Thin films of Cu_2ZnSnS_4 for solar cells: optical and structural properties

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The structure of Cu_2ZnSnS_4 films was investigated by Raman spectroscopy, scanning electron microscopy, energy dispersive X-ray spectrometry, optical reflectance and photoluminescence. The films were formed by thermal annealing layers of copper, zinc and tin sulfides on glass substrates at different substrate temperature and ambient atmosphere. It was revealed that the films have the dominant structure of kesterite with possible inclusions of stannite Cu_2ZnSnS_4 structure. Under certain growth conditions, however, segregation of $Cu_{2-x}S$ occurs, as proved by registering the characteristic peak in Raman spectra. No traces of secondary phases of zinc or tin sulphides are found.

Методами рамановской спектроскопии, сканирующей электронной микроскопии, энергетически-дисперсионной рентгеновской спектрометрии, оптического отражения и фотолюминесценции исследованы структуры пленок Cu_2ZnSnS_4, сформированных термическим отжигом предварительно осажденных слоев меди и сульфидов цинка и олова на стеклянные подложки при различных температурах подложек и окружающей атмосферы. Установлено, что пленки имеют структуру кестерита с возможными включениями структуры станнита. Показано, что при определенных технологических режимах формирования пленок в них может иметь место сегрегация фазы $Cu_{2-x}S$. В спектрах не проявились возможные включения фаз сульфидов цинка и олова.

Introduction

Photovoltaic devices provide today nearly 20 GW of electrical power worldwide. Almost 90 % of such power is produced by silicon solar cells, the efficiency of which has almost reached the theoretical limit. Due to constant annual growth of photovoltaic energy production by 30–40 %, the area of solar panels and the amount of material required for their manufacture increases significantly. An optimal solution of this problem is using of thin-film technology in manufacturing of solar cells. However, in this aspect silicon is not efficient material because of its indirect-gap and, consequently, low efficiency of absorption of solar radiation in visible and near infrared (1–2 eV). A transition to direct-gap materials can significantly reduce a thickness of the absorber layer needed for full absorption of an incident light.

For implementation of this perspective a number of binary and ternary chalcogenide semiconductors, which can be promising materials for second generation solar cells due to an appropriate band gap (1–1.5 eV), were intensively investigated in past years [1]. The efficiency of thin film solar converters based on CdTe, $CuInS_2$ (CIS) and $Cu(In,Ga)Se_2$ (CIGSe) has rapidly — during several years — reached values above 20 % [2]. However, the resources of In and Ga in the crust are little and the cost of these

materials is relatively high [3], while the large-scale use of toxic Cd and Te in solar cells is undesirable from the viewpoint of ecology.

Therefore, in the last few years, as a promising alternative for the development of the novel solar cells quaternary chalcogenides like Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe), and $Cu_2ZnSn(S,Se)_4$ are considered. In these compounds, the relatively expensive chemical elements of the third group, In and Ga, are replaced by cheap elements of second (Zn) and fourth (Sn) groups. After a rather short time of investigations, the efficiency exceeding 10 % has already been reported for CZTS-based solar cells [4]. However, the transition from atomic (Si) or binary (CdTe) compounds to ternary (CIS) or quaternary (CZTS) compounds generates a number of technological and fundamental physical problems. They are related to close values of formation energies for various crystallographic forms of these materials (e.g. kesterite and stannite for CZTS), an influence of possible significant non-stoichiometry (excess or deficiency of Cu and groups II and IV elements), and very high concentration of different structural defects [5−7].

Therefore, the main task of the researchers working on CZTS is obtaining homogeneous stoichiometric structures without inherent defects and inclusions of secondary phases of binary (ZnS, SnS, $Cu_{2-x}S$) and ternary (Cu_2SnS_3, Cu_3SnS_4) compounds. The presence of structural or phase inhomogeneities in CZTS dramatically deteriorates the solar cells characteristics [8−10].

The aim of this work was to determine the type of structure, composition homogeneity and identification of possible secondary phases in Cu_2ZnSnS_4 films formed by thermal annealing of preliminary deposited layers of copper, zinc and tin sulfides on glass substrates.

Experimental details

The films Cu_2ZnSnS_4 studied in this work were obtained by thermal annealing of layers of copper, zinc sulphide and tin sulphide deposited on a glass substrate caped by a layer of molybdenum. Annealing was carried out at 370 or 390°C in atmosphere of air or nitrogen. Utilizing relatively low temperatures of annealing was conditioned by potential possibility of usage of flexible organic polymer films in the technology of such structures formation.
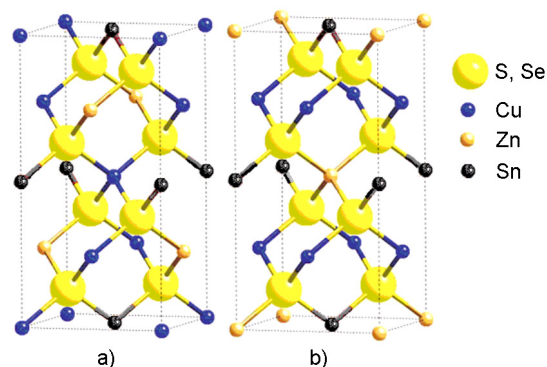

Fig. 1. Schematic of kesterite (a) and stannite (b) structures [9].

Optical reflection spectra of CZTS films under study were recorded by Shimadzu UV-3600 spectrometer, surface morphology was investigated by scanning electron microscope (SEM) Tescan Mira 3 LMU. Chemical composition was determined using energy dispersive spectroscopy (EDS) included in SEM. Structural properties of the films were investigated by micro-Raman spectroscopy. For excitation of Raman spectra the 514.5 nm wavelength of Ar^+-laser was used. The laser power was adjusted for the power density on the sample surface not exceeding 0.1 mW/μm^2, in order to avoid affecting the structure of the film in the process of measuring Raman spectra. All measurements were performed at room temperature. Photoluminescence (PL) spectra were recorded at temperature of liquid nitrogen and excited with a second harmonic (532 nm) of Nd:YAG laser.

Results and discussion

CZTS crystals can be found in nature [11] in the form of mineral that can crystallize in structures of kesterite (space group $I\bar{4}4$) and stannite (space group $I\bar{4}2m$) (Fig. 1).

As can be seen from Fig. 1, these crystalline structures are very similar and differ only by distribution of cations in tetrahedral sites [12]. Type of the cation arrangement in Cu_2ZnSnS_4, and thus its crystallographic structure, strongly depends on technological conditions [13]. Identification of the crystallographic structure of CZTS by conventional X-ray diffractometry is hardly possible since kesterite and stannite reflections almost coincide. The reason is a tiny difference in their X-ray scattering due to similarity of energy spectra and atomic masses of Cu and Zn. For the same reasons the X-ray methods are not informative
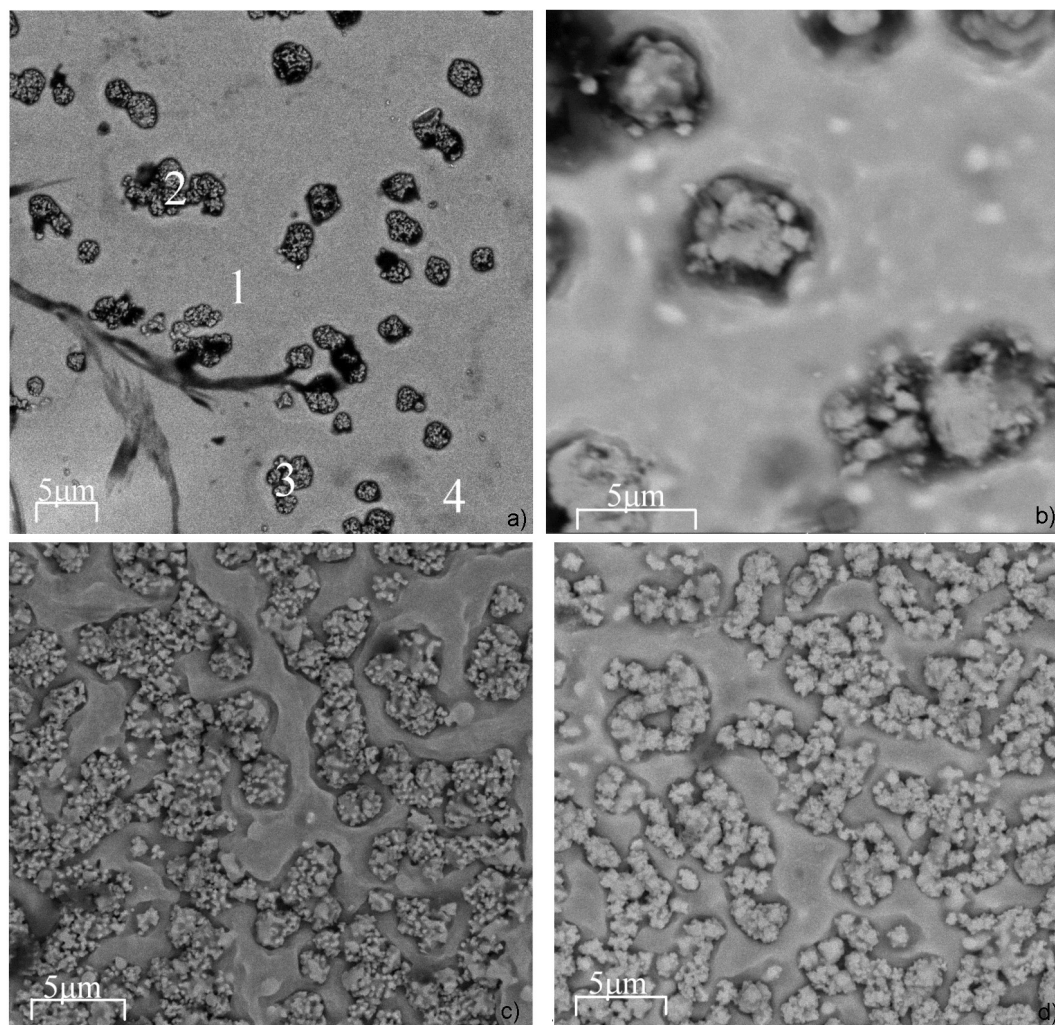
Fig. 2. SEM images of the films formed at 370°C (a, b) and 390°C (c, d) under nitrogen atmosphere (a, c) and air (b, d).

enough for an identification of the secondary phases of ZnS or Cu_2SnS_3 in CZTS.

As can be seen from Fig. 2, the surface morphology of the films strongly depends on technological conditions, such as annealing temperature and atmosphere in which the annealing was carried out. An increase of the synthesis temperature by only 20°C from 370 to 390°C causes the considerable increase of the surface density of some secondary phase. The local EDS analysis was carried out in different areas of the films (marked in Fig. 2, a) in order to determine the chemical composition of the flat areas (markers 1 and 4) and of the morphological inhomogeneities (markers 2 and 3). The EDS method does not allow to obtain the data on the composition of just thin surface layer, because the probing electrons penetrate the whole film. The large energy of the probing electron was required for

achieving high enough spectral resolution in the EDS measurements.

Therefore, the composition obtained by EDS in every spot is averaged over the whole film thickness. Nevertheless, even in this case, one can obtain some information about component composition of the inhomogeneities, which are located at the film surface. It is seen from Table that the areas with morphological inhomogeneities (2 and 3) are Cu-rich. At the same time, for the flat and homogeneous areas (1 and 4) the ratio of the components Cu:Zn:Sn:S is very close to the stoichiometric one — 2:1:1:4. However, some excess of Cu content and deficiency of Sn is measured even for the apparently homogeneous areas. The enrichment by Cu in areas 2 and 3 can be an evidence of $Cu_{2-x}S$ formation. This assumption has to be checked, however, by other method(s), which are sensitive to the par-
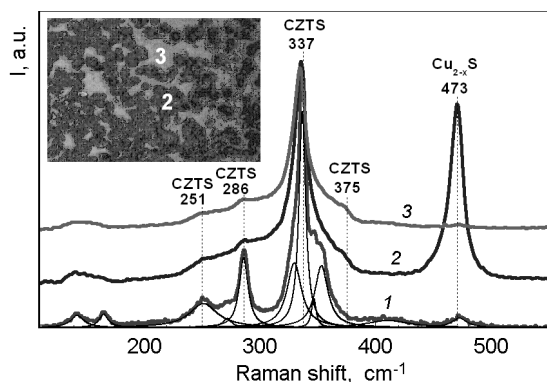
Fig. 3. Raman spectra of Cu_2ZnSnS_4 crystal (*1*) and films formed at 370°C in nitrogen atmosphere. The film spectra were obtained in dark (*2*) and light (*3*) areas of the surface, as indicated optical microscope image (×100) in the inset.

ticular compound rather than overall content of certain chemical elements. One of the most efficient tools for this purpose was proved to be Raman spectroscopy [14].

Before studying the thin film samples by Raman spectroscopy, we obtained Raman spectrum of a reference Cu_2ZnSnS_4 crystal (Fig. 3, curve *1*). It reveals intense peaks at 251 cm^{-1}, 286 cm^{-1}, and 337 cm^{-1} related with kesterite structure [15–22]. The frequency of the most intensive band of the Raman spectrum of Cu_2ZnSnS_4 correlates well with theoretically calculated mode for the kesterite structure (335.2 cm^{-1}), while for stannite it is expected at 332.7 cm^{-1} [16]. One can see from the spectrum shown in Fig. 3 that the Raman spectrum of the crystal CZTS sample also possesses weaker bands at 143, 166, 271, 347, and 353 cm^{-1}, which can be also assigned to the kesterite modes [19–22].

From the fitting of experimental Raman spectrum of the reference Cu_2ZnSnS_4 crystal by a set of Lorentzian components we can conclude that at the low-frequency side of the most intense band (337 cm^{-1}) a weaker component at about 330 cm^{-1} is observed (Fig. 3, curve *1*). Most probably this Raman band is related with disorder of Zn and Cu atoms in Cu_2ZnSnS_4 lattice, as was
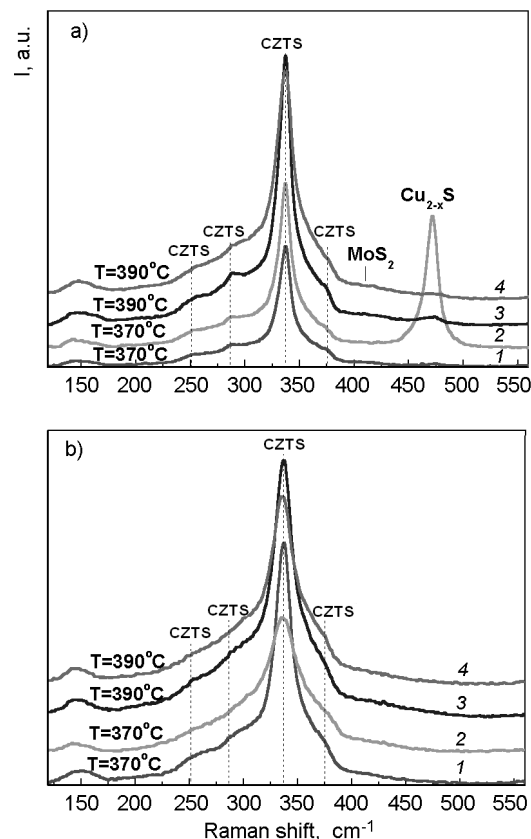

Fig. 4. Raman spectra of dark (a) and light (b) areas of the films synthesized under air (*1*, *3*) and nitrogen (*2*, *4*).

supposed in [22]. This disorder is often caused by so-called anti-sites defects, such as Zn atoms on the place of $Cu(Cu_{Zn})$ and vise versa (Zn_{Cu}). The assignement made in [22] was based on the fact that disorder in cation sublattice leads to the change of lattice symmetry and thus can induce new band(s) in the Raman spectrum [8, 9]. Another possible origin of this extra band can be related with inclusions of stannite structure, because the calculated frequency of the strongest Raman-active (A_1) mode of stannite, 332.7 cm^{-1} [16] is very close to the frequency of the additional experimental mode of 330 cm^{-1}.

Fig. 3 shows the Raman spectra of films formed at 370°C in nitrogen atmosphere. The measurement was performed in the

Table. Peak frequency, ω, and width, Ω, of the main Raman band, obtained from fitting

Sample	370°C, air		370°C, N$_2$		390°C, air		390°C, N$_2$	
Frequency	half-width	ω, cm^{-1}	Ω, cm^{-1}	ω, cm^{-1}	Ω, cm^{-1}	ω, cm^{-1}	Ω, cm^{-1}	ω, cm^{-1}
Light areas	336	18	335	31	336	20	335	24
Dark areas	337	14	337	13	337	13	337	18

light (curve *2*) and dark (curve *3*) areas on the film surface, as marked in the inset to Fig. 3. We can see that both spectra are qualitatively similar to the spectrum of the reference Cu_2ZnSnS_4 crystal which has the structure of kesterite. At the same time, in the spectrum obtained from the dark area (2) an additional strong band is observed at 473 cm^{-1} which is related with $Cu_{2-x}S$ [17–19]. This result is in a good agreement with the discussed above EDS data which shows excess of Cu content in the dark areas. Therefore, at these technological conditions the CZTS film homogeneity is deteriorated by inclusions of $Cu_{2-x}S$.

In Fig. 4 Raman spectra of films formed at various technological conditions are shown for the dark (a) and light (b) areas of the surface (as they appear under the light microscope). The spectra of films synthesized under air atmosphere differ from those formed under nitrogen atmosphere by more sharp peaks for both the dark and light areas. The peak frequency and width of the most intense CZTS mode (A_1) were obtained by multi-Lorenzian fitting of the spectra (as in Fig. 2) and are summarized in Table. It is seen from Table 1 that the peak width is smaller for the dark area of the films, despite $Cu_{2-x}S$ being observed in the same areas (curve *2* in Fig. 4a). Therefore, we may assume that the reason of the large Raman peak width for light areas (Fig. 4b) is not the inclusions of $Cu_{2-x}S$ but the disorder in the cation sublattice of CZTS lattice itself. The peak at 410 cm^{-1} in the spectrum of the dark areas of the film obtained at 390°C under N_2 corresponds to MoS_2 [13] which is obviously formed at Mo/CZTS interface.

The optical reflectance measurements and based on them calculation of the absorption spectra allowed to estimate the bandgap of the films. The value obtained of about 1.3 eV is smaller than values expected for purely kesterite structure [23]. This deviation can be due to the inclusions of defects and secondary phases. This assumption was confirmed by results of Raman spectroscopy (Fig. 3) which determined formation of Cu_{2-x} in certain samples, as well as inclusions of stannite modification of CZTS.

The PL spectra of the films almost coincide for all the samples and have a similar asymmetric broad band with a maximum at 1.26±0.01 eV (Fig. 5). PL of Cu_2ZnSnS_4 is known to be usually dominated by recombination of donor-acceptor pairs [24] or tran-
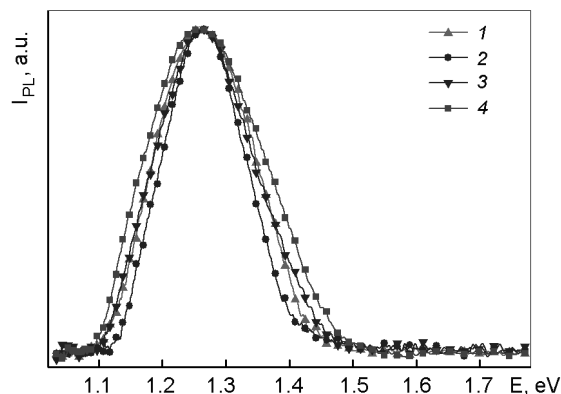

Fig. 5. Photoluminescence spectra of CZTS films at $T = 80$ K, synthesized in air (*1, 2*) and nitrogen (*3, 4*).

sition from conduction band to acceptors states [25]. Note that in the PL measurements both dark and light areas of the films contributed to the spectra, because they were excited not under microscope with a laser but in macro-configuration with less focused diode light source.

Conclusions

Structural properties of Cu_2ZnSnS_4 films formed by thermal annealing of layers of copper, zinc, and tin sulfides on glass substrates have been studied. Raman spectroscopy proves that the films are of kesterite structure with possible inclusions of disordered areas of stannite. Raman spectroscopy also identified segregation of $Cu_{2-x}S$ phase at the certain technological conditions. The influence of the annealing temperature and atmosphere in which the formation of structures occurs on the film composition was established. The interpretation of reflectance spectra is significantly complicated by the formation of $Cu_{2-x}S$ clusters, which contribute to the optical spectra.

References

1. T.Unold, H.W.Schok, *Annu.Rev.Mater.Res.*, **41**, 297 (2011).

2. I.Repins, M.A.Contreras, B.Egaas et al., *Prog. Photovolt.Res.Appl.*, **16**, 235 (2008).

3. S.Siebentritt, S.Schorr, *Prog.Photovolt.Res. Appl.*, **20**, 512 (2012).

4. D.Aaron, R.Barkhouse, O.Gunawan et al., *Prog.Photovolt.Res.Appl.*, **99**, 262105 (2011).

5. H.Matsushita, T.Maeda, A.Katsui, T.Takizawa, *J. Cryst. Growth*, **208**, 416 (2000).

6. O.V.Parasyuk, L.D.Gulay, Ya.E.Romanyuk, L.V.Piskach, *J. Alloys Comp.*, **329**, 202 (2001).

7. Ya.E.Romanyuk, O.V.Parasyuk, *J. Alloys. Comp.*, **348**, 195 (2003).

8. S.Schorr, H.-J.Hoebler, M.Tovar, *Eur. J. Mineral.*, **19**, 65 (2007).

9. S.Schorr, *Solar Energy Mater and Solar Cells*, **95**, 1482 (2011).

10. X.Fontane, L.Calvo-Barrio, V.Izquierdo-Roca et al., *Appl. Phys. Lett.*, **98**, 181905 (2011).

11. S.A.Kissin, *Can. Mineral.*, **27**, 689 (1989).

12. S.R.Hall, J.T.Szymanski, J.M.Stewart, *Can. Mineral.*, **16**, 131 (1978).

13. S.Chen et al., *Phys. Rev.*, **B 79**, 165211 (2009).

14. J. Alvarez-Garcia, V. Izquierdo-Roca, A. Perez-Rodriguez, Raman Spectroscopy on thin films for solar cells, in Advanced Characterization Techniques for Thin Film Solar Cells. Ed. U. Rau, D. Abou-Ras, T. Kirchatz, Wiley - VCH Verlag, 365 (2011)

15. M.Himmrich, H.Haeuseler, *Spectrochim. Acta*, **47A**, 933 (1991).

16. T.Gurel, C.Sevik, T.Cgin, *Phys. Rev.*, **B 84**, 205201 (2011).

17. P.A.Fernandes, P.M.P.Salome, A.F.daCunha, *Thin Solid Films*, **517**, 2519 (2009).

18. K.Muska, M.Kauk, M.Altosaar et al., *Energy Procedia*, **10**, 203 (2011).

19. K.Woo, Y.Kim, J.Moon, *Energy Environ. Sci.*, **5**, 5340 (2012).

20. M.Altosaar, J.Raudoja, K.Timmo et al., *Phys. Stat. Sol.*, **205**, 167 (2008).

21. H.Yoo, J.K.Kim, *Thin Solid Films*, **518**, 6567 (2010).

22. X.Fontane, V.Izquierdo-Rosa, E.Saucedo et al., *J. Alloys and Comp.*, **539**, 190 (2012).

23. R.B.V.Chalapathy, G.S.Jung, B.T.Ahn, *Solar Energy Mater. and Solar Cells*, **95**, 3216 (2011).

24. J.P.Leitao, N.M.Santos, P.A.Fernandes et al., *Phys. Rev.*, **B 84**, 024120 (2011).

25. M.Grossberg, J.Krustok, J.Raudoja, T.Raadik, *Appl. Phys. Lett.*, **101**, 102102 (2012).

Тонкі плівки Cu_2ZnSnS_4 для сонячних елементів: оптичні та структурні властивості

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Методами раманівської спектроскопії, скануючої електронної мікроскопії, енергетично-дисперсійної рентгенівської спектрометрії, оптичного відбивання та фотолюмінесценції досліджено структуру плівок Cu_2ZnSnS_4, сформованих термічним відпалом попередньо осаджених шарів міді та сульфідів цинку та олова на скляні підкладки при різних температурах підкладок та оточуючої атмосфери. Встановлено, що плівки мають структуру кестеріту з можливими включеннями структури станіту. Показано, що при певних технологічних режимах формування плівок в них може мати місце сегрегація фази $Cu_{2-x}S$. В спектрах не проявилися можливі включення фаз сульфідів цинку та олова.