*Semiconductor Physics, Quantum Electronics & Optoelectronics, 2021. V. 24, No 3. P. 272-276.*

*Semiconductor physics*

# Preparation of quaternary compounds $Cu_2ZnSnS_4$ by using the self-propagating high-temperature synthesis

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**Abstract.** Possibility to prepare finely dispersed $Cu_2ZnSnS_4$ by using the method of self-propagating high-temperature synthesis has been studied in this work. Investigations of Raman scattering and IR-Fourier spectroscopy of the synthesized finely dispersed material have been carried out. The analysis of the Raman and IR-Fourier spectra showed that the synthesized material in the process of preparing is formed with a kesterite structure with the inclusion of a certain amount of secondary phases in the form of sulfides and stannites.

**Keywords:** self-propagating high-temperature synthesis, quaternary semiconductors, kesterite, Raman scattering, FTIR spectroscopy.

https://doi.org/10.15407/spqeo24.03.272
PACS 78.30.Er, 88.40.jm

Manuscript received 10.06.21; revised version received 09.07.21; accepted for publication 18.08.21; published online 26.08.21.

## 1. Introduction

At the moment, alternative energy is based on solar cells (SCs), among which several main groups can be distinguished: silicon and non-silicon SCs ($CuInSe_2$, CdTe, GaAs/Ge, *etc*.) [1–3]. It turned out that the process of manufacturing silicon-based structures is technologically complex and expensive, and the use of structures that include elements such as In, Cd, Te, As also turned out to be unprofitable because of their environmental harm and relatively high cost [3]. This stimulated the search for new materials with similar properties, but less harmful and expensive to manufacture. One of these materials is $Cu_2ZnSnS_4$ with a kesterite structure [4]. Analysis of the literature data showed that the methods for obtaining $Cu_2ZnSnS_4$ are quite different [5–7], but they have a number of significant drawbacks. First of all, this is their technological complexity and multistage nature, the need for post-technological processing, which in turn leads to a deterioration in the quality of the material obtained and significantly increases its cost. So, for example, the method of direct fusion of elements in vacuum [5] requires a complex expensive equipment, moreover, due to the specifics of the technique, it is not possible to control the stoichiometry of the obtained material, as well as its phase composition. In [6], it was shown that in the process of obtaining $Cu_2ZnSnS_4$ by using the method of growing in liquid solutions, a large number of reaction by-products is formed on the surface of the material, which requires additional processing of the synthesized material. When using the solvothermal method [7] for obtaining $Cu_2ZnSnS_4$, a significant amount of organic compounds from the solvents used in the synthesis remains on the surface of material. At the same time, there is no information in the literature on the possibilities of the self-propagating high-temperature synthesis (SHS) method for obtaining $Cu_2ZnSnS_4$. This method makes it possible to obtain the necessary compounds in one technological cycle, which makes SHS a more energy efficient, low-cost and more environmentally friendly method. The SHS technology is based on a solid-state exothermic reaction due to the internal energy of the reagents. The reaction proceeds at sufficiently high temperatures (~ 1200 °C), which can lead to an uneven course of the reaction. This, in turn, can facilitate formation of various lattice defects, secondary phases, point defects, *etc*. during the synthesis. SHS will make it possible to obtain high quality materials without the aforementioned disadvantages of other methods. Consequently, the preparation of such complex compounds as $Cu_2ZnSnS_4$ with the kesterite structure by using the SHS method is quite urgent. This makes the study of the modes of synthesis of complex compounds $Cu_2ZnSnS_4$ with the kesterite structure by using the SHS method quite relevant.

Therefore, the purpose of this work is to elucidate the possibility of obtaining $Cu_2ZnSnS_4$ with the kesterite structure by using the SHS method.

## 2. Experimental technique

The finely dispersed $Cu_2ZnSnS_4$ ($Cu_2ZnSnS_4$-SHS) obtained by using the method of self-propagating high-temperature synthesis (SHS) was investigated. The charge components were taken in the stoichiometric ratio (2:1:1:4), sulfur and metals (Cu, Zn, Sn) were fine powder. To maintain the stoichiometric composition of the material, the starting reagents were carefully weighed on the high-precision analytical balance Radwag AS 110/X, accuracy class EN 45501-1, resolution 0.00001 g. To mix the starting reagents, the planetary mill Retch PM 100 was used, at 200 rpm with reverse every 15 min, stirring duration 240 min.

Before starting the synthesis, atmospheric air was evacuated from the reactor to remove oxygen. The evacuation was carried out using a foreline pump, the first evacuation lasted 60 min, then argon was inflated, after which the next evacuation was carried out for 60 min with repeated argon inflating and evacuation. Before beginning the synthesis, an argon pressure of 2 atm (202650 Pa) was set in the reactor. In the course of synthesis, due to the heating of the charge and inert medium in the reactor, the pressure increases, which in turn can lead to a deterioration in the quality of the synthesized material. Therefore, a 3 atm. outlet valve was installed in the reactor.

The synthesis was carried out in a silica crucible. The density of the reagents in the charge was selected in such a way that the speed of propagation of the combustion front in the charge was ~ 0.5 cm/s. To initiate the reaction, a copper coil was used, an alternating voltage of 16 V was applied to this coil. After the reaction proceeded, the reactor was cooled to room temperature, after which the reactor was disassembled. After extraction, the material was ground in an agate mortar.

Raman spectra were measured on an INTEGRA Spectra LS PNL at room temperature according to the method [8]. The Raman spectrum was excited by radiation from a helium-neon laser with the wavelength 633 nm (output power up to 35 mW), wavelength resolution 0.03 nm.

FTIR measurements were performed using a Thermo Scientific ™ Smart ™ iTX ATR Accessory instrument. Sample preparation was carried out according to the method [8].

## 3. Results and discussion

Fig. 1 shows the Raman spectra of the quaternary compound $Cu_2ZnSnS_4$ obtained by using the SHS method.

From Fig. 1, it is shown that the frequency position of the most intense band with the frequency 336 $cm^{-1}$ corresponds to the vibrations of the A-mode of the kesterite structure [9–12]. The spectrum also contains a band with the frequency 285 $cm^{-1}$, which also refers to the vibrations of the $Cu_2ZnSnS_4$ A-mode, which is less pronounced in the spectrum [13]. In addition, the spectrum also contains a peak with the frequency 469 $cm^{-1}$, which corresponds to the $Cu_{2-x}S$ phase [9].

The broadening of the band in the region of 350 $cm^{-1}$ may be caused by the fact that in this region the stannite ($Cu_2SnS_3$) and ZnS phases can contribute to the spectrum [13, 14]. However, the strong overlap of these bands with the main peak 336 $cm^{-1}$ does not allow more accurate identification of these bands. It should be noted that, despite the presence of a certain amount of secondary phases in the synthesized powder, the spectra also contain repetitions (second and third orders) of vibrations of the A-mode of kesterite within the range 600 to 700 $cm^{-1}$ and 1000 to 1100 $cm^{-1}$, respectively.

As noted earlier, the SHS reaction proceeds under rather non-equilibrium thermodynamic conditions. During the synthesis, the temperature reaches ~ 1200…1400 °C, while the reaction rate is quite high. This can lead to uneven propagation of the combustion front, uneven heating of the reaction bulk of material, *etc*. It should be also noted that, as shown in [15], annealing of $Cu_2ZnSnS_4$ at the temperatures close to 550…600 °C leads to decomposition of the initial material with the kesterite structure into binary and ternary sulfides ($Cu_{2-x}S$, SnS, $Cu_2SnS_3$, *etc*.). The authors of [15, 16] indicate that the main reason for this process is evaporation of sulfur and SnS during annealing. At the same time, many authors note an improvement in the quality of the $Cu_2ZnSnS_4$ structure during annealing at the temperatures within the range 230 to 450 °C due to transformation of secondary phases in $Cu_2ZnSnS_4$ with the kesterite structure [17–20].

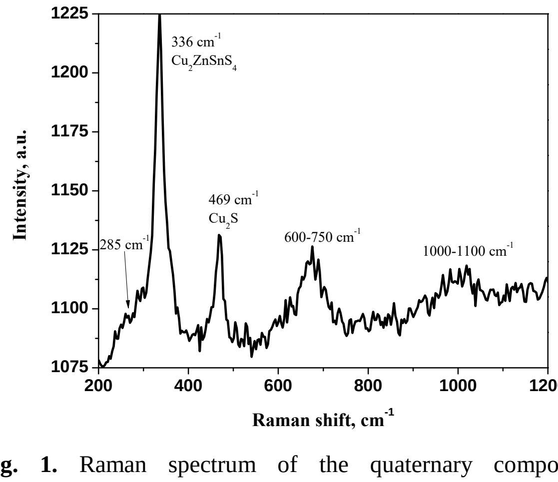

**Fig. 1.** Raman spectrum of the quaternary compound $Cu_2ZnSnS_4$-SHS.

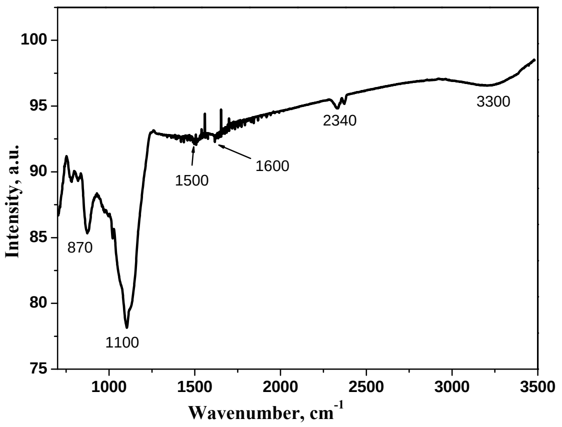

**Fig. 2.** FTIR spectrum of the quaternary compound $Cu_2ZnSnS_4$-SHS.

It should be also noted that the cooling of the material synthesized by us using the SHS method to room temperature occurs rather quickly (~ 20–30 min). Excessive pressure of an inert atmosphere most likely interferes with evaporation of sulfur and SnS. This is evidenced by the low intensity of the peaks from the secondary phases in the Raman spectra. Therefore, it can be assumed that in our case, during the course of the SHS reaction and subsequent cooling, there is both the process of decomposition of $Cu_2ZnSnS_4$ into binary and ternary phases at the temperatures above 600 °C and the reverse process – at the temperatures below 500 °C, as indicated in [17–20].

Fig. 2 shows the FTIR spectrum of $Cu_2ZnSnS_4$-SHS. The spectrum has the form of a complex wide band with several maxima: ~ 870, ~ 1100, ~ 1500, ~ 1600, ~ 2340, ~ 3300 $cm^{-1}$. In the literature, these bands ~ 870, ~ 1100 $cm^{-1}$ are associated with the resonant interaction between the vibrations of sulfide ions in crystallites [21]. The bands ~ 1500, ~ 1600 $cm^{-1}$ are caused by formation of complexes of sulfur and metal (most likely copper and tin or $Cu_{2-x}S$, $Cu_2SnS_3$) [22]. The band ~ 2340 $cm^{-1}$ is associated with formation of an extension of the bond between Zn–S ions [23]. The wide band ~ 3300–3400 $cm^{-1}$ is due to the presence of water on the surface of the material [24]. The presence in the spectrum of bands with the peaks ~ 1500, ~ 1600 $cm^{-1}$ associated with formation of complexes of sulfur with metals, in our opinion, indicates the presence of sulfide phases in the material, which agrees with the data of Raman scattering.

Note that the SHS technology makes it possible to obtain materials of different sizes, including finely dispersed ones, with the particle sizes of the order of ~ 100 nm and less. This also applies to $Cu_2ZnSnS_4$ with the kesterite structure. Therefore, the use of finely dispersed material $Cu_2ZnSnS_4$ together with organic semiconducting polymers of *p*-type can make it possible to deposit the layers including $Cu_2ZnSnS_4$ with the kesterite structure on flexible substrates by using printer technologies. This will greatly simplify the creation of solar cells based on $Cu_2ZnSnS_4$.

## 4. Conclusions

The presented results have shown that the method of self-propagating high-temperature synthesis makes it possible to prepare finely dispersed $Cu_2ZnSnS_4$ material in one technological cycle. Raman scattering studies have shown that the synthesized material has a kesterite structure and also contains a certain amount of secondary phases in the form of sulfides and stanites. Further research is needed to improve the quality of the finely dispersed $Cu_2ZnSnS_4$ material.

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## Отримання почетверених сполук $Cu_2ZnSnS_4$ за допомогою самопоширюваного високотемпературного синтезу

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**Анотація.** У роботі досліджена можливість отримання дрібнодисперсного $Cu_2ZnSnS_4$ методом самопоширюваного високотемпературного синтезу. Проведено дослідження комбінаційного розсіювання світла та ІЧ-Фур'є спектроскопії синтезованого дрібнодисперсного матеріалу. Аналіз спектрів КР та ІЧ-Фур'є показав, що синтезований матеріал у процесі отримання формується зі структурою кестерит із включенням деякої кількості вторинних фаз у вигляді сульфідів та станитів.

**Ключові слова:** самопоширюваний високотемпературний синтез, почетверені напівпровідники, кестерит, комбінаційне розсіювання світла, ІЧ-Фур'є спектроскопія.