Features of IR reflection spectra of $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ single crystals ($0 \leq X \leq 0.015$)

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Abstract. The method of long-wave spectroscopy made it possible to study the IR reflection spectra of layered single crystals $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ ($0 \leq X \leq 0.015$) in the frequency range of 40-500 cm$^{-1}$ and the temperature range of 84 ÷ 300 K. It was shown that partial substitution of thallium atoms with copper atoms leads to a decrease in the frequencies of the corresponding oscillations in the frequency range of 40-500 cm$^{-1}$ and does not lead (at these concentrations) to local oscillations. It was found that solid solutions $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ ($X= 0 \div 0.015$) exhibit the characteristic single-mode behavior. It was shown that partial substitution of thallium atoms with copper atoms in single crystals $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ ($X = 0.005; 0.010; 0.015$) weakens the ionic bond in Tl – S, as a result of which the frequencies of “internal” oscillations shift towards low temperatures.

1. Introduction
In recent years, the researchers have been paying great attention to the study of the zone structure, lattice dynamics and physical properties of semiconductor compounds of TlB$_3$C$_6$ class [1, 7-24]. This allows identifying the patterns that determine the dependence of properties on the composition, structure and nature of the chemical bond, which, in turn, makes it possible to conduct a targeted search for materials that ensure a given combination of physical properties. Highly dispersed and thin film materials with characteristic dimensions of tens and units of nanometers are increasingly used in semiconductor opto- and quantum electronics. The quality of such films and, as a rule, the parameters of the devices based on them depend on the conditions of thin films formation, the size and orientation of crystallites, and the kinetic parameters of phase transformations.

This makes the compounds TIB$_3$C$_6$ particularly interesting both from the point of view of understanding the fundamental features of the crystalline structure of layered semiconductors and from...
the point of view of practical application. The ability of these layered crystals to fold into plates with reflecting edges resulting from the sharp asymmetry of the chemical bond makes them promising materials for photoelectric converters.

It is known that the constituents TlB\(^3\)C\(^6\)\(_2\) (B-In, Ga; C- S, Se) of cations Tl\(^{+1}\) and B\(^{+3}\) are the elements of the third group and ensure various coordination of atoms, valence states and the nature of chemical bonds. These features cause sharp anisotropy of the physical properties of this group of materials. Physical characteristics and phase composition are also critical for thin-film solar cells.

2. Materials and methods
The paper presents the results of an experimental study of the IR reflection spectra of \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) \((0 \leq X \leq 0.015)\) single crystals in the frequency range of 40-500 cm\(^{-1}\) and the temperature range of 84 ÷ 300 K.

Single crystals were grown using a modified Bridgman-Stockbarger method. The resulting crystals were p-type and had the resistivity of \(10^8 - 10^{10}\) Ohm-cm at 300 K. The band gap width = 2.18 eV, mobility = 65 cm\(^2\)/V·s. The samples for measurements were obtained by folding along the cohesion plane from massive \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) single crystals and had dimensions of 5 x 8 x 2 mm\(^3\). Since the samples after shearing had pronounced mirror surfaces, they were not filled and polished.

The IR spectra were measured at the DVIX unit (long-wave vacuum IR spectrometer) created on the basis of the FIS-21 spectrometer [2]. The DVIX unit differs from the branded FIS-21 by the fact that an additional focus is created in the cuvette compartment of the spectrometer using the IPO-22 attachment. The IR reflection in the temperature range of 84 ÷ 300 K was measured from the planes of the fresh chipping of \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) \((X = 0 ÷ 0.015)\) single crystals in geometry \(E \perp C\). The resolution throughout the spectrum was about 1 cm\(^{-1}\). The spectra of the imaginary portion of the dielectric constant \(\varepsilon'\) and the loss function \(\text{Im}[\varepsilon^{-1}]\) were calculated based on the Kramers-Kronig analysis [2].

Low temperature measurements of IR reflection were carried out using a cryostat device [3]. The temperature pitch made 5 ÷ 10° C. The system allows stabilizing the established intermediate temperature with an accuracy of at least ± 0.5 K.

3. Results and discussion
The analysis of the state of the oscillations' spectra \(\beta\)-TlInS\(_2\) crystals [4] showed, in particular, that the section of the IR reflection spectrum 250 ÷ 350 cm\(^{-1}\) is associated with oscillations of Tl –S atoms. Since thallium atoms in \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) single crystals are partially replaced by copper atoms, all the intended features were to be observed precisely in the above frequency region. Proceeding from it, all our attention was drawn to the study of concentration and temperature features of IR-reflection ranges of \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) \((X = 0 ÷ 0.015)\) single crystals in the frequency range of 250 ÷ 350 cm\(^{-1}\).

Figure 1 shows the IR-reflection spectra of \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) \((X = 0 ÷ 0.015)\) single crystals at 84 K and 300 K. The figure shows that the frequency range of \(\varepsilon > 250\) cm\(^{-1}\) on IR-reflection spectra of \(\beta\)-Tl\(_{0.0985}\)Cu\(_{0.015}\)InS\(_2\) single crystals shows a shift of the corresponding oscillations towards low frequencies. Besides, in the frequency range of 250 ÷ 350 cm\(^{-1}\) at a temperature drop to 84 K, the IR-reflection spectrum splits.
Figure 1. Reflection spectra of $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ single crystals at 300 K (a) and 84 K (b): 1 - $x = 0.0$; 2 - $x = 0.015$.

Figure 2. Reflection spectra of $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ single crystals at 84 K (a) and 300 K (b): 1 - $x = 0.0$; 2 - $x = 0.005$; 3 - $x = 0.010$; 4 - $x = 0.015$.

Figure 3. Dispersion of the imaginary component of dielectric permeability $\varepsilon'(\nu)$ of $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ single crystals at 84 K (a) and 300 K (b): 1 - $x = 0.0$; 2 - $x = 0.005$; 3 - $x = 0.010$; 4 - $x = 0.015$. 
Figures 2, 3 shows the spectra of IR reflection and $\varepsilon'(\nu)$ of $\beta$-Tl$_{1-x}$Cu$_x$In$_2S$ ($X = 0$-$0.015$) single crystals at 84 K and 300 K. As expected, the analysis of the figures makes it possible to conclude that partial substitution of thallium atoms with copper atoms leads to a decrease in the frequencies of the corresponding oscillations in the indicated section of the spectrum. This decrease is most noticeable at low and to a much lesser extent at room temperature.

![Figure 2: Spectra of IR reflection and $\varepsilon'(\nu)$](image1)

![Figure 3: Spectra of IR reflection and $\varepsilon'(\nu)$](image2)

**Figure 4.** Dispersion of function $\text{Im}[-\varepsilon(\nu)^{-1}]$ of $\beta$-Tl$_{1-x}$Cu$_x$In$_2S$ single crystals at 84 K (a) and 300 K (b): 1 - $x = 0.0$; 2 - $x = 0.005$; 3 - $x = 0.010$; 4 - $x = 0.015$.

![Figure 5: Dependence of IR active phonon frequencies on the composition of solid solutions $\beta$-Tl$_{1-x}$Cu$_x$In$_2S$ at 84 K](image3)
A similar effect of copper atoms is observed on spectra $\text{Im} [-\varepsilon (\nu)^{-1}]$ (Figure 4). Figure 5 shows the dependence of the IR active phonon frequencies on the composition of solid solutions $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ ($X = 0 \div 0.015$).

The analysis of IR-reflection ranges shows that partial replacement of thallium atoms with copper atoms in an atomic sublattice of $\beta$-TlInS$_2$ crystals does not lead (at these concentration) to local fluctuations. Solid solutions $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ ($X = 0 \div 0.015$) show characteristic features of single-mode behavior $\varepsilon''(\nu)$. According to the existing concepts [5], when replacing a heavy atom with a lighter one, the frequency of the corresponding oscillation should shift towards large frequency values. In solid solutions $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ ($X = 0.005; 0.01; 0.015$) the opposite is observed, i.e. partial substitution of thallium atoms with copper atoms leads to a decrease in the frequencies of the corresponding optical phonons. It seems that in addition to the mass factor, a sharp change in the bond force between atoms plays a significant role here. In our opinion, the partial substitution of thallium atoms with copper atoms leads to a significant decrease in the Tl – S bond force. As the concentration of copper atoms increases, the frequencies of the corresponding oscillations decrease.

On the other hand, the substitution of thallium atoms with copper atoms reduces the temperature dependence of the frequencies of the corresponding oscillations (Figures 2, 3). As follows from [6], the temperature dependence of frequencies of normal modes can be caused by two mechanisms – thermal expansion of the crystal lattice and anharmonic coupling of oscillations. It should be noted that the above mechanisms of different anharmonicity of paired interaction potential between atoms are that the first is associated with intramodal anharmonicity, and the second – with intermodal. Since in $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ crystals (Figure 3), when the temperature decreases, there is a narrowing of the bands to a half-width value, the most likely reason for the weakening of the temperature dependence of the bands is often considered a decrease in the coefficient of thermal expansion. This means that the introduced copper atoms quite strongly disturb the $\beta$-TlInS$_2$ crystal lattice, especially at low temperatures.

Table 1. Frequencies of longitudinal ($LO$), transverse ($TO$) optical phonons and optical constants of $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ single crystals at 84 K

|   | $x = 0$  | $x = 0.005$ | $x = 0.01$ | $x = 0.015$ |
|---|----------|-------------|------------|-------------|
| $\nu$, cm$^{-1}$ | $4\pi \nu$ | $\nu$, cm$^{-1}$ | $4\pi \nu$ | $\nu$, cm$^{-1}$ | $4\pi \nu$ |
| $TO_1$ | 314 | 1.349 | 308 | 2.222 | 308 | 2.109 | 309 | 0.950 |
| $LO_1$ | 342 | 336 | 336 | 337 |
| $TO_2$ | 302 | 149 | 298 | 2.222 | 297 | 2.109 | 295 | 0.910 |
| $LO_2$ | 329 | 325 | 323 | 323 |
| $TO_3$ | 287 | 1.207 | 281 | 2.450 | 282 | 2.331 | 282 | 0.850 |
| $LO_3$ | 311 | 309 | 305 | 307 |
| $TO_4$ | 277 | 0.639 | 273 | 0.351 | 272 | 0.333 | 272 | 0.150 |

The frequencies of longitudinal ($LO$), transverse ($TO$) optical phonons and optical constants of $\beta$-Tl$_{1-x}$Cu$_x$InS$_2$ ($X = 0 \div 0.015$) single crystals at 84 K are given in Table 1. The static dielectric constant was determined from the Liddane-Sachs-Teller ratio:
Oscillator forces were determined from the ratio:

\[ 4\pi\rho = \varepsilon_0 - \frac{\nu^2}{V_n^2} \]

Table 2. Frequencies of longitudinal (\(LO\)) and transverse (\(TO\)) optical phonons of \(\beta\)-TlInS\(_2\) and \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) single crystals at 300 k

|       | \(v\), cm\(^{-1}\) [o.d.] | \(v\), cm\(^{-1}\) [8] | \(v\), cm\(^{-1}\) [8] | \(v\), cm\(^{-1}\) [o.d.] |
|-------|----------------------------|-------------------------|-------------------------|--------------------------|
| \(TO_1\) | -                         | 33                      | -                       | -                        |
| \(LO_1\) | -                         | 38                      | -                       | -                        |
| \(TO_2\) | 47                        | 48                      | -                       | 48                       |
| \(LO_2\) | 55                        | 54                      | -                       | 52                       |
| \(TO_3\) | 90                        | 89                      | 79                      | 88                       |
| \(LO_3\) | 98                        | 97                      | 96                      | 97                       |
| \(TO_4\) | 123                       | 129                     | 123                     | 126                      |
| \(LO_4\) | 142                       | 142                     | 142                     | 142                      |
| \(TO_5\) | 266                       | 265                     | 264                     | 263                      |
| \(LO_5\) | 277                       | 278                     | 280                     | 275                      |
| \(TO_6\) | 293                       | 297                     | 295                     | 292                      |
| \(LO_6\) | 324                       | 329                     | 380                     | 320                      |
| \(TO_7\) | 459                       | -                       | -                       | 444                      |
| \(LO_7\) | 496                       | -                       | -                       | 484                      |

Note: o.d. – our data

Table 2 shows the results of comparative analysis of literature data regarding frequencies (\(TO\)) and (\(LO\)) of \(\beta\)-TlInS\(_2\) crystal phonons with the data obtained from our experiments for \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) (\(X = 0 \div 0.015\)) at 300 K. The comparison of the results of low-temperature studies was not possible, since there are no research results of low-temperature measurements.

By analyzing Tables 1, 2 and having tracked the change of the corresponding oscillations with transition from \(\beta\)-TlInS\(_2\) to \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) (\(X = 0 \div 0.015\)) it is possible to conclude that copper atoms, in fact, replace thallium atoms in Tl – S systems.

4. Conclusion

It was shown that partial substitution of thallium atoms with copper atoms leads to a decrease in the frequencies of the corresponding oscillations in the frequency range of 40-500 cm\(^{-1}\) and does not lead (at these concentrations) to local oscillations. It was found that \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) (\(X = 0 \div 0.015\)) solid solutions show characteristic features of single-mode behavior. It was shown that partial substitution of thallium atoms with copper atoms in \(\beta\)-Tl\(_{1-x}\)Cu\(_x\)InS\(_2\) (\(X = 0.005; 0.010; 0.015\)) single crystals leads to a weakening of the Tl – S ionic bond thus resulting in the shift of the frequencies of “internal” oscillations towards low temperatures.

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