ABSTRACT

Of dissertation for the doctor of philosophy degree (PhD)

6D072000 – Chemical technology of inorganic substances

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Preparation of functional chalcogenide crystals from melt-solution

General description of work. The work is devoted to the preparation of functional chalcogenide crystals of the kesterite family, which are considered as a promising material for the adsorption layer of solar cells. Various approaches to the synthesis of Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe) and their solid solution (CZTSSe) in the form of single crystals and single crystal powders have been studied. The modes of crystal growth are determined, which provide a monophase product with optimal stoichiometry.

Relevance of the research topic. Due the depletion of non-renewable resources, there is an increasing interest in alternative methods of obtaining energy, for example, in solar energy. Despite the development of this topic in the form of silicon PVCs, their high cost and the complexity of the manufacturing technology forces us to search for cheaper analogs that can meet the growing demand. The most important advantages of CZTS(Se) are their low cost, environmental friendliness and abundance of constituent elements in nature. At the same time, CZTS(Se) has optimal physical properties - a band gap of 1.0–1.6 eV and a high absorption coefficient (10^4–10^5 cm^{-1}), due to which the theoretical maximum efficiency of batteries based on them is ~ 33%.

The degree of elaboration of the topic. A large number of methods for producing thin films of kesterite are described in the literature, each of which has its own advantages and disadvantages. The record for the achieved efficiency of conversion of sunlight is 12.6% with an average value of published results at the level of 8-10%. Low efficiency is associated with deviation from stoichiometry and the presence of side phases. In addition, the kesterite manufacturing process is characterized by low reproducibility. At the moment, the monograin technology is one of the promising methods for the manufacture of PVC, where the absorber layer is a thin film, which consists of a monolayer of monocrystalline powder. This technology was presented as an alternative to thin-film solar cells and, in fact, is a kind of hybrid between monocrystalline and thin-film solar cells. In the literature, halides of alkali and transition metals (KI, CdI_2) are used as a flux that promotes the recrystallization process. Until now, a number of unsolved problems remain - the control of excess phases and stoichiometry in the synthesized material. Also, it is relevant to reduce the complexity of the synthesis process, which is associated with the use of vacuum equipment.

The aim of the thesis is to optimize the process of obtaining crystals CZTS, CZTSe (CZTS (Se)) and their solid solutions.

To achieve this goal, the following tasks have been set:

1.Search for new fluxes suitable for recrystallization of CZTS (Se).

2.Development of approaches to ensure the absence of off-target phases in the CZTS (Se) synthesis products.

3.Evaluation of the influence of experimental parameters on the stoichiometry of crystals for the development of optimal production technologies.

4.Testing the method without vacuum preparation of solid solutions $Cu_2ZnSnS_xSe_{4-x}$.

Research objects: Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$, $Cu_2ZnSnS_xSe_{4-x}$.

Subject of scientific research: melt-solution synthesis of kesterite, phase composition, morphology, phase formation.

Research methods. When performing research on the topic of the dissertation, the following methods of synthesis and analysis were used: dry synthesis from elementary components, melt-solution synthesis under isothermal conditions and at a temperature gradient, powder X-ray phase analysis, scanning electron microscopy with an energy dispersive attachment, Raman spectroscopy.

The source base and research materials are 206 literature sources on methods of obtaining thin films, single crystals, single-crystalline kesterite powders, as well as on other areas of natural science related to the topic of this research.

Scientific novelty:

- New solvents for obtaining CZTS (Se) crystals have been proposed and experimentally tested.
- A comparison of the methods of isothermal and non-isothermal recrystallization of CZTSe in a previously unused KI-KCl solvent is carried out.
- An efficient method has been developed for the two-stage synthesis of crystals of the kesterite family with the possibility of changing the stoichiometry due to the addition of elementary precursors at the second stage of the synthesis.
- For the first time, the solvents $CuCl_2$, $ZnCl_2$, $SnCl_2$ were tested to obtain monophase CZTS by the melt-solution method.

For the first time, CZTS crystals were obtained by parallel recrystallization and sulfurization of polycrystalline CZTSe without using a vacuum. For the first time, the method of liquid-phase sulfur encapsulation was applied for the sulfurization of single-crystalline powders in order to obtain solid solutions based on CZTS and CZTSe. The dependence of the morphology and compositional composition of grains on the temperature and duration of the experiment was revealed.

The theoretical significance of the study. The conditions found for the melt-solution recrystallization to obtain kesterite crystals, as well as the developed vacuum-free technology for the synthesis of kesterite and its solid solutions, are of significant theoretical interest.

Practical value. The scientific significance of the work lies in the experimental analysis of phase formation in the systems CZTS (Se) - solvent (KI-KCl, KI-NaCl, CsCl-NaCl, CsCl-KCl, LiCl-KCl). The results of vacuum-free annealing of CZTSe in sulfur vapor will make a great contribution to the optimization of methods for obtaining crystals of S-containing solid solutions of the kesterite family. In addition, the demonstrated approaches to the selection of the optimal solvent and growth conditions will improve the methods for obtaining other functional crystals of chalcogenides.

The main provisions for the defense:

- Synthesis of single-phase product CZTS (Se) effectively extends from elementary compounds in the presence of the eutectic melt KI-KCl at 1000 C in the first stage with intermediate grinding charge before resynthesis at 750 C.
- Recrystallization in $SnCl_2$ solvent provides CZTS crystals with optimal stoichiometry Cu/(Zn + Sn) ~ 0.96, Zn / Sn ~ 1.11, corresponding to the composition of the adsorption layer of solar cells with record characteristics.
- An innovative way to obtain solid solutions $Cu_2ZnSnS_x Se_{4-x}$ is to anneal CZTSe in the presence of elemental sulfur in an open quartz flask.

The main results of the dissertation research are published in 4 scientific papers, including:

- 1 article published in an international scientific journal, which, according to the information base of the Thomson Reuters company (ISI Web of Knowledge, Thomson Reuters), has a non-zero impact factor and is in the first quartile (Q1); The personal contribution of the doctoral student to the preparation of the publication consisted in carrying out experimental work on obtaining Cu_2ZnSnS_4 crystals by recrystallization from such solvents as $CuCl_2$, $ZnCl_2$ and $SnCl_2$; and participation in the characterization of Cu_2ZnSnS_4 crystals, as well as in the interpretation of the results obtained.

- 1 article published in a journal recommended by the Committee for Control in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan. The personal contribution of the doctoral student to the preparation of the publication consisted in conducting experimental work on obtaining crystals, and in participating in physical and chemical research, as well as in participating in the interpretation of the results.

- in 2 theses of reports at international conferences and symposia.

The structure and scope of the thesis.

The dissertation work consists of an introduction, 4 main sections, a list of references, from 206 titles. The work is presented on 124 pages, contains 73 figures and 13 tables.

Based on the results of the dissertation research , the following conclusions were made:

1. Eutectic mixtures of salts CsCl-KCl, CsCl-NaCl, KI-NaCl, KI-KCl, LiCl-KCl, as well as $SnCl_2$ and $ZnCl_2$ are potential solvents for obtaining kesterite crystals due to the absence of any chemical reactions between the charge and the solvent.

2. Eutectic mixtures of $PbCl_2$ -NaCl, $PbCl_2$ -KCl and $CuCl_2$ salts are not suitable for the melt-solution growth of kesterite. In the case of $PbCl_2$ -NaCl and $PbCl_2$ -KCl, lead chalcogenides were found in the composition, and in the case of $CuCl_2$, the formation of the kesterite phase was not detected.

3. It was found that the $Cu_2SnS(Se)_3$ phase can dissolve a large amount of zinc, which makes its composition very similar to kesterite, and only Raman spectroscopy can reliably identify these phases. In addition, this region of solid solutions is not indicated on the phase diagrams, which requires their repeated study.

4. The optimum temperature of the second stage of recrystallization of CZTSe in the presence of a KI-KCl solvent is 750° C. At 650° C, the reaction time significantly increases, and at 850° C, peritectic decomposition of kesterite occurs.

5. Correction of the stoichiometry of kesterite at the second stage of recrystallization is realized due to the addition of metal precursors to the charge: the addition of zinc led to a shift in the zinc-rich region with cation ratios about Cu / (Zn + Sn) = 1.5 and Zn / Sn = 1.2; the addition of copper to the cation ratios around Cu / (Zn + Sn) = 0.8 and Zn / Sn = 0.9; adding tin to a small tin rich range with cation ratios around Cu / (Zn + Sn) = 0.9-1.1 and Zn / Sn = 0.975.

6. The recrystallization of kesterite in a temperature gradient is apparently limited by the diffusion of the components through the solvent. It is economically more expedient to carry out the process under isothermal conditions, when the synthesis reaction is completely completed in 14 hours at 750 C.

7. Recrystallization of polycrystalline CZTS in $SnCl_2$ flux leads to the formation of chlorine-free crystals with an optimal cation ratio; twinned individuals are observed in large crystals.

8. Vacuum free sulfurization CZTSe at 675 C leads to the deterioration of morphology of the grains due to the rapid replacement of selenium by sulfur, but by reducing the process temperature to 575° C it was possible to preserve the integrity of the grains and improve the distribution of sulfur atoms in the grain structure.

9. Raman spectroscopy is a reliable and simple method for phase identification in kesterite systems. Powder diffractometry requires precision measurements at 2theta far angles to distinguish CZTS(Se) from CTS(Se)

Evaluation of the completeness of solutions to the assigned tasks. All the tasks set for solving the goal of this dissertation work have been solved in full. The optimal solvents were selected from among the chlorides of alkali metals. An efficient method was developed for obtaining monophase monocrystalline kesterite powders under isothermal conditions using the molten salt assisted technology, as well as a method for regulating the stoichiometry of crystals by adding an excess of cations in the form of elementary substances to the charge. An innovative non-vacuum method for preparing solid solutions of kesterite was developed in which selenium atoms are partially replaced by sulfur atoms. The temperature and time conditions for the melt-solution recrystallization were determined. The phase composition of the obtained samples and the stoichiometry of the kesterite phase were determined by physicochemical methods.

Thus, the objectives of the dissertation research have been achieved - optimization of the process of obtaining crystals CZTS, CZTSe and their solid solutions.

Assessment of the technical and economic efficiency of the solutions proposed in the dissertation work. The solutions proposed in the framework of this dissertation work can form the basis for the production of monocrystalline kesterite powders for the manufacture of thin-film PVCs using monograin technology.

Compliance with directions of development of science or government programs. The dissertation work was carried out within the framework of the grant funding program of the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan "Development of technology for the synthesis of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ chalcogenide crystals for thin-film solar cells" (Grant No. AP08052719).