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Photoluminescence of Yb^{3+}-doped $CuInS_2$ single crystals prepared by In-flux and chemical vapor transport methods

N. Tsujii*, Y. Imanaka, T. Takamasu, H. Kitazawa, G. Kido

National Institute for Materials Science, Sengen 1-2-1, Tsukuba 305-0047, Japan

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Abstract

We ⋊ have grown bulk single crystals of Yb-doped $CuInS_2$ by In-flux and chemical vapor transport methods, and have studied their magnetic and optical properties. Magnetic susceptibility measurements reveal that the concentrations of Yb actually doped are in the range of 1×10^{18} to $3 \times 10^{19}\,cm^{-3}$, one order of magnitude smaller than the nominal concentrations. Photoluminescence from the Yb^{3+} center has been clearly observed at low temperatures. The spectra shapes show that the Yb ions occupy crystallographically one site. The crystals grown by the chemical vapor transport exhibited most pronounced luminescence from the Yb center.

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Keywords: Semiconductors; Crystal growth; Impurities in semiconductors; Luminescence

1. Introduction

Chalcopyrite compounds of the I-III-VI_2 type formula have been attracted as candidate materials for optoelectronic devices. They are known to show high efficiency for solar cell applications. We have been interested in these compounds as promising materials for light emitting applications as well. They have several advantages for host materials in which rare-earth ions can be effectively incorporated as luminescence centers: most of the chalcopyrite compounds have direct energy gaps with energies ranging from ultraviolet to infrared region, so they can effectively excite rare-earth ions by the electron-hole recombination energy. Moreover, the chalcogen atoms like S or Se have larger electronegativity than the pnictogen atoms like P or As of III–V semiconductors, which possibly enables high concentration of rare-earth ions to be incorporated in thermally stable forms.

Although rare-earth doped semiconductors have been widely studied, only a few works have been reported for rare-earth doped chalcopyrite systems. These include $CuAlS_2$:Tb [1], $CuAlSe_2$:Er [2], and Yb-doped $CuGaS_2$, etc. [3]. We have chosen the compound $CuInS_2$ as a host material. Although rare-earth doped $CuInS_2$ system has not been studied so far, this compound seems to be most suitable to dope rare-earth ions, because ionic radius of In atom is comparable to those of rare-earths.

$CuInS_2$ has a direct band gap of 1.53 eV. We hence have prepared single crystals of Yb-doped $CuInS_2$. The intra-*f* transition of Yb^{3+}, $^2F_{5/2}$–$^2F_{7/2}$, needs the energy of 1.2 eV, well matches to the band gap energy of $CuInS_2$. We have previously reported the photoluminescence of $CuInS_2$:Yb single crystals prepared by an indium-flux technique [4]. This work was motivated to investigate the spectra variation of Yb^{3+} in high magnetic fields. However, the Yb-related luminescence was relatively weak for the In-flux crystal. In this paper, we have prepared $CuInS_2$:Yb crystals with several different conditions and technique, in order to test the efficiency of $CuInS_2$:Yb compound as luminescent materials.

2. Experimental

Single crystals of $CuInS_2$:Yb have been prepared by an In-flux technique as well as a chemical vapor transport method.

* Corresponding author.
E-mail address: tsujii.naohito@nims.go.jp (N. Tsujii).

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For the In-flux grown crystals, details of preparation were described previously [4]. Nominal compositions of Yb were 0.3 and 3 mol%. Hereafter, we refer these samples to 'Yb-1' and 'Yb-2', respectively. Non-Yb-doped crystals were also prepared by the In-flux technique.

Chemical vapor transport (CVT) grown crystals were prepared in an evacuated silica tube using I_2 as a transport agent. The nominal composition of Yb was 1 mol%. I_2 was charged in the ratio of 5 mg/cm^3. The silica tube was heated in an electric furnace, keeping one end at 850 °C and the other at 830 °C for 2 weeks.

Single crystals were obtained with sizes of several millimeters as shown in Fig. 1. (1 0 1) plane was found to be the dominating face by X-ray diffraction. Powder X-ray diffraction was performed to check the sample quality, the results of which showed that the single phased samples with the chalcopyrite structure were formed without any second phase. Magnetic susceptibility was measured in order to estimate the concentration of Yb, using a superconducting quantum interference device (SQUID) magnetometer of Quantum Design Co. at the field of $H = 1$ T. Photoluminescence spectra were measured at low temperatures (1.6 or 4.2 K, and 77 K). A solid green laser (532 nm) was used for an excitation source. Signals were collected with a CCD detector.

3. Results and discussion

In Fig. 2, magnetic susceptibilities $\chi(T)$ of $CuInS_2$:Yb crystals are shown. $\chi(T)$ of the non-doped $CuInS_2$ is temperature independent and diamagnetic. Those of Yb-doped crystals increase at low temperature, which is attributed to Yb^{3+} ions. The data follow a Curie-Weiss law:

$$\chi(T) = \frac{C}{T-\theta} + \chi_0, \tag{1}$$

where C, θ, and χ_0 are the Curie constant, Weiss temperature, and the temperature independent susceptibility, respectively. The Curie constant is written as $C = Np_{\mathrm{eff}}^2/3k_{\mathrm{B}}$, where N, p_{eff}, and k_{B} represent the number of magnetic ions, effective Bohr magneton of the ion, and the Boltzmann constant, respectively. Since the expected value of p_{eff} for Yb^{3+} around room temperature is 4.54 μ_{B}, one can estimate the concentration of Yb^{3+} from the Curie constants. We have fitted the $\chi(T)$ data in Fig. 2, and have estimated the Yb^{3+} concentration. The results are listed in Table 1.

The concentrations of doped Yb ions are found to be one order of magnitude smaller than the nominal compositions. Nevertheless, Yb concentration of the order of 10^{18} cm^{-3} is much higher than the solubility limit of Tm^{3+} ions to GaAs

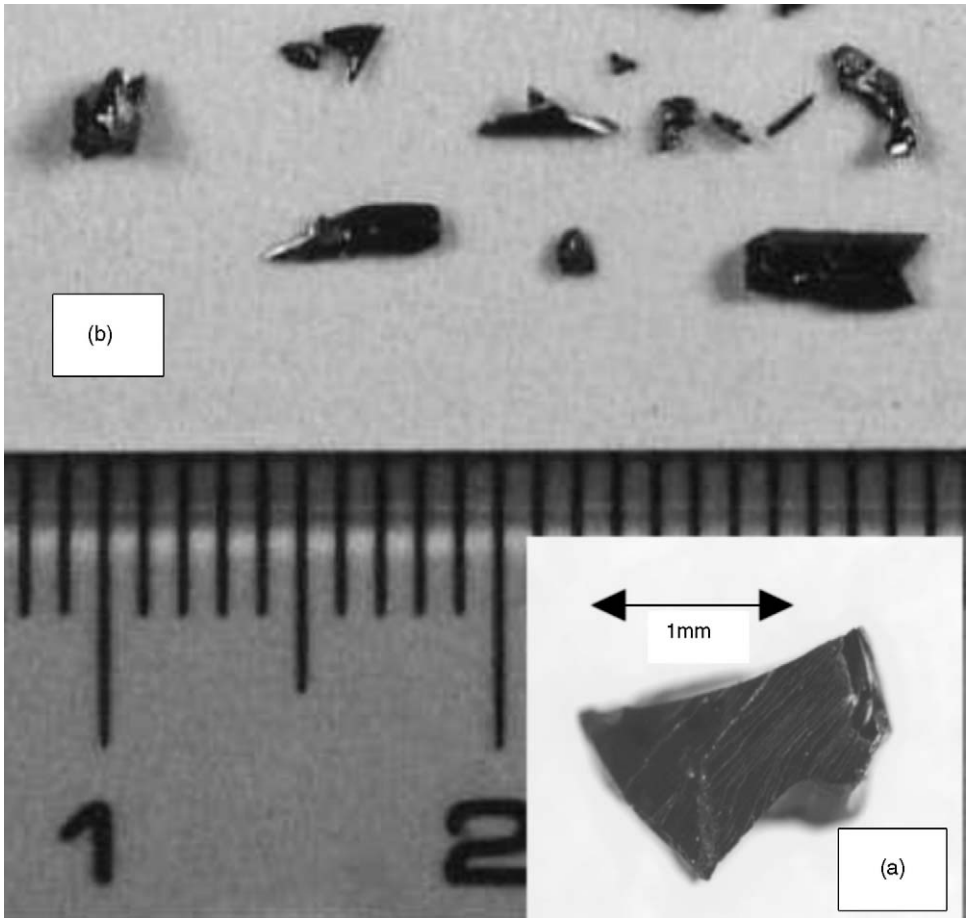

Fig. 1. Crystals of $CuInS_2$:Yb grown by an In-flux technique (a), and by a chemical vapor transport method (b).

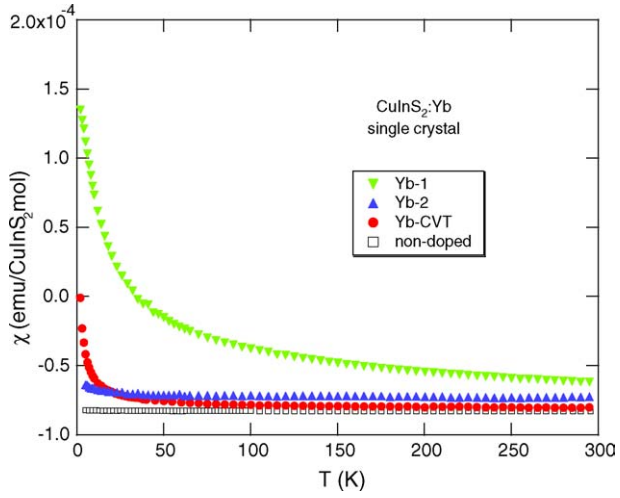

Fig. 2. Magnetic susceptibility χ of the $CuInS_2$:Yb single crystals measured at $H = 1$ T.

[5]. We can hence conclude that $CuInS_2$ is suitable as a host material to which rare-earth ions are doped in relatively high concentration.

From the Curie-Weiss fitting for the data of Yb-2 crystal, we have obtained a large negative Weiss temperature $\theta \sim -70$ K. This indicates a strong antiferromagnetic interaction. However, one cannot attribute this to the magnetic interaction between Yb^{3+} ions, because the Yb ions are too dilute to develop such a strong interaction. We therefore suggest that the large negative θ is due to the single-site interaction, possibly the coupling between 4*f* and the valence electrons. Similar results are reported for InP:Yb bulk crystals [6]. It is notable that InP:Yb exhibits remarkable phonon-side-band luminescence [7], implying the strong coupling of 4*f* and the host band. To elucidate these coupling effect, microscopic measurements such as nuclear magnetic resonance/relaxation on bulk crystals would be powerful.

In Fig. 3, photoluminescence spectra of $CuInS_2$:Yb crystals are shown. Several peaks are observed, and are classified into three kinds of luminescences, as are marked by E, D, and Yb. The wavelength of the peaks E corresponds to the energy gap of $CuInS_2$, 1.53 eV $\simeq$ 810 nm. They are hence attributed to the recombination of free and/or bound excitons [8]. The excitonic peak is broader in Yb-2 crystal than in Yb-1. This is consistent with the higher Yb concentration in Yb-2 crystal. For the non-doped $CuInS_2$ crystal, the excitonic peak is

Table 1
Concentration of Yb ion nominal and estimated from the magnetic susceptibility

Crystals	Nominal Yb	Estimated
Yb-1	0.003	$1 \times 10^{-4}(1 \times 10^{18}\,\mathrm{cm}^{-3})$
Yb-2	0.03	$3.7 \times 10^{-3}(3 \times 10^{19}\,\mathrm{cm}^{-3})$
CVT	0.01	$3 \times 10^{-4}(3 \times 10^{18}\,\mathrm{cm}^{-3})$
Non-doped	–	$\leq 2 \times 10^{-5}(\leq 2 \times 10^{17}\,\mathrm{cm}^{-3})$

The unit of concentration is per $CuInS_2$ formula unit. Concentration of non-doped crystal is that for spin $S = 1/2$ and $g = 2$ paramagnetic impurities.

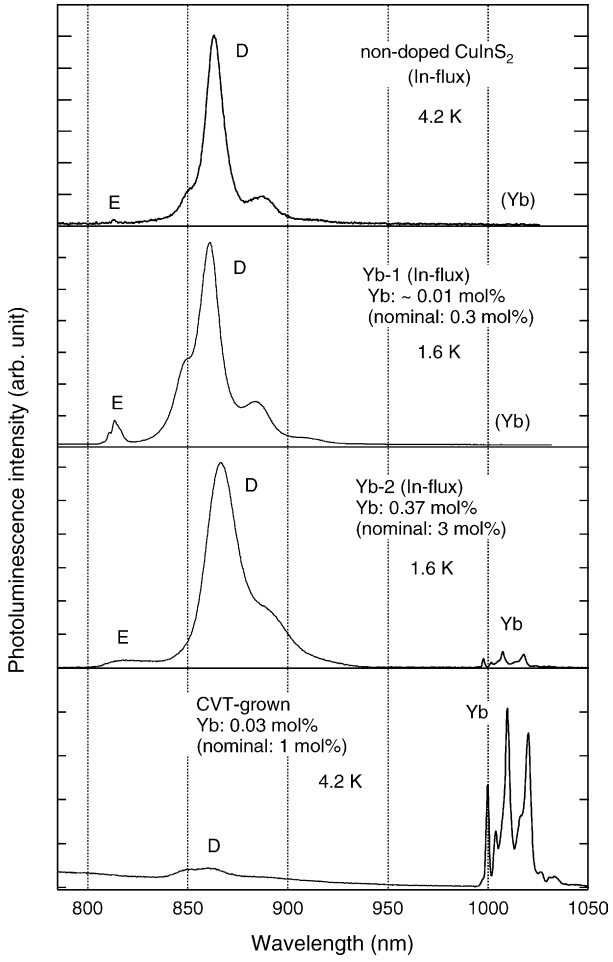

Fig. 3. Photoluminescence spectra of $CuInS_2$:Yb single crystals excited by a green laser (532 nm) measured at $T = 4.2$ or 1.6 K. Peaks marked by E, D and Yb indicate luminescences from the exciton, defects and Yb^{3+} center, respectively.

weaker than in the Yb-doped crystals. This is provably because the non-doped crystal was measured at slightly higher temperature (4.2 K) than Yb-1 and Yb-2 (1.6 K).

Peaks marked by D are observed at longer wavelength than that of the band gap. Similar peaks are also observed for non-doped $CuInS_2$ crystals [4,8,9], and are assigned to the defect (donor–acceptor recombination) luminescences [9].

The most important feature in Fig. 3 is the observation of sharp luminescence peaks around the wavelength of 1000–1040 nm. These are assigned to the luminescence of Yb^{3+} intra-*f* transition between $^2F_{5/2}$-$^2F_{7/2}$ spin-orbit levels. There are several split peaks in this energy region. This is due to the crystal field effect, which lifts the degeneracy of the spin-orbit multiplets. The peak shapes of Yb-2 and the CVT-grown crystals are essentially identical, though the relative intensity differs significantly. In addition, our previous study has shown that the magnetic-field variation of the peaks are explained by a Yb^{3+} center in the tetragonal symmetry [4,10]. These facts suggest that Yb ions occupy crystallographically one-site, most likely the In-site.

For Yb-1 crystal, Yb-related luminescence has not been observed though magnetic susceptibility has indicated the existence of Yb^{3+}. Higher Yb concentration may be needed to observe Yb-related luminescence. For the CVT-grown crystal, D peaks are remarkably suppressed and the Yb-related luminescence is pronounced compared to the data for Yb-2. This indicates that the CVT grown crystal is very pure with less defects.

Although the observation of excitonic peaks in Yb-1 and Yb-2 crystals indicates that the crystals are well grown, their defect-related peaks are much larger than that for the CVT-grown crystal. This may be partially due to the difference of the surface state; photoluminescence measurements for Yb-1 and Yb-2 crystals were performed on a cleaved plane (cleaved at room temperature in air), whereas an as-grown surface was used for the case of the CVT-grown crystal. Therefore, defects are easily formed at the surface of Yb-1 and Yb-2 crystals, while surface defects would be terminated for the CVT-grown crystal.

It is also noted that no excitonic peaks are observed for the CVT-grown crystal. This fact suggests that the electron-hole recombination energy is effectively transferred to Yb ions, resulting in the absence of excitonic peaks. For the In-flux grown crystal (Yb-2), the coexistence of the excitonic and the Yb-related peaks suggests that the electron-hole recombination energy is not effectively transferred to Yb ions. The origin of this difference is unclear. Meanwhile, the strong Yb-related emission in the CVT grown crystal would suggest that $CuInS_2$:Yb is a useful material for light emitting source and is also suitable to investigate the energy transfer mechanism from host to 4*f* elements, which is still under debates [11]. In addition, it is notable that the bandgap of $CuInS_2$ is very close to that of GaAs (1.5 eV). This fact limits the probability of non-doped $CuInS_2$ for a light-emitting material, because commercial GaAs for this purpose is already available. On the other hand, GaAs is not useful for the Yb-related luminescence, owing to the deep electron-trap level around Yb [12]. Comparison of rare-earth doped $CuInS_2$ and GaAs would be interesting from the basic point of view.

In Fig. 4, photoluminescence spectra of $CuInS_2$:Yb measured at 1.6 or 4.2 K and 77 K are shown. Panel (a) shows the data for Yb-2 crystal, but the measurement was performed several month after the measurement for Fig. 3. This delay resulted in the enhancement of the D peaks, as can be seen in the figures, suggesting that the D peaks are mainly due to the surface defects. Notably, the D peaks drastically suppressed at 77 K, while the intensity of the Yb-related peaks are not so affected. Similar tendency is seen in the data for the CVT-grown crystal, shown in the panel (b). At 77 K, the D peaks completely vanish. This may be due to that the donor and/or acceptor levels are occupied by thermally excited holes and electrons. These facts indicate that the Yb-related luminescence is the most efficient relaxation process among the relaxation mechanisms in $CuInS_2$:Yb crystals. Luminescence properties of $CuInS_2$:Yb

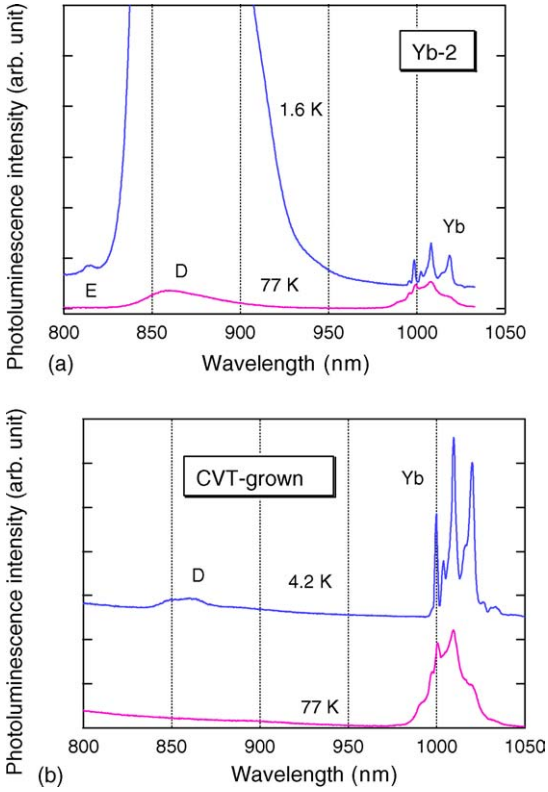

Fig. 4. Photoluminescence spectra of $CuInS_2$:Yb measured at different temperatures; (a) for flux-grown (Yb-2) crystal, (b) for CVT-grown crystal.

at elevated temperatures are of great interest, and are now studied.

4. Conclusion

We have prepared single crystals of $CuInS_2$:Yb by In-flux and chemical vapor transport methods with different nominal Yb concentrations. Magnetic susceptibilities of these crystals revealed that Yb ions can be doped in a high concentration of $10^{18}cm^{-3}$ by thermal equilibrium conditions. Photoluminescence spectra of these crystals have shown the existence of three kinds of luminescence peaks: excitonic recombination, defect (donor–acceptor) related, and the Yb-related luminescences. Although the In-flux grown crystals (Yb-1 and Yb-2) have demonstrated the excitonic peaks, suggesting the high quality of samples, Yb-related peaks of these crystals are found to be very weak or invisible even at 1.6 K. On the other hand, strong Yb-related peaks have been observed for the CVT grown crystal, with much suppressed defect-related peaks. The absence of excitonic peaks and the weak intensity of defect-related peaks in the CVT grown crystal suggest that the energy of exciton recombination is effectively transferred to Yb site. Moreover, it is revealed that the luminescence intensity of the Yb-related peaks is less temperature dependent rather than the defect related peaks, the latter of which rapidly

diminish by 77 K. This implies that $CuInS_2$:Yb is promising for light emitting materials available at relatively high temperatures.

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