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Photoluminescence studies of rare-earth-doped CuAlS$_2$ single crystals

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Abstract

The infrared photoluminescence spectra of CuAlS$_2$ doped with Tm or Er ions have been investigated. The PL emission differed strongly depending on preparation conditions. The Tm-doped crystals showed the group of PL lines due to f–f transition of Tm^{3+} at around 1130 and 1500 nm in Cu-poor crystals. On the other hand, in Er-doped crystal the well-known PL lines of Er^{3+} at around 1540 nm have been observed at 20 K. In CuAlS$_2$ crystal doped with both Er and a very small amount of Fe, not only the 1540 nm emission but also emissions at around 1210 and 1320 nm were observed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Optical communication systems based on silica fibers constitute the backbone of long distance and high-speed telecommunications. The demand for the systems has made active the investigations related to the optical device operated at energy region of intrinsic attenuation and dispersion loss minima of the fibers. Among these investigations doping of rare-earth (RE) elements, such as Er, in semiconductors attracts interest, since RE-doped semiconductors emit sharp and temperature-stable luminescence due to the RE intra-4f-shell transition as decoupled from valence interactions. Recently, in wide band gap III–V compound, such as nitrides, the strong emission peaked at 1.54 μm due to Er^{3+} has been obtained at room temperature [1], whose intensity is stronger than the emission intensity in Er-doped narrow gap semiconductor.

CuAlS$_2$ is the widest band-gap member of I–III–VI$_2$-type chalcopyrite-type semiconductor with an energy gap of 3.5 eV, wide enough to accommodate visible emission centers such as transition metal ions and RE elements. We have been working with the material doped

with RE and found sharp photoluminescence (PL) spectra due to f–f transitions in the wavelength region of 350–900 nm (1.33–3.54 eV) [2–5]. However, emissions of 1.5 μm wavelength band have not been observed in any RE-doped CuAlS$_2$. Nevertheless, we think that this material is superior to the III–V or II–VI semiconductors for doping of RE ions, since it has two cation sites different in valence (i.e., monovalent Cu and trivalent Al), although they are crystallographically equivalent. This leads to a peculiar feature for doping of RE ions. For example, in CuAlS$_2$ crystal, in which Er occupies the Cu-site, the green emission of Er^{3+} is substantially enhanced in comparison with that of Er^{3+} at the Al-site. This site preference was found to be controllable by co-doping with Fe [5]. In this paper, we report on the IR emission spectra in RE-doped CuAlS$_2$ crystals and discuss the PL spectra of RE ions in relation with the site-occupancy of the RE^{3+} ions.

2. Experimental detail

RE (Tm and Er)-doped CuAlS$_2$ single crystals were grown by the chemical vapor transport (CVT) method under three different growth conditions. In the first case, the starting materials were CuAlS$_2$ powder obtained by the direct melting and Er elements with a molar ratio of

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$CuAlS_2$ versus RE being $0.95:0.05$ (type-I crystals), whereas in the second case the crystal growth was carried out from the constituent elements (Cu, Al, S-99.9999%, RE-99.99%) at molar ratio of $Cu:Al:S:RE = 0.95:1:2.0:0.05$ (type-II crystals). In the last case the molar ratio was $Cu:Al:Fe:S:RE = 0.95:0.9995:0.0005:2.0:0.05$ using $CuFeS_2$ powder as a Fe co-dopant source (type III crystals). The source materials were sealed in a quartz ampoule (13 mm inner diameter and 200 mm in length) in vacuum (10^{-6} Torr) with iodine in the concentration of 5 mg/cm. The ampoule was placed in a two-zone furnace and the transport carried out for seven days with the temperature of the source zone being 900°C and that of the growth zone being 750°C. The resulting crystals were transparent and were either blue (type I crystals), yellow (type III crystals) in color, or colorless (type II) with the typical dimensions of $0.5 \times 1 \times 3$ mm^3, and exhibited a well-developed $\{1\,1\,2\}$ facet. For photoluminescence (PL) measurement, crystals were placed on the cold finger of a low-temperature cryostat. The emission was excited by the 514.5 nm line of an argon-ion laser, dispersed by a JASCO CT-25C monochromator, and detected by a liquid-nitrogen-cooled Ge detector (Northcoast EO-817L) and amplified by a lock-in amplifier. Corrections for the spectral response were made for all the spectra obtained.

3. Results and discussion

3.1. Tm-related emission

The IR-PL spectrum in a type II Tm-doped crystal of $CuAlS_2$ at 20 K is shown in Fig. 1(b). Some broad emission bands were observed, as well as a series of two sharp emission lines with peaks at 1136 nm and at around 1500 nm. These broad bands have been observed in $CuAlS_2$ crystals doped with high concentration of relatively large ions, which have also been observed in the type I crystals as shown in Fig. 1(a). We tentatively ascribe the broad band to some emission centers inherent to the host $CuAlS_2$, which was introduced by doping of

an ion of the larger size. The three sharp emission lines observed at 1136, 1460 and 1500 can be associated with f–f transitions in Tm^{3+} ions. Based on the Dieke's diagram the PL line at 1136 nm can be assigned to either one of the f–f transitions, $^1G_4 \rightarrow {}^3F_4, {}^3F_3 \rightarrow {}^3H_4$ and $^3H_5 \rightarrow {}^3H_6$ between the LS-coupling terms of Tm^{3+}. The fine structure emission lines at 1460 and 1500 nm were tentatively assigned to $^1G_4 \rightarrow {}^3F_3$ transitions, which share the same excited term $^1G_4$ with the blue emission due to $^1G_4 \rightarrow {}^3H_6$ transition at 477 nm, since both show a quite similar temperature quenching [3].

Temperature dependence of these emission lines between 77 K and room temperature (RT) is shown in Fig. 2. Since the 1136 nm emission disappeared above 77 K due to an overlap of the strong broad bands. As the temperature is increased the 1.5 μm line not only loses the integrated intensity but also shows a change in the line shape. The latter is caused by the appearance of new fine structures in the longer wavelength side of the 20 K emissions, which can be explained by the thermal redistribution among the crystal-field split sub-levels of the excited state $^1G_4$.

In Tm-doped type I crystals of $CuAlS_2$ the sharp emissions could not be observed as shown in Fig. 1(a) although this crystal showed 477 and 800 nm emission due to f–f transition of Tm^{3+} as reported previously [3]. The intensity of the emission at 800 nm decreased with an increase of temperature, whose temperature dependence has been interpreted in terms of the thermal redistribution of the electrons between the excited states of 477 and 800 nm emissions ($^1G_4$ and $^3F_4$ levels) via charge transfer states (CTS) of $4f^{13}L$ with Tm ions peaked at 3.1 eV, where L denotes a valence band hole. However, the 800 nm line in type II shows typical thermal quenching behavior like a B-emission at 1500 nm as shown in Fig. 2. It is suggested that the other energy transfer pass which cause thermal quenching is formed by occupation of RE on some of the other sites. We suspect that the site in question is the Cu site. Further, PLE measurements of Tm^{3+} emissions in Tm-doped type II crystals of $CuAlS_2$ are necessary.
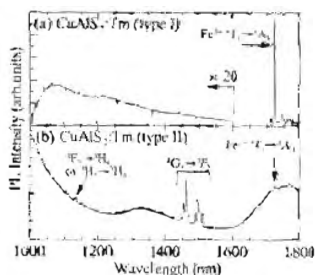

Fig. 1. IR-PL spectrum of $CuAlS_2$:Tm in (a) type I and (b) type II crystals at 20 K.

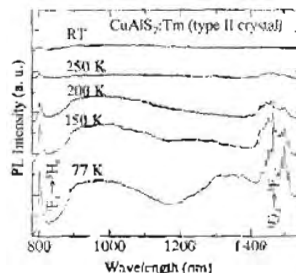Fig. 2. Temperature dependence of Tm^{3+}-related PL in $CuAlS_2$:Tm single crystal of type II.

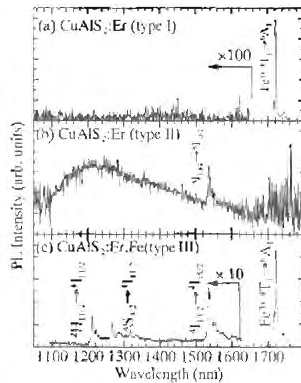Fig. 3. PL spectra of $CuAlS_2$: Er single crystal (a) type I, (b) type II, and (c) type III crystal at 20 K.

3.2. Er-related emission

All the Er-doped $CuAlS_2$ crystals show green and red emissions of Er^{3+} ion at room temperature [5]. The relative emission intensities of the three types of crystals are type I < type II < type III. Infrared emission spectra in types I, II and III single crystals of Er-doped $CuAlS_2$ are shown in Fig. 3. In types II and III crystals the well-known Er^{3+} emission lines at around 1540 nm could be obtained, which were assigned to the electronic transitions, $^4I_{13/2} \rightarrow {}^4I_{15/2}$ between the LS-coupling terms of Er^{3+} ions having $4f^{11}$ electronic configuration. The strongest line peaks at 1536 nm. Type III crystals emitted not only 1540 nm lines but also the sharp lines at around 1210 and 1320 nm. These sharp emissions were tentatively assigned from Dieke's diagram to $^2H_{11/2} \rightarrow {}^4I_{11/2}$ and $^4S_{3/2} \rightarrow {}^4I_{11/2}$ intra-4f shell transition, respectively. The levels of $^2H_{11/2}$ and $^4S_{3/2}$ are also the excited states of the Er^{3+} green emissions in the same crystals [5]. A sharp strong emission at 1720 nm as shown in Fig. 3(a) and (c) is responsible for the ligand field transition of Fe^{3+} ion [6] that is a typical impurity in $CuAlS_2$ crystal grown by CVT. In type II crystal, the Fe^{3+}-related emission could not be detected. It has been revealed that the emission is due to the substitution of the copper site of $CuAlS_2$ by iron [7]. The disappearance of the emission in type II crystal suggests that substitution of Er atoms at Cu site induces substitution of the most Fe atoms at the Al sites. The similar effect of Fe-substitution was also observed in Mo-doped $CuAlS_2$ crystals grown by CVT [8]. It is expected that the Fe ion at Al site becomes divalent to compensate the broken charge neutrality by putting the Er^{3+} at the Cu site. Although the existence of Fe^{3+} on Cu site is clear, existence of Fe^{2+} ions has also been confirmed [5]. This fact indicates that co-doping with Fe decreases the copper composition in type III crystals. $CuAlS_2$ has two kinds of bonds between a cation and an anion site; one is ionic (Al–S bond) and the other covalent (Cu–S bond) [9]. If we assume that Er-ion substitutes for the Cu-site, the environment surrounding Er can be regarded as ionic, since the second nearest neighbors consist of eight Al ions and four Cu ions. Therefore, in the Cu-poor crystals the environment may become more ionic due to an increase in Al_{Cu} antisites.

Favennec et al. [10] have reported a strong dependence of the emission intensity of the Er^{3+} ions on the band gap of the host semiconductor. In general, optical emission in the semiconductors is not as efficient as in the dielectric materials. Probably ionic bonds in dielectrics favors a formation of the required RE^{3+} than the covalent bonds. Therefore, the enhancement effect of RE^{3+}-related emission by co-doping with Fe is due to the impurity atoms inducing formation of the local bond with a more ionic state surrounding the RE atoms.

4. Conclusion

The Er- and Tm-doped $CuAlS_2$ showed several sharp emission lines in the near-infrared region. The Er^{3+}-related emissions at 1200, 1300 and 1550 nm were assigned to the electronic transition between the multiplets in $4f_{11}$ configuration, that is, $^2H_{11/2} \rightarrow {}^4I_{11/2}, {}^4S_{3/2} \rightarrow {}^4I_{11/2}$, and $^4I_{13/2} \rightarrow {}^4I_{15/2}$, respectively. The IR emissions due to Tm^{3+} with $4f_{12}$ configuration around 1500 nm were attributed to $^1G_4 \rightarrow {}^3F_3$ transitions.

The effective doping with RE on more ionic site in $CuAlS_2$ crystal enhanced RE^{3+}-related emission intensity, which is controllable by co-doping with Fe.

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