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Synthesis and crystal and defect structures of polycrystalline Cu_2SrSnS_4 and $Cu_{1.9}SrSnS_4$ powders

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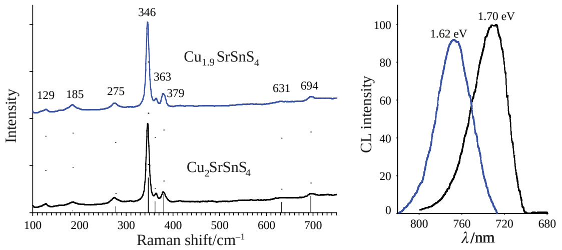
The polycrystalline samples of $Cu_{2-\delta}SrSnS_4$ with a trigonal structure were prepared by solid-phase ampoule synthesis with a long annealing time (1944 h), and their crystal lattice parameters were refined and Raman spectra were obtained. For the first time, the effect of defect structure on the lifetimes of photogenerated current carriers in the polycrystalline powders was examined by combining time-resolved microwave photoconductivity and cathodoluminescence methods. A significant increase in the lifetimes during the conversion of Cu_2SrSnS_4 into $Cu_{1.9}SrSnS_4$ was found, which was probably due to changes in the defect structure.

$$(2-\delta)Cu + Sn + 3S = Cu_{2-\delta}SnS_3$$
$$Cu_{2-\delta}SnS_3 + SrS_3 = Cu_{2-\delta}SrSnS_4$$



$2Cu_{Sr} + Sn_{Sr}$ replacement with V_{Cu}

Keywords: copper quaternary compounds, $Cu_{2-\delta}SrSnS_4$, polycrystalline powders, defect structure, cathodoluminescence, lifetimes of photogenerated current carriers.

Copper quaternary compounds,[1–4] which include $Cu_{2-\delta}ZnSnS_{4-x}Se_x$ [CZTS(Se)] with a kesterite structure, occupy a special place among various semiconductors used to construct absorbing layers for solar cells. However, currently, the efficiency of solar cells based on the CZTS(Se) compounds does not exceed 13% due to the specific structure of these materials. It was assumed that the similarity of ionic radii of Zn^{2+} and Cu^+ caused a large number of Cu_{Zn} and Zn_{Cu} anti-structural defects, which serve as traps for photogenerated current carriers.[5,6] The replacement of ions in a cationic sublattice with larger ions is of interest to obtain materials such as the Cu_2SrSnS_4 (CSTS) thin films,[2,7] which can be used in solar cells.[8–11] However, it is difficult to study the effect of defects on electrophysical properties in thin film materials because the composition of the films[8–10] is difficult to control. Therefore, it is useful to study model systems such as the CSTS powders of a given composition obtained by solid-phase synthesis in evacuated quartz ampoules with the subsequent long-term annealing[12,13] in order to optimize the composition of CSTS films and increase the efficiency of solar cells based on them.

Here, we describe the solid-phase ampoule synthesis of Cu_2SrSnS_4 and $Cu_{1.9}SrSnS_4$ polycrystalline powders and a study of their phase composition and defect structure and the lifetime of photogenerated current carriers in them.

The CSTS samples (m = 2 g) were synthesized from copper (99.99%), tin (99.99%), SrS (99.99%, Alfa Aesar), and sulfur (99.9%). At the first step, the ternary compounds Cu_2SnS_3 and $Cu_{1.9}SnS_3$ were produced from the elements in evacuated sealed quartz ampoules (p_{res} = 0.27 Pa) and annealed at T = 1100 °C for 10 h.

At the second step, the ampoule contents were ground in an agate mortar with a required amount of SrS (pre-annealed in a vacuum at $T \approx 750$ °C to remove excess sulfur).

The resulting mixtures were sealed in evacuated quartz ampoules and annealed at T = 1100 °C for 10 h.

At the last step, the ingots obtained were ground in an agate mortar for homogenization and annealed again in evacuated sealed quartz ampoules at T = 620 °C for 1944 h.

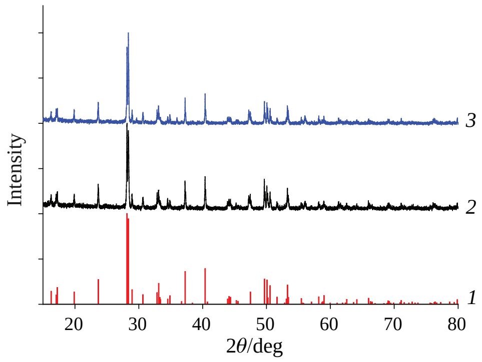


Figure 1 XRD data: (*1*) standard reference sample (PC PDF4 04-009-0385), (*2*) Cu_2SrSnS_4, and (*3*) $Cu_{1.9}SrSnS_4$.

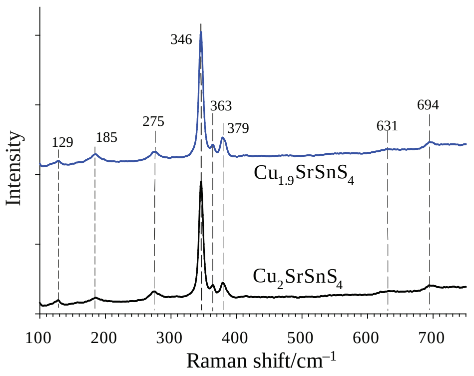


Figure 2 Raman spectra of the CZTS samples.

The phase composition of the samples was studied by a combination of XRD analysis and Raman spectroscopy.† Figure 1 shows that all samples were single-phase ones. The crystal structure is trigonal, and the space group is $P3_1$. Table 1 summarizes the refined values of crystal lattice parameters, which are consistent with published data.[7]

Figure 2 shows the Raman spectra of the Cu_2SrSnS_4 and $Cu_{1.9}SrSnS_4$ samples, which are close to those of the films obtained previously[11] but markedly different from the theoretical spectrum[11] (see Online Supplementary Materials). No lines of impurity phases were found.

Figure 3 shows the cathodoluminescence (CL) spectra‡ of the powders obtained at 78 K, which exhibit maximums at about 1.70 and 1.62 eV for Cu_2SrSnS_4 and $Cu_{1.9}SrSnS_4$, respectively. The absence of exciton peaks from the spectra unambiguously indicates a band-to-band transition, and these maximums can be associated with levels in a band gap. Since the band gap shifted with decreasing the copper content, it is possible to associate a maximum of E = 1.62 eV with defects caused by V_{Cu} copper vacancies or associates of such defects.

Table 1 Crystal lattice parameters of $Cu_{2-\delta}SrSnS_4$ (space group $P3_1$).

Compound	a/Å	c/Å	V/Å^3
Cu_2SrSnS_4	6.288 (3)	15.591 (7)	534.05 (3)
$Cu_{1.9}SrSnS_4$	6.288 (4)	15.576 (8)	533.4 (4)
Cu_2SrSnS_4[5]	6.29	15.578	533.7

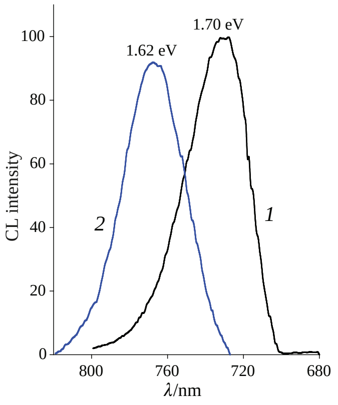


Figure 3 CL spectra of (*1*) Cu_2SrSnS_4 and (*2*) $Cu_{1.9}SrSnS_4$ powders obtained at 78 K.

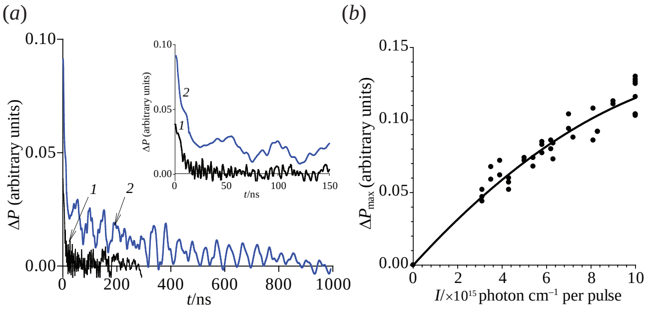


Figure 4 (*a*) The decay of microwave photoconductivity for (*1*) Cu_2SrSnS_4 and (*2*) $Cu_{1.9}SrSnS_4$ and (*b*) the dependence of photoresponse amplitude on light intensity for $Cu_{1.9}SrSnS_4$. The curves of microwave photoconductivity decay were smoothed using a 9-point linear filter, $I_0 = 10^{16}$ photon cm^{-2} per pulse.

Note that band gap data for CSTS are contradictory:[2] according to Crovetto *et al.*,[8] the band gap energy for this compound is E_g = 1.95–1.98 eV; a proximate value of E_g = 1.93 eV was obtained by Xiao *et al.*,[10] whereas the value of E_g for CSTS was 1.78 eV according to Tong *et al.*[9] Thus, we can assume that the peak at 1.70 eV for Cu_2SrSnS_4 corresponds to the donor level in the band gap.

Figure 4(*a*) shows microwave photoconductivity decays§ for Cu_2SrSnS_4 and $Cu_{1.9}SrSnS_4$. It can be seen that as the copper content of samples decreased, the times at which the photoresponse dropped to zero increased sharply from 20 ns to about 1 ms, which is significantly longer than that for the CSTS films described by Tong *et al.*[9] ($\tau < 2.06$ ns). The dependence of photoresponse amplitude on incident light intensity, $\Delta P_{max}(I)$, was nonlinear for $Cu_{1.9}SrSnS_4$ [Figure 4(*b*)]; this may be due to second-order reaction processes (free electron and hole recombination) in the sample:[15]

$$e^- + p^+ \xrightarrow{k_{rec}} h\nu \quad \text{(in radiative processes),} \tag{1}$$

where k_{rec} is the reaction rate constant of electron–hole recombination. According to published data,[17,18] the nonlinear dependence of photoresponse amplitude on incident light intensity indicates electron–hole recombination in loss kinetics of photogenerated current carriers. Microwave photoresponse for the Cu_2SrSnS_4 sample was small, and it was not possible to measure its dependence on incident light intensity.

A significant increase in decay times of photogenerated current carriers with a decrease in the copper content of copper quaternary compounds $Cu_{2-\delta}CdSnS_4$ was explained[19,20] by the formation of complex $2Cu_{Cd} + Sn_{Cd}$ clusters with an increase in δ and their replacement with copper vacancies V_{Cu}. By analogy with these systems, it can be assumed that the maximum at E = 1.70 eV observed in the CL spectrum of Cu_2SrSnS_4 (Figure 3) refers to clusters of defects, for example, $2Cu_{Sr} + Sn_{Sr}$, whereas the peak at E = 1.62 eV for $Cu_{1.9}SrSnS_4$ (Figure 3) corresponds to copper vacancies V_{Cu} or complexes of defects based on them.

The lifetimes of photogenerated current carriers in a semiconductor are key parameters determining the efficiency of a solar cell. Thus, the use of the CSTS copper-deficient films is

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† X-ray studies of the deposited films were carried out on a PANalytical AERIS diffractometer (Cu-Kα radiation). Raman spectra were studied using a Bruker Senterra micro-Raman system (532 nm).

‡ The samples were excited by a pulsed 40 keV electron beam. The CL spectra were recorded with a DFS-13 monochromator. The CL method was described in detail elsewhere.[14]

§ To study the loss kinetics of photogenerated current carriers, the time-resolved microwave photoconductivity (MPC) method was applied (a unique research facility: System for photogenerated current carrier lifetime measurements by a Microwave photoconductivity method in the 36 GHz frequency range) in the frequency range of 36 GHz at room temperature. The time resolution of recording circuit was ~5 ns.[15,16] The photoconductivity was excited by an LGI-505 nitrogen laser with the wavelength λ = 337 nm and a pulse duration of 8 ns. The maximum density of the light flux incident on the sample (exposure) was $I_0 = 10^{16}$ photon cm^{-2} per pulse. The light intensity was changed using light filters.

a possible way to create efficient solar cells based on such materials.

In conclusion, we have prepared the Cu_2SrSnS_4 and $Cu_{1.9}SrSnS_4$ single-phase powders by solid-phase ampoule synthesis, refined the crystal lattice parameters by XRD analysis, and obtained detailed Raman spectra. The microwave photoconductivity method allowed us to reveal a significant increase in the lifetimes of photogenerated current carriers during the conversion of Cu_2SrSnS_4 into $Cu_{1.9}SrSnS_4$, which was apparently due to the replacement of defect clusters caused by copper vacancies, and explain changes in the CL spectra.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.02.037.

References

1 Q. Tian and Sh. F. Liu, *J. Mater. Chem. A*, 2020, **8**, 24920.
2 M. V. Gapanovich, V. V. Rakitin and G. F. Novikov, *Russ. J. Inorg. Chem.*, 2022, **67**, 1 (*Zh. Neorg. Khim.*, 2022, **67**, 3).
3 I. N. Odin, M. V. Gapanovich, M. V. Chukichev, A. V. Vasiliev and G. F. Novikov, *Mendeleev Commun.*, 2020, **30**, 124.
4 I. N. Odin, M. V. Gapanovich, M. V. Chukichev and G. F. Novikov, *Mendeleev Commun.*, 2020, **30**, 666.
5 M. S. Kumar, S. P. Madhusudanan and S. K. Batabyal, *Sol. Energy Mater. Sol. Cells*, 2018, **185**, 287.
6 *Copper Zinc Tin Sulfide-Based Thin-Film Solar Cells*, ed. K. Ito, Wiley, 2015.
7 C. L. Teske, *Z. Anorg. Allg. Chem.*, 1976, **419**, 67.
8 A. Crovetto, R. Nielsen, E. Stamate, O. Hansen, B. Seger, I. Chorkendorff and P. C. K. Vesborg, *ACS Appl. Energy Mater.*, 2019, **2**, 7340.
9 Z. Tong, J. Yuan, J. Chen, A. Wu, W. Huang, C. Han, Q. Cai, C. Ma, Y. Liu, L. Fang and Z. Liu, *Mater. Lett.*, 2019, **237**, 130.
10 H. Xiao, Z. Chen, K. Sun, C. Yan, J. Xiao, L. Jiang, X. Hao, Y. Lai and F. Liu, *Thin Solid Films*, 2020, **697**, 137828.
11 A. Crovetto, Z. Xing, M. Fischer, R. Nielsen, C. N. Savory, T. Rindzevicius, N. Stenger, D. O. Scanlon, I. Chorkendorff and P. C. K. Vesborg, *ACS Appl. Mater. Interfaces*, 2020, **12**, 50446.
12 V. Kheraj, K. K. Patel, S. J. Patel and D. V. Shah, *J. Crystal Growth*, 2013, **362**, 174.
13 E. R. Baek, V. Astini, A. Tirta and B. Kim, *Curr. Appl. Phys.*, 2011, **11**, S76.
14 M. V. Gapanovich, I. N. Odin, M. V. Chukichev, V. F. Kozlovskii and G. F. Novikov, *Inorg. Mater.*, 2016, **52**, 53 (*Neorg. Mater.*, 2016, **52**, 56).
15 G. F. Novikov, *J. Renewable Sustainable Energy*, 2015, **7**, 011204.
16 M. V. Gapanovich, D. N. Varseev, E. V. Rabenok, B. I. Golovanov and G. F. Novikov, *High Energy Chem.*, 2019, **53**, 429 (*Khim. Vys. Energ.*, 2019, **53**, 432).
17 G. F. Novikov and N. A. Radychev, *Russ. Chem. Bull.*, 2007, **56**, 890 (*Izv. Akad. Nauk, Ser. Khim.*, 2007, 856).
18 M. V. Gapanovich, N. A. Radychev, E. V. Rabenok, D. N. Voilov, I. N. Odin and G. F. Novikov, *Inorg. Mater.*, 2007, **43**, 1065 (*Neorg. Mater.*, 2007, **43**, 1190).
19 H. Guo, Y. Li, X. Fang, K. Zhang, J. Ding and N. Yuan, *Mater. Lett.*, 2016, **162**, 97.
20 S. Hadke, S. Levcenko, G. S. Gautam, C. J. Hages, J. A. Márquez, V. Izquierdo-Roca, E. A. Carter, T. Unold and L. H. Wong, *Adv. Energy Mater.*, 2019, **9**, 1902509.

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