

# Optical Absorption Spectra in $\text{CuInS}_2$ Doped with Fe, Mn and Cr

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(Received April 20, 1988; accepted for publication May 28, 1988)

Optical absorption spectra were measured in single crystals of  $\text{CuInS}_2$  doped with Fe, Mn and Cr grown by the chemical transport technique. Intense absorption bands characteristic of individual transition elements were observed. Absorption bands introduced by Fe and Mn were attributed to the photoionization transition, while those by Cr were assigned to the ligand-field transition.

**KEYWORDS:** compound semiconductor, chalcopyrite type crystal, copper indium disulfide, transition atom impurity, optical absorption spectrum, photoconductivity spectrum, ligand-field transition, photoionization transition

In recent years, ternary compounds with a chalcopyrite-type crystal structure have received much interest among researchers of compound semiconductors as candidates of materials for new optoelectronic devices. The authors have been working with the characterization of below-gap absorption bands due to transition atom impurities in several chalcopyrite-type compounds.<sup>1-4)</sup> Among these compounds,  $\text{CuInS}_2$ , which has an energy gap around 1.4 eV, has been investigated for the purpose of a solar energy conversion. The present note describes optical and electrical studies on transition atoms in  $\text{CuInS}_2$ .

Single crystals of  $\text{CuInS}_2$  doped with transition atoms were grown by the chemical vapor transport technique using iodine as a transporting agent. The starting materials were powders of polycrystalline  $\text{Cu}_2\text{S}$  and  $\text{In}_2\text{S}_3$  prepared by sintering in a vacuum the mixture of constituent elements with appropriate molar ratio. Transition elements were doped by adding appropriate amounts of the corresponding sulfides into the starting materials. The source materials were sealed in a silica ampule in a vacuum with iodine (15 mg/cm<sup>3</sup> for the volume of the ampule). The ampule was placed in a two-zone furnace with the source zone-temperature 850°C and the growth zone-temperature 700°C. The typical shape of obtained crystals was a platelet with the dimensions 5 mm × 5 mm × 0.2 mm. One side of the major surface of the crystal was flat in most cases, while the other side was rough with a dendritic growth in some cases. The rough side was mirror-polished using the lapping films (3 μm, 1 μm and 0.3 μm).

Although the concentrations of transition atom impurities denoted below are only nominal, it is known from previous experiences that the nominal values can be used for the sake of the estimation of approximate concentration of transition atom impurities in chalcopyrite type crystals obtained by the chemical transport.<sup>2)</sup> Absorption spectra were measured at room temperature with a conventional single beam spectroscopic system: a halogen-tungsten lamp, a chopper, a monochromator (focal length 250 mm, with gratings blazed at 0.75 μm and 1.6 μm), a photodetector (a silicon-photocell and a liquid nitrogen-cooled InSb photocell) and a lock-in amplifier. The correction for the blank absorption was

performed by a personal computer data acquisition system. Photoconductivity spectra were also measured at room temperature by employing the same system and were corrected for the spectral response of the light measured with a thermopile.

Figure 1 shows the absorption spectra in  $\text{CuIn}_{1-x}\text{Fe}_x\text{S}_2$  with  $x=0.01$  and 0.03. Photoconductivity spectra of these crystals are also shown in the same figure indicating a good correspondence with the absorption spectrum. In this figure, a threshold of the absorption band at 0.8 eV and a shoulder at 1.0–1.1 eV can be observed. Similar below-gap absorption bands have been observed in Fe-doped crystals of  $\text{CuGaS}_2$  and  $\text{CuAlS}_2$  with a shoulder at 1.2 eV and 1.3 eV, respectively.<sup>1)</sup> The absorption band of the latter crystals has been associated with the photoionization transition of charge transfer type, i.e. the transition from the valence band to the unoccupied Fe-related deep level.<sup>5)</sup> From these considerations we assigned the below-gap absorption band observed in  $\text{CuIn}_{1-x}\text{Fe}_x\text{S}_2$  to the photoionization transition of the charge-transfer type.

In the same spectra, we also observe an increase of absorption coefficient toward the lower energy side. The increase of absorption is the tail of the absorption band centered at the energy position lower than 0.5 eV, which can be assigned to the ligand-field transition  $^5E \rightarrow ^5T_2$  in the  $d^6$  manifold of  $\text{Fe}^{2+}$  from the comparison with the case of  $\text{ZnS}:\text{Fe}^{2+}$  reported by Slack *et al.*<sup>6)</sup> We have observed the ligand-field transition of  $\text{Fe}^{2+}$  in photon

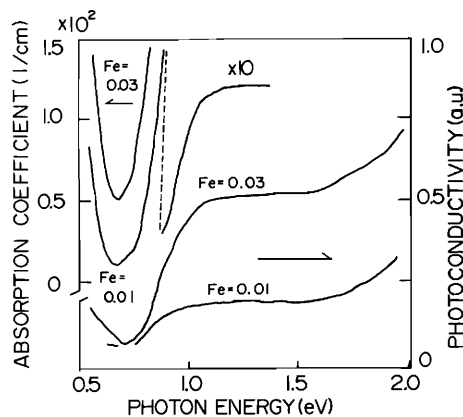


Fig. 1. Optical absorption spectra (left scale) in  $\text{CuInS}_2$  doped with Fe. Nominal concentration of Fe is described in the figure. Photoconductivity spectra (right scale) in  $\text{CuInS}_2$  doped with Fe are also plotted for comparison.

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energies ranging from 0.3 to 0.65 eV in CuGaS<sub>2</sub> doped with 6 mol% Fe.<sup>4</sup> It is a problem for future investigation to ascertain the existence of the absorption band.

In Fig. 2 a spectrum of CuIn<sub>0.99</sub>Mn<sub>0.01</sub>S<sub>2</sub> measured at room temperature is shown. An absorption band with a broad peak around 0.65 eV is extending below the absorption edge of the host material. The ligand-field transition of Mn<sup>2+</sup> in chalcopyrite was investigated in CuAlS<sub>2</sub> and the lowest excited state <sup>4</sup>T<sub>1</sub> was located above 2 eV.<sup>3</sup> It can be postulated that the crystal field strength does not differ greatly between CuAlS<sub>2</sub> and CuInS<sub>2</sub> since the ligand atom is the same for both materials. Therefore, we assume that the absorption band introduced by the manganese doping is not due to the ligand-field transition of Mn<sup>2+</sup> but to some kind of photoionization transition. We reached this assumption taking into account the absorption band observed in GaAs:Mn, in which a broad absorption band located in low energies has been attributed to photoionization from the valence band to the Mn-related deep level.<sup>7</sup> Photoconductivity studies should help the above assumptions. However, measurements of photoconductivity spectra have been unsuccessful due to the low resistivity of the manganese-doped samples and are rendered to future studies.

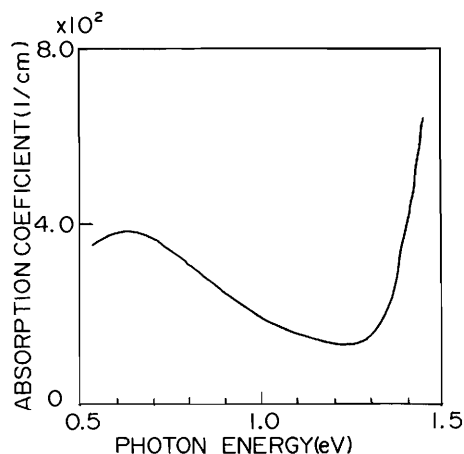


Fig. 2. Optical absorption spectrum measured in a single crystal of CuIn<sub>0.99</sub>Mn<sub>0.01</sub>S<sub>2</sub> at room temperature.

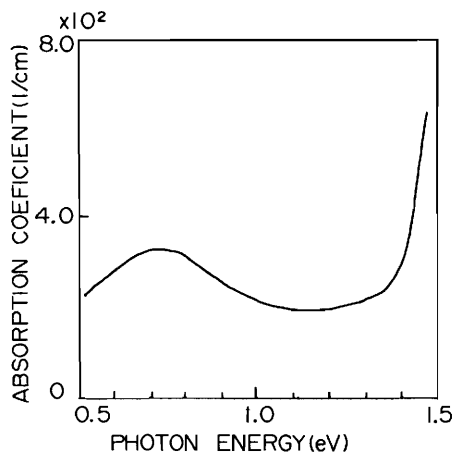


Fig. 3. Optical absorption spectrum measured in a single crystal of CuIn<sub>0.99</sub>Cr<sub>0.01</sub>S<sub>2</sub> at room temperature.

An absorption spectrum of CuIn<sub>0.99</sub>Cr<sub>0.01</sub>S<sub>2</sub> is plotted in Fig. 3. An absorption band peak at 0.75 eV, similar to that in Mn-doped crystal, is observed. However, the band width of the 0.75 eV peak is considerably narrower than that in the Mn-doped sample. No photoconduction can be observed at the absorption band. This peak may be associated with the ligand-field transition <sup>5</sup>E → <sup>5</sup>T<sub>2</sub> by comparing it with chromium doped II-VI compounds, such as ZnS:Cr.<sup>8</sup> The values of ligand-field parameters cannot be determined due to lack of data for higher excited states.

Electrical conductivity measurements were also carried out in these transition atom-doped CuInS<sub>2</sub> crystals by means of the four-probe method. The surfaces of the crystals were polished with sheets of lapping paper and etched using 60% HNO<sub>3</sub>. Gold films were evaporated for electrodes. All samples used in the present study were tested by means of the thermal-probe method and found to be of the p-type. Undoped CuInS<sub>2</sub> showed a conductivity of 1.5 × 10<sup>3</sup> Ωcm. Even with 1%Fe, the resistivity increased only by one factor. In a sample doped with 5%Fe, resistivity decreased to 5 × 10<sup>2</sup> Ωcm. The activation energy deduced from a temperature-dependence measurement was about 60 meV, indicating an existence of a rather shallow acceptor state. We also measured the resistivity in a Mn-doped sample, which showed a much reduced value of 2 × 10<sup>2</sup> Ωcm. Among the three transition atoms investigated, chromium was found to be the most suited element for increasing the resistivity of the crystal; 1%Cr-doped samples showed resistivity ranging between 3 × 10<sup>4</sup> Ωcm and 3 × 10<sup>5</sup> Ωcm. It should be noted that the resistivities were low in the samples doped with the atomic species which cause photoionization absorption below the band gap of the host crystal. Resistivity change was not so drastic in transition atom-doped samples as in vacuum-annealed samples. Detailed studies, including the temperature-dependence measurements, are now in progress to gain further information on the electronic structures of the deep levels relating to the transition atoms.

This work has been partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 62604006) from the Ministry of Education, Science and Culture which is deeply appreciated.

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