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Mechanism of band-edge luminescence in cuprous iodide single crystals

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ABSTRACT

The photoluminescence spectra of CuI crystals using synchrotron radiation as an excitation light source were obtained at 60 K. The emission peaks at 405, 415, 420 and 443 nm were observed. The possible origins of these peaks were discussed by the temperature dependence of luminescence spectra for CuI material. Meanwhile, the photoluminescence spectra of CuI powder with different excitation intensity were measured and the ultrafast luminescence component of CuI crystals was warranted to be attributed to the recombination of donor acceptor pair. Furthermore, the excitation process was studied by measuring the photoluminescence excitation spectra of CuI crystals and powder.

1. Introduction

Cuprous iodide (CuI) has attracted a great deal of attention [1–3] because of its unusual properties such as wide band gap, negative spin–orbit splitting [4], anomalous diamagnetism behavior [5], and large ionicity [6]. CuI has three crystalline phases: α, β and γ [7], and normally exists in the low-temperature γ-phase with zinc blend structure. In recent years, γ-CuI has attracted steadily growing interest due to its ultrafast scintillation property [8,9] with a decay time of about 90 ps at room temperature and it is the fastest inorganic scintillation crystal at present.

It is known that the photoluminescence is one of the most important properties of a scintillator material [10,11]. Thus the luminescent characteristics of CuI are of primary importance for its scintillation use. However, previous research on luminescence properties of CuI film and crystalline material has mainly focused on its photoluminescence spectra at room temperature [2,3,12]. To our knowledge, there are few papers about the temperature dependence of photoluminescence spectra of CuI crystals and there is little research on the photoluminescence excitation (PLE) spectra of CuI material, especially in the vacuum ultraviolet (VUV) region. Recently, large CuI single crystals up to 1 cm on edge have been successfully obtained by solution method in our laboratory [13]. Therefore, it is necessary to study the luminescence properties of CuI crystals so as to understand its luminescence mechanism and these results can help us to improve the luminescence intensity of CuI crystals for its scintillator applications.

2. Experimental

In this paper, the CuI single crystals were prepared from acetonitrile solvent by evaporation technique [14]. The different CuI samples such as transparent, brown and black crystals were obtained with different growth conditions. The X-ray diffraction patterns revealed that all the samples belong to the γ-phase CuI with zinc blende structure. The photoluminescence (PL) spectra of CuI crystals and powder were measured at the vacuum ultraviolet (VUV) Station (Energy of electrons = 800.0 MeV) of National Synchrotron Radiation Laboratory, Hefei, China. The typical spectral resolution of the primary monochromator (1 m Seya-Namioka) and the secondary monochromator (Spectrapro-275) is 0.4 and 2 nm, respectively. The pressure in the vacuum chamber during the measurements was 1×10^{-4} Pa. The excitation and emission spectra were detected by a Hamamatsu H5920-01 photomultiplier. The excitation spectra were corrected by the photoflux of the excitation beam using the excitation spectrum of sodium salicylate as standard. The spectra were measured in the temperature range of 60–296 K. In order to research the influence of the excitation intensity on the CuI luminescence, the PL spectra of CuI powder on a Perkin-Elmer LS 55 luminescence spectrophotometer were also measured at room temperature. The LS 55 uses a pulsed Xenon flash lamp (power equivalent to 20 kW for 8 μs duration, pulse width at half height <10 μs) as a source of excitation.

3. Results and discussion

Fig. 1 shows the PL spectra of different CuI crystals under the excitation of synchrotron radiation vacuum ultraviolet–ultra violet (VUV–UV) at 60 K. The inset of Fig. 1 presents the enlarged drawing of the PL spectrum of black CuI crystals. Due to the increase of the defect concentration in the brown and black CuI crystals [15], the

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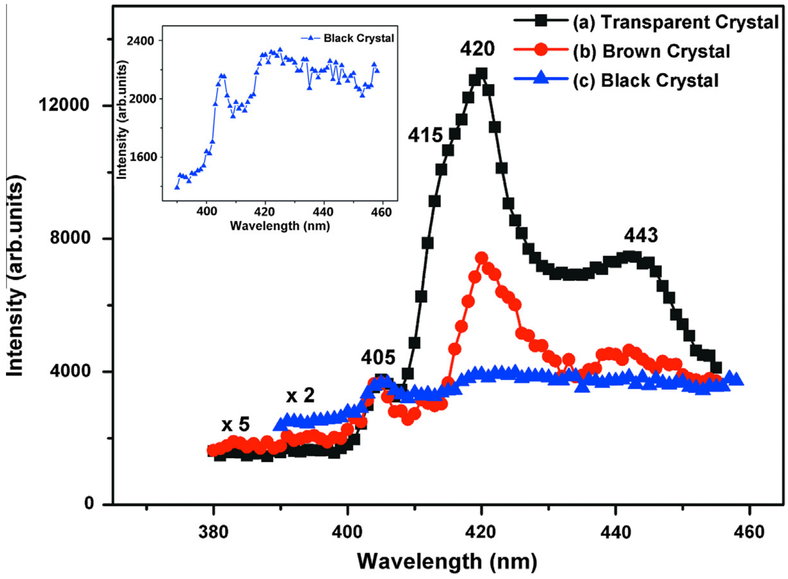
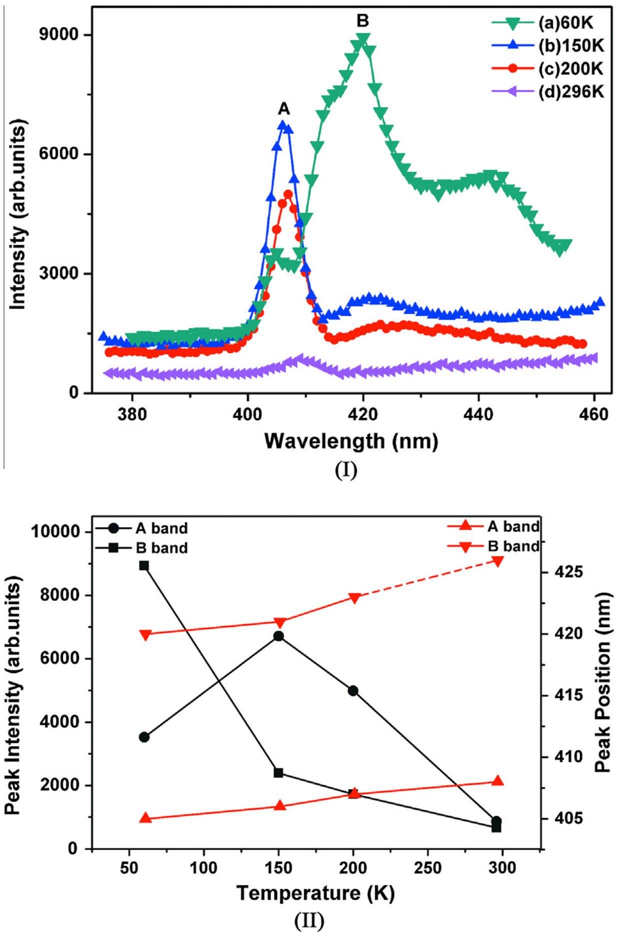


Fig. 1. PL spectra of as-grown CuI crystals at 60 K with excitation wavelength of 232 nm: (a) transparent crystal; (b) brown crystal; (c) black crystal. The inset showing the magnification of curve c. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

photoluminescence (PL) spectra vary with different crystal quality. There are two significant peaks in all the spectra. One peak situated at about 405 nm, which has been proved to be due to free-exciton (FE) emission [16]. The other peak of 420 nm may be assigned to the DAP recombination. Also, it was also found that the relative luminescence intensity ratio of 420 nm peak to 405 nm peak is the lowest for black CuI crystals and it is the highest for transparent CuI crystals. Therefore, it can be concluded that the luminescence of CuI is greatly influenced by the quality of as-grown crystals and the intensity of the fast luminescence component in transparent CuI crystals is very high, which indicates this material is an ideal ultrafast scintillator at low temperature [8]. On the other hand, it can be seen that there are one peak at 443 nm and one feature at 415 nm from the spectrum of transparent crystal (Curve of transparent CuI crystal in Fig. 1).

In order to understand the origin of the emission peaks, the temperature-dependent photoluminescence of transparent CuI crystals is shown in Fig. 2(I). The emission peaks at around 405 and 420 nm are marked as A and B, respectively. From Fig. 2(I), it can be seen that the emission feature at 415 nm and the emission peak at 443 nm disappear with increasing the temperature to 150 K. This thermal quenching behavior of CuI crystals is rather similar to that of bound-exciton (BE) recombination in other semiconductors, such as ZnO, GaN and AlN [17,18]. Meanwhile, the 415 nm emission feature lies between the region of FE emission and DAP emission, thus it is reasonable to believe that the origin of 415 nm emission feature is attributed to the BE emission [19]. In other CuI experiment [12], the similar temperature dependence of 443 nm emission peak is also observed. Its origin is assumed to be very complex and it may be attributed to the recombination interaction of various luminescence centers.



(I)

(II)

Fig. 2. (I) Temperature-dependent emission spectra of transparent CuI crystal under excited by 232 nm of synchrotron radiation; (II) Temperature dependence on the intensity and position of A and B emission peaks. The black lines represent the peak intensity and the red lines represent the peak position. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

As shown in Fig. 2(I), the emission peaks at A and B are always present in the spectra of CuI crystals from 60 K to 296 K. Fig. 2(II) shows the temperature dependence of the luminescence intensity and position of A and B emission peaks. It can be seen that the luminescence intensity of the FE emission (labeled as A) is increased with increasing temperature from 60 K up to 150 K and then it is decreased with further increasing temperature to room temperature. At low temperature, the free excitons are trapped to defects or impurities, forming bound excitons. It results the