Photoluminescence and Raman spectroscopy of polycrystalline AgInTe$_2$

Andri Jagomägi*, Jüri Krustok, Jaan Raudoja, Maarja Grossberg,
Ilona Oja, Malle Krunks, Mati Danilson

Department of Materials Science, Tallinn University of Technology, 5 Ehitajate tee, Tallinn 19086, Estonia

Abstract

We studied the photoluminescence characteristics of polycrystalline chalcopyrite AgInTe$_2$. The spectra showed three bands. The first band has the maximum at 1.023 eV, and it has one LO-phonon replica with the energy of 25 meV. The second band has the maximum at 0.959 eV and two phonon replicas with the same LO-phonon energy. The third broad band has the maximum at 0.741 eV. The dependence of the spectra on the temperature and the excitation power were recorded. According to the observed j-shift and thermal quenching, the 0.959 eV band can be assigned to a donor–acceptor pair recombination with the activation energy of 35 meV. Room temperature unpolarised Raman spectrum revealed six peaks. The lines observed at 122, 140, 217, and 266 cm^{-1} are assigned to A$_1$, E$_1$, or B$_1$, E+B$_2$, and longitudinal optical E modes, respectively.
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1. Introduction

High absorption coefficient and optimal bandgap energy ($E_g \approx 1.02$ eV) make AgInTe$_2$ (AIT) an excellent material for a solar cell absorber layer. These two properties are common to other ternary chalcopyrite compounds. Accordingly, some of them like CuInSe$_2$, CuGaSe$_2$, and CuInS$_2$ have already found application in the solar cell industry. However, the cost-effectiveness of commercial solar cells still does not meet the market requirements; thus, we must continue the investigation of new materials and technologies.

AIT is one of the less studied ternary chalcopyrite compound. There are few papers where optical [1–6] and electrical [2,4,7] properties of AIT are studied. Nevertheless, there is still very little known about its defect structure. To our knowledge, only one paper is published on the PL properties of AIT [8]. The paper reports one broad band at about 0.97 eV. The same is true for the phonon studies of AIT; only one Raman spectrum of AgInTe alloy [9] can be found in the literature.

This contribution presents the first detailed PL studies of AIT. Possible origins for the bands found are discussed. In addition, we introduce the first Raman spectrum of chalcopyrite AIT and match the fitted peaks with the most probable phonon modes.

2. Experimental

Polycrystalline AIT was synthesised from high-purity (5N) elements. The components were weighed out according to stoichiometric ratio and loaded into a quartz ampoule. The ampoule with precursor materials was degassed and evacuated up to 0.0133 Pa. Then, the ampoule was sealed. The synthesis of the material started at 710 °C for 24 h. Then, the temperature of the furnace was slowly reduced with the rate of 1 °C/8 h to the crystallisation point of the AIT (692 °C; [10]). After the crystallisation, the material was cooled down to the room temperature with the rate of 10 °C/h. For the PL measurements, the freshly cleaved sample was cooled inside the closed-cycle He cryostat (tuneable from 8 to 300 K) and excited with 441.6 nm He–Cd laser, which has the maximum output power of 40 mW.

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* Corresponding author. Tel.: +372 620 3210; fax: +372 620 2798.
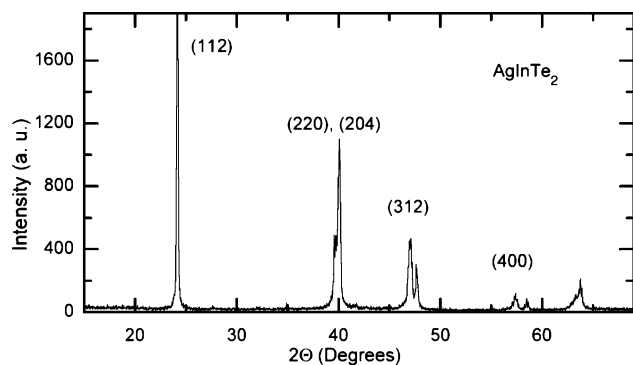*E-mail address:* andri@kiri.ee (A. Jagomägi).

Fig. 1. Measured X-ray diffraction spectrum of the AIT sample.

The PL signal was detected using the standard lock-in technique, computer-controlled SPM-2 grating monochromator (f=40 cm) and an InGaAs detector. The signal detected was corrected according to the detector sensitivity spectrum. To determine the origins of the PL bands, the spectra dependencies on temperature and excitation power were recorded. For the Raman study, the scattering of Nd/YVO$_4$ laser emission with the wavelength of 532 nm was recorded. The signal was guided through the Spex 340E monochromator and detected with the N$_2$ cooled CCD camera (Princeton Instruments LN/CCD-1100PB). The Raman studies were carried out at the room temperature.

3. Results and discussion

The XRD analysis of the synthesised samples confirmed the expected chalcopyrite AIT structure (see Fig. 1). No other phases were detected.

3.1. Photoluminescence results

The typical PL spectrum of AIT is shown in Fig. 2, where three different PL bands can be clearly distinguished. The first band (E1) has relatively narrow peak at 1.023 eV, and it has one visible LO-phonon replica with the energy of
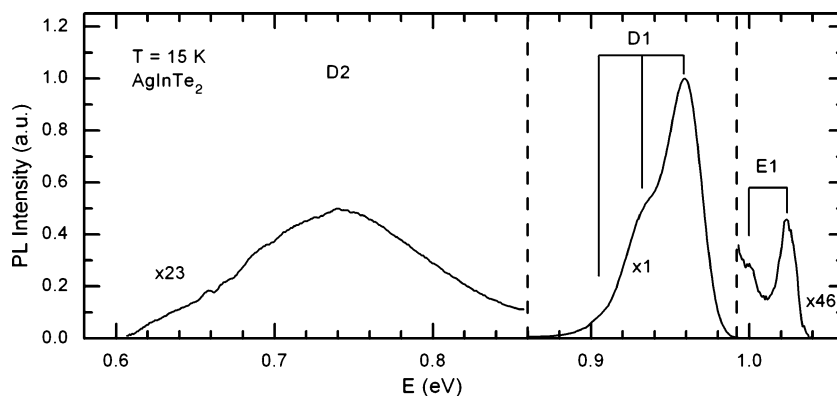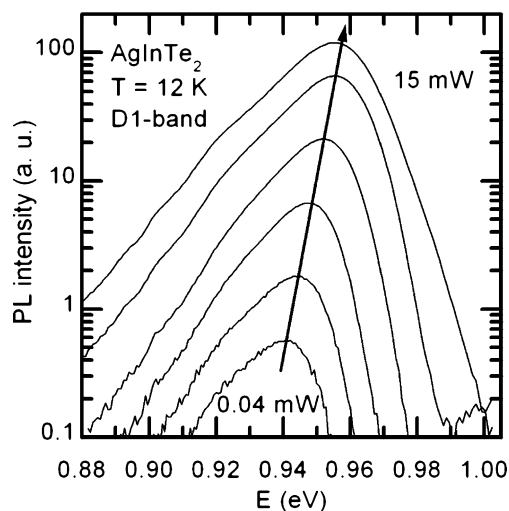

Fig. 3. Laser power dependence of the D1-band. To avoid the warming of the sample, the laser power was varied from 15 to 0.04 mW. The rate of the peak position shift is 6 meV per decade.

$\hbar\omega_{LO}$=25 meV. The second and most intensive band D1 has the main peak at 0.959 eV, and it has two LO-phonon replicas with the same phonon energy. The third band D2 is the broadest and is centred approximately at 0.741 eV. Unfortunately, neither the intensity of the E1-band nor the D2-band was high enough to record the temperature and laser power dependencies. Nevertheless, due to its narrowness, we believe that E1 may have an excitonic origin, and due to its deepness and broadness, the D2 is caused by some deep defects.

However, the intensity of the D1-band was sufficient to conduct the temperature and the laser power dependence measurements. The spectra recorded at various excitation powers from 0.04 to 15 mW are shown in Fig. 3. As it is seen, the peak position of the D1-band shifts towards higher energies with the increasing excitation power. The rate of the shift is 6 meV per decade of the laser power. This so-called j-shift is characteristic for donor–acceptor pair (DAP) recombination, because at high excitation powers, the

Fig. 2. PL spectrum of AgInTe$_2$ at 15 K. Different scales are used for different bands. Vertical lines show the positions of the LO-phonon replicas of the E1- and D1-bands. The fitting gave the corresponding phonon energy of $\hbar\omega_{LO}$=25 meV.

recombination through distant DAPs saturates. In the case of increasing laser power, the recombination rate can only increase through closely situated donors and acceptors which emit photons with higher energies than distant pairs.

To obtain information about the energy levels of the involved donor and acceptor states, the thermal quenching of the PL bands is often used. The temperature dependence of the D1-band in Fig. 4 shows the shift of the peak position towards lower energies with the rising temperature. The shift is predominantly influenced by the temperature dependence of the band gap energy. Indeed, according to Ref. [11], the band gap dependence of AIT is in the order of -36 meV from 0 to 300 K. At the same time, the shift of the D1-band in our spectra is about -12 meV from 15 to 140 K.

According to Ref. [12], the thermal quenching of DAP recombination spectrum can be fitted with the expression

$$\Phi(T) = \frac{\Phi_0}{1 + a_1 T^{3/2} + a_2 T^{3/2}\exp(-E_a/kT)},\qquad(1)$$

where Φ is integrated intensity, a_1 and a_2 are the process rate parameters, T is the temperature, and E_a is the activation energy. The fitting shows (see Fig. 5) that the activation energy of the D1-band is 35 meV.

3.2. Raman results

The unit cell of chalcopyrite structure contains eight atoms which gives rise to 24 vibrational modes. Three of them are acoustic modes, and 21 are optical modes. At the Γ
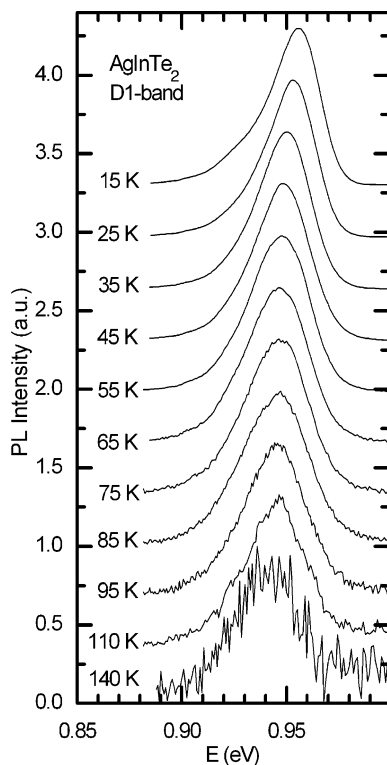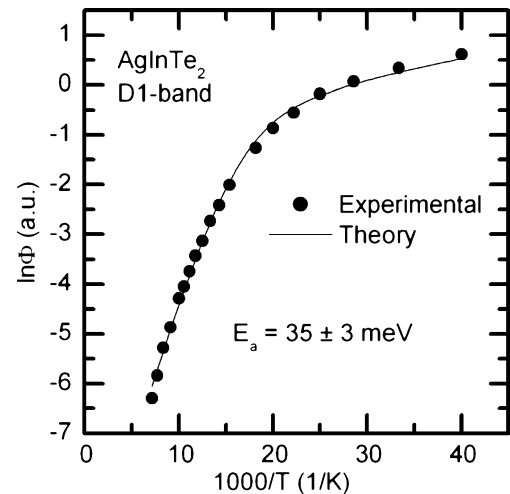
Fig. 5. Arrhenius plot of the D1-band. Solid line represents the fitting result using Eq. (1).

point, the optical modes transform like $A_1 + 2A_2 + 3B_1 + 3B_2 + 6E$. From those, only $3B_2$ and $6E$ modes are infrared-active. On the other hand, all these modes, except the A_2, are Raman active [13].

The room temperature unpolarised Raman spectrum of AIT has six peaks (see Fig. 6). The spectrum was fitted using multiple Lorentzians. The peak at 122 cm^{-1} is evidently caused by A_1 mode. This mode cannot be detected by infrared studies, but it is estimated theoretically in Ref. [14] that in AIT, it will give a peak at 127 cm^{-1}. This is very close to our experimental result. Yet, the A_1 mode in AIT seems to be at lower energy than in other ternary tellurides (125 cm^{-1} in CuInTe$_2$ [15], 135 cm^{-1} in CuGaTe$_2$ [16]). A very intense peak is also at 140 cm^{-1}. According to IR measurements [17], this peak can be related to one of the E modes, but at the same time, there is no other experimental data confirming this assertion. For that reason, it can also be one of the B_1 modes.

Fig. 4. Temperature dependence of the D1-band. The spectra are normalised.
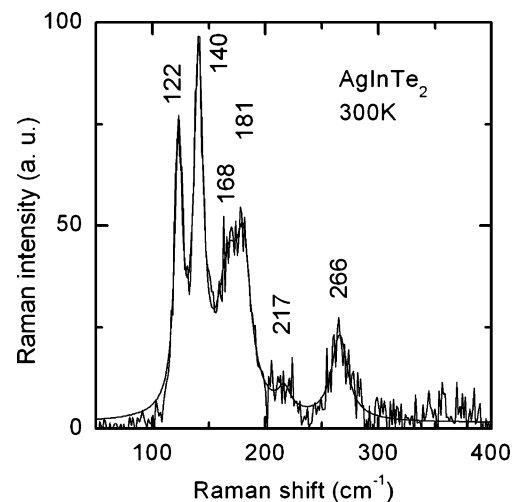
Fig. 6. Room temperature Raman spectra of AIT. The solid curve is the result of fitting with multipeak Lorentzian.

Because the other Raman peaks in our spectrum are not so well resolved, it is difficult to draw any conclusions for those peaks. However, in analogy to the Raman data of other tellurides, we can assume that the peak at 266 cm^{-1} is a combination of E and B$_2$ modes. Likewise, the low intensity 217 cm^{-1} band is most probably related to the longitudinal optical E mode. Although, the results of the PL measurements showed that the energy of the LO-mode is close to 201 cm^{-1} ($\hbar\omega_{LO}$=25 meV), the corresponding peak was not so well resolved in the Raman spectra. Therefore, it is possible that the band at 217 cm^{-1} consists of several peaks.

4. Conclusion

We conducted PL and Raman measurements on polycrystalline AIT samples. The PL spectra showed three bands. Because of the narrowness and closeness to the bandgap energy, we assign the first band at 1.023 eV to excitonic emission. The second PL band at 0.959 eV is assigned to DAP recombination. This conclusion is based on the results of laser power dependence measurements that reveal the j-shift 6 meV per decade. The third PL band at 0.741 eV is most probably caused by the recombination between deep defect states. However, to identify the responsible defects for the E1 and D2 bands, further research is necessary.

The Raman studies revealed six peaks. We assign the peak at 122 cm^{-1} to the A$_1$ mode. The neighbouring peak at 140 cm^{-1} is caused by the E or the B$_1$ mode, and the peak at 266 cm^{-1} is a combination of E and B$_2$ modes. The peak at 217 cm^{-1} is in good accordance with the fitting of the PL spectra where the phonon replicas were detected with the energy of $\hbar\omega_{LO}$=25 meV. Accordingly, this mode is assigned to longitudinal optical E mode.

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