal shows that it is of pure γ -CuI crystals without extra impurities. In the following, influence of impurities on the optical property of the as-grown crystal will be discussed.

3.3 Optical properties characterization of the γ -CuI crystals

Crystal platelets with thickness of about 1 mm were cut along (111) face and polished for optical measurements. Transmittance spectra of the as-grown γ -CuI crystals are plotted in Fig. 4(a). All the crystals show transparent windows in the range of visible light and exhibit a maximum transmittance exceeding 70%, which indicates the as-grown crystals have high optical quality. After the careful observation, we find that the transmittance of γ -CuI^c crystal is higher than that of γ -CuI^a and γ -CuI^b crystals. Besides, the γ -CuI^a, γ -CuI^b and γ -CuI^c crystals also display sharp cut down edges located at 412, 417 and 411 nm, respectively, which were the characteristics for direct-gap interband transitions [9]. The difference is possibly due to the existence of trace Cl⁻¹ or Br⁻¹ impurities in γ -CuI^a or γ -CuI^b, respectively.

Fig.4(b) exhibits the photoluminescence spectra of the as-grown γ -CuI crystals at room temperature. An asymmetrical band-edge emission of a two-peak structure is located at around 412

nm in the spectrum of γ -CuI^b crystal, while the symmetrical emissions at 412 nm and 411 nm are observed in the spectra of γ -CuI^a crystal and γ -CuI^c crystal, respectively. It should be mentioned that all the band-edge emission are sharp and has a strong intensity, indicating that the appearance of interband excitonic transition, which are also evidence for the high quality of the crystal.¹⁴ The emission band of γ -CuI^b crystal was fitted with Gaussian lineshape, and the results show that there are two luminescent peaks at approximately 411 and 419 nm, respectively. The broad band at 419 nm is the defect emission band and possibly originated from the recombination of donor-acceptor pair (DAP) emission.¹⁵ In general, the emission energy of DAP depends on the power intensity of excitation light according to previous theory.¹⁶ Thus, we tested the emission at 419 nm of the same γ -CuI^b crystal under different excitation power of incident 325 nm laser to speculate if the emission comes from DAP. As shown in Fig.4(c), P_0 is the initial power of excitation light, $P_0/e^{0.3}$ and P_0/e represents that the power is attenuated to $1/e^{0.3}$ and $1/e$ times, respectively. It shows that the peak position of the broad emission band trends toward lower energy slightly with decreasing the power of excitation light. Considering the XPS characterization, as the ion radius of Br⁻¹ ion is smaller than I⁻¹ ion, trace Br⁻¹ impurities exists in the γ -CuI^b crystal. Thus, we assume the existing Br⁻¹ ion may act as acceptor level, and the Cu interstices acts as the donor of the DAP emission. The emission at 419 nm may come from the DAP. In order to confirm the origination, the bulk γ -CuBr crystal with the size up to 5 mm was also grown using the above mentioned temperature difference method from 3 mol/L HBr aqueous solutions. The room temperature photoluminescence spectrum of γ -CuBr crystal was measured under the same condition of γ -CuI^c, as shown in Fig.4(d). As can be seen, the peak position of the emission of γ -CuBr crystals is located at 419 nm in the band-edge region ($E_g=2.95$ eV¹⁷), which is close to the broad emission band of γ -CuI^b crystal. The results indicate that the appearance of γ -CuBr phase in the as-grown γ -CuI^b crystal is another possible reason for the emission at 419 nm.¹⁸ The exact origin remains unclear and a more detailed investigation is in progress.

4. Conclusion

In this paper, we have proposed a facile and efficient approach for growing high quality γ -CuI single crystals by temperature difference method with NH_4X (X=Cl, Br, I) as cosolvents. The cosolvents have a remarkable influence both on the morphology of γ -CuI micro-crystals and the optical properties. The correlation between the crystal growth habit and the cosolvent will make it possible to produce crystallites with a desired morphology. In addition, the as-grown crystals exhibit excellent optical properties with a maximum transmittance exceeding 70% and a sharp band-edge emission. The sharp emission at 411 nm is attributed to the interband excitonic transition. While the broad emission band of the as-grown γ -CuI^b crystal at 419 nm may come from DAP emission or γ -CuBr phase in the γ -CuI^b crystal. These results provide an important reference for investigating the luminescence mechanism of γ -CuI crystals and improving the luminescence property, especially the fast component luminescence, by doping under mild growth conditions.

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Figure captions:

Fig. 1 Experimental apparatus for the temperature difference method using NH_4X (X=Cl, Br, I) as cosolvents. A positive temperature gradient was employed, where polycrystalline nutrient was placed at the bottom of the container (hot zone, 60 °C) and the seed was placed at the top of the container (cold zone, 40 °C). Owing to steady convection caused by the temperature difference, the fluid flows from the dissolution zone to the growth zone, as a result the crystal growth proceeds.

Fig. 2 γ -CuI crystallites prepared by spontaneous crystallization and bulk γ -CuI crystals grown on the seed crystals using temperature difference method from the solutions: (a) NH_4Cl , (b) NH_4Br (c) NH_4I .

Fig. 3 (a) Powder X-ray diffraction patterns and (b) XRD patterns of the exposed surfaces of the as-grown γ -CuI single crystals using different cosolvents; (c) The representative Cl 2p core level spectrum of γ -CuI^a crystal; (d) The representative Br 3d core level spectrum of γ -CuI^b crystal.

Fig. 4 (a) Optical transmission and (b) Photoluminescence spectra of different as-grown γ -CuI crystals; (c) Photoluminescence spectra of γ -CuI^b crystal under excitation of different power of incident laser; (d) The comparison of room temperature photoluminescence spectra of the γ -CuI^c and γ -CuBr single crystal.

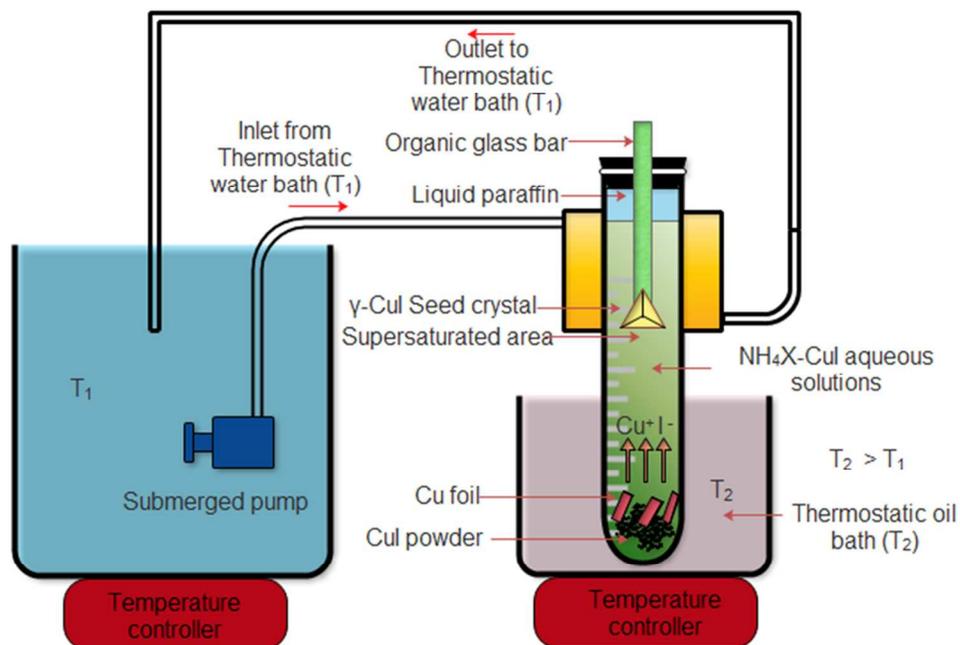


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99x65mm (300 x 300 DPI)

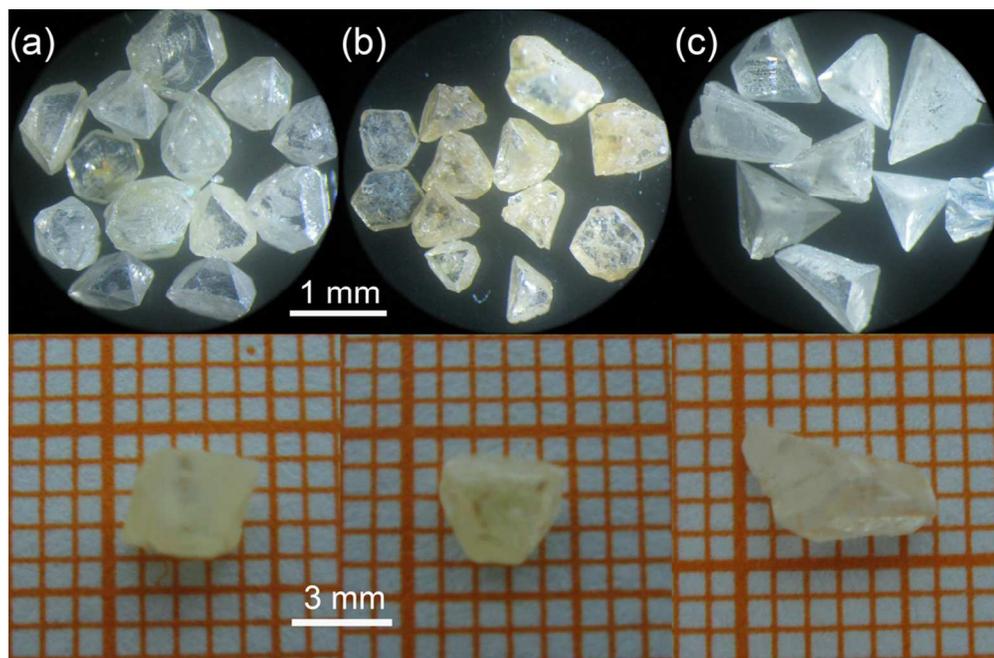


Fig. 2 $\gamma\text{-CuI}$ crystallites prepared by spontaneous crystallization and bulk $\gamma\text{-CuI}$ crystals grown on the seed crystals using temperature difference method from the solutions: (a) NH_4Cl , (b) NH_4Br (c) NH_4I .
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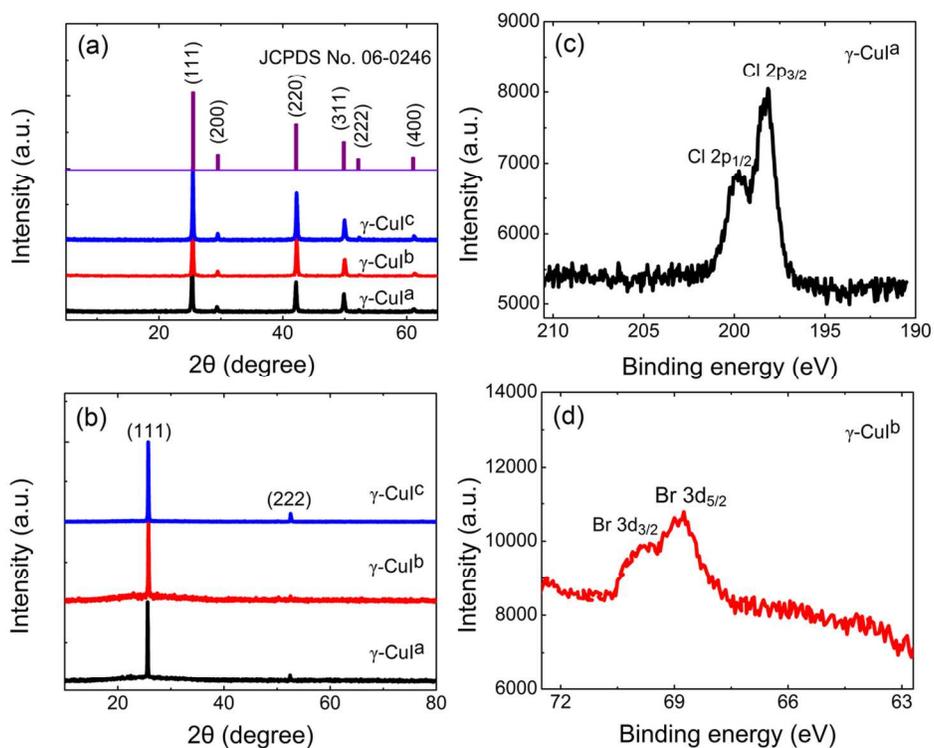


Fig. 3 (a) Powder X-ray diffraction patterns and (b) XRD patterns of the exposed surfaces of the as-grown γ -CuI single crystals using different cosolvents; (c) The representative Cl 2p core level spectrum of γ -CuI^a crystal; (d) The representative Br 3d core level spectrum of γ -CuI^b crystal.
120x97mm (300 x 300 DPI)

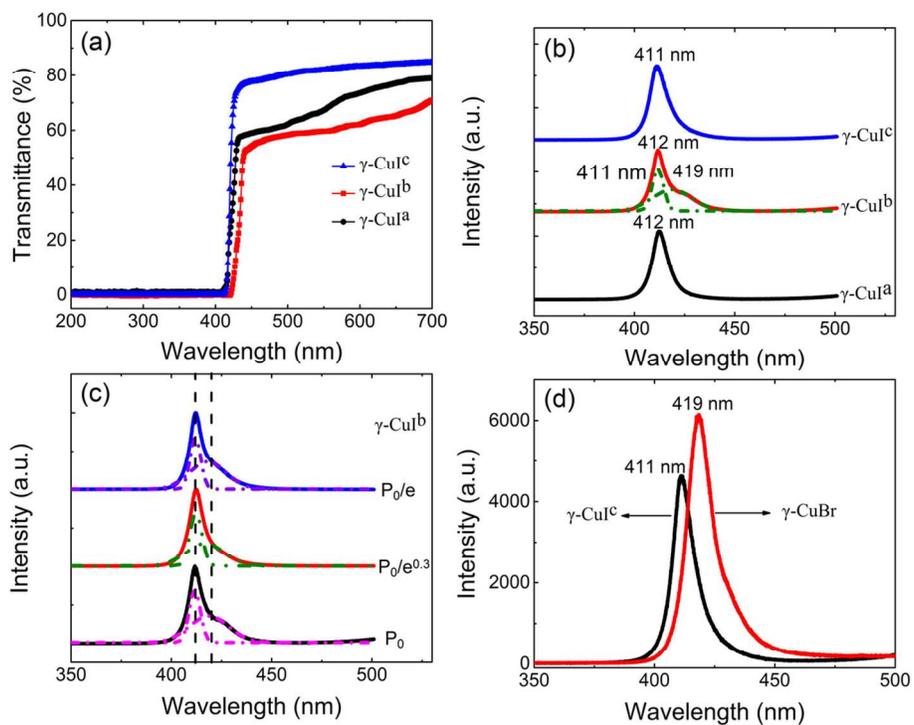


Fig. 4 (a) Optical transmission and (b) Photoluminescence spectra of different as-grown γ -CuI crystals; (c) Photoluminescence spectra of γ -CuI^b crystal under excitation of different power of incident laser; (d) The comparison of room temperature photoluminescence spectra of the γ -CuI^c and γ -CuBr single crystal. 116x90mm (300 x 300 DPI)