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Preparation of High-Purity Chalcogens

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Abstract

The development of advanced laser technologies demands optical materials with definite operation performance such as high optical homogeneity, low absorption and high damage threshold. Insufficient purity of initial materials used for the synthesis and growth of crystals is responsible for deterioration of optoelectronic material performances. The results of experiments aimed at the preparation of high-purity sulphur, selenium and tellurium using a complex of physical and chemical purification methods are considered. Gaseous and gas-forming impurities are shown to be the principal impurities that cause worsening of the optical characteristics of chalcogenide materials. The studies of gas-forming impurities behaviour at different technological stages during the manufacture of high purity chalcogens and synthesis of chalcogenide compounds have been carried out. A technological scheme has been chosen that provides the preparation of high-purity chalcogens with the decreased total impurities content by a factor of 10^3–10^4 in comparison with the initial material.

INTRODUCTION

The development of advanced laser technologies demands optical materials with definite operation performance such as high optical homogeneity, low absorption and high damage threshold. Insufficient purity of starting materials, used for synthesis and growth of crystals, is responsible for impairment of optoelectronic material performances.

The study of impurity structure of the initial materials has shown their main impurities to be gaseous and gas-forming. Carbon and water mass of initial sulphur of the "os. ch. 16–5" specification (specially pure grade) is up to 10^{-1}–10^{-2} %. Carbon and oxygen contents of initial selenium of the "os. ch. 22–4" specification is up to 10^{-2} %. The principal impurity in tellurium of the TV-4, TVCh and Tellurium refined specifications is oxygen, with 10^{-1} % mass proportion in fine fraction material.

Therefore, principal attention was paid to the studies of the behaviour of these impurities at different technological stages. At the same time, gas chromatographic techniques have been developed for the determination of carbon and gaseous impurities both directly in the materials obtained, and at different technological stages.

ANALYSIS OF IMPURITIES

The methods used to study purification and to perform certificate tests of the obtained products include the following.

1. Determination of metal impurities has been conducted by spectrochemical analysis, followed by vacuum distillation of the base, atomic absorption, neutron activation, inversion voltammetry, spark source mass spectrometry, glow discharge mass spectrometry analyses.

2. Determination of carbon has been carried out by burning out in oxygen followed by gas chromatography analysis.

3. Determination of bitumen has been performed by spectrophotometric analysis.

4. Determination of gaseous impurities (CO, CO_2, H_2O, O_2, H_2, N_2, CS_2, COS, SO_2, SO_3, H_2S) has been performed by gas chromatography, mass spectrometry, and by measuring the pressure in the ampoule after a technological stage [1].

The detection limit of metal impurities was 10^{-5} to 10^{-8} %. The detection limit of carbon and gaseous impurities by gas chromatographic analysis was 10^{-5} %.

TELLURIUM

The methods most widely used at present to obtain high-purity tellurium involve crystallization and the methods based on transport in the gas phase. By means of these methods, low concentrations of most electroactive impurities may be achieved. Either reducing melting or flow hydrogen distillation are usually used to remove oxygen. Hydrogen flow through tellurium melt leads also to the decrease of selenium content. As a rule, the content of impurities in tellurium after purification is not reported.

We used the following methods when choosing an optimal scheme [2]: distillation, directional solidification, melting in vacuum and in reducing atmosphere, crystallization from the gas phase. Realization of unidirectional crystallization after which one breaks ampoules and pumps out the gases evolved (repeating this procedure two or three times) was found to purify tellurium from CO_2 and H_2O impurities. Removal of oxygen is accompanied by significant dissolution of hydrogen in tellurium melt. It was not easy to remove hydrogen by directional solidification. Two- or three-stage directional solidification must be carried out.

As a result of our investigations, the following technological scheme of tellurium purification has been chosen:

a) purification from gaseous and metal impurities by distillation through TeO_2 layer in dynamic vacuum;

b) removal of gas-forming impurities (CO_2, H_2O) by directional solidification;

c) removal of oxygen by melting in hydrogen atmosphere;

d) removal of hydrogen by directional solidification.

Spectrochemical analysis showed that the mass content of impurities (with respect to 32 elements) in tellurium purified according to the suggested scheme is less than $5 \cdot 10^{-6}$ %. Gas chromatographic analysis has shown gaseous impurities (CO_2, H_2O, H_2, *etc.*) mass content to be less than $1 \cdot 10^{-5}$ %. The data have been verified by glow discharge mass spectrometry.

Elemental high-purity Te was used for the synthesis of both CdTe and CdTe-based solid solutions, and chalcogenide glasses from As − Se − Te system. Tests of electrophysical characteristics of cadmium telluride single crystals at the St. Petersburg Institute of Nuclear Physics, RAS, showed that this material is among the world's best samples for its detector characteristics. Comparative measurements (performed at the State Optic Institute, RAS, St. Petersburg) of transmission spectra involved chalcogenide glasses synthezied using both Te refined by crystallization in rotating container and Te purified by the above-suggested scheme. The comparison showed that the material purified from gas and gaseous impurities allowed to obtain glasses with absorption coefficient (at 10.6 μm) 80 times less, in spite of practically equal metal impurities content.

SULPHUR

Elemental sulphur of "os. ch. 16−5" was used as the initial material. Gas chromatography and chemical analyses have shown that principal impurities in this sulphur were bitumen (mass content up to 10^{-1} %), H_2O (up to $5 \cdot 10^{-1}$ %), sorbed and dissolved gases. Chalcogenide compounds synthesis and growing are strongly influenced by these impurities. Impurities have a negative effect on functional characteristics of chalcogenides. The following techniques were used for additional purification: thermal method (under dynamic and static vacuum), thermal method with high-temperature zone [3], directed crystallization. The removal of oxygen-contained gases (CO_2, H_2O, SO_2, SO_3) proceeds at the initial purification stage. CS_2, COS and H_2S are eliminated at the final stage. The appearance of SO_2 at the final stage is the evidence of the violation of technology and means that sulphur interacts with the atmosphere.

The best results were obtained with the combination of thermal methods: treatment of sulphur under dynamic vacuum at 125–150 °C and under static vacuum at 300–400 °C, followed by packing in amounts sufficient for synthesis charge preparation. High-temperature treatment in the presence of oxygen was found to be the most effective technique for elimination of carbon-containing impurities.

The technological scheme selected for the preparation of high-purity sulphur provides the decrease in total impurities content by a factor of 10^2–10^3 in comparison with the initial material. Sulphur purity with respect to metals corresponds to seven-nines (7N). The total mass content of gas and gas-forming impurities is not more than $2 \cdot 10^{-5}$ %. High-purity sulphur thus obtained was used for synthesis and growth of single crystals of proustite, silver thiogallate and for the preparation of chalcogenide glasses. The use of high-purity initial materials enabled the preparation of material possessing high optical homogeneity and low absorption coefficient in transparence range (infrared). The comparison of optical characteristics of As_2S_3 glasses obtained from unpurified initial sulphur material, and that prepared from sulphur purified according to the above scheme, has shown that the absorption coefficient of the latter is an order of magnitude less.

SELENIUM

As in the case of sulphur, when developing the technology for the preparation of high-purity selenium, the following techniques were used: thermal methods (distillation, vacuum and oxidizing melting) and unidirectional crystallization. The major impurities of the initial material – selenium of the "os. ch. 22–3" specification – were carbon, oxygen and gaseous impurities (N_2, CO, CO_2, H_2O) with mass content up to $5 \cdot 10^{-2}$ %. Quartz container often got destroyed during cooling liquid selenium. This caused additional difficulties. Investigation of temperature features of devitrification permitted to choose cooling conditions excluding possible seal failure of quartz container. In our opinion, the following scheme is most efficient for selenium purification:

a) elimination of gaseous impurities by heating selenium under dynamic vacuum;

b) purification from carbon by oxidizing melting;

c) removal of selenium oxide;

d) final purification by multiple distillation.

By using the complex of above-mentioned purification techniques, we obtained selenium with the total impurities mass proportion not more than $1 \cdot 10^{-4}$ %.

The samples of high-purity chalcogens have been certified and exhibited at the Exhibition of Special-Purity Substances Collection (Nizhniy Novgorod, Russia).

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