Determination of the composition of chalcogenid glasses $\text{AS}_x\text{SE}_{1-x}$ by the method of X-ray fluorescent analysis

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Abstract. The features of X-ray fluorescence analysis of chalcogenide glassy semiconductors are considered in the research. The standard method was used to determine the concentrations of arsenic and selenium $\text{AS}_x\text{SE}_{1-x}$ alloys. The use of this method allows determining the quantitative composition of glasses with an accuracy of $\pm 0.0002$.

1. Introduction

The peculiarity of chalcogenide glassy semiconductors is that they belong to the group of compounds of variable composition, thus, in the glassy state it is possible to get homogeneous materials in a wide range of compositions. However, the absence of long-range order in glasses excludes the arsenic-selenium types of the non-destructive method of X-ray phase analysis from the control methods of the chemical composition of the systems [3, 4, 6–8].

The research objects were glassy and crystalline alloys of the $\text{AS}_x\text{SE}_{1-x}$ systems ($\text{AS}_{0.02}\text{SE}_{0.98}$, $\text{AS}_{0.1}\text{SE}_{0.9}$, $\text{AS}_{0.286}\text{SE}_{0.714}$, $\text{AS}_{0.4}\text{SE}_{0.6}$, $\text{AS}_{0.55}\text{SE}_{0.45}$, $\text{AS}_{0.6}\text{SE}_{0.4}$). The compositions of these samples are given by the composition of the initial mixture, determined with an error of $\pm 0.001$.

Glassy alloys of arsenic-selenium systems were synthesized at a temperature of 700 °C. During the synthesis of alloys containing selenium, the temperature in the furnace was raised to a maximum at a rate of 4 °C per minute and the melts were kept at this temperature for 6 hours. The synthesis of alloys containing sulfur was carried out in two stages. Initially, the ampoules in the furnace were heated at a rate of 3 °C per minute to a temperature of 450 °C (melting of sulfur and its interaction with arsenic occur with the formation of $\text{AS}_2\text{S}_3$). At 450 °C, the ampoules were kept for 5 hours. In the second stage, the heating rate of the ampoules to a maximum temperature was 4 °C per minute and the melts were kept at this temperature for 6 hours. The melt was hardened in the air [1, 5, 9–15].

2. Experiments

Glassy specimens weighing ~ 5 grams were monolithic ingots; the top of the ampoule did not contain traces of sublimation. The criteria for the vitreous state were a fibrous fracture, the absence of lines on the patterns, the absence of inclusions and irregularities when viewing polished surfaces in a MIM-7 metal microscope and an MIK-1 infrared microscope. Glassy alloys were not subjected to special machining (grinding, polishing, etc.).

X-ray fluorescence spectra were recorded on an X-ray M-analyzer, which was designed to determine the qualitative and quantitative elemental composition of solid, liquid and powdery substances. The effective excitation of the fluorescence of chemical elements in the analyzed sample (from Mg to U) was carried out by the X-ray flux generated by the X-ray tube. To obtain qualitative,
The spectrometer guarantees the most accurate, reliable and high-performance automatic microanalysis of samples of any shape and size from 0.1 mm and more. The spectrometer allows detecting and determining impurities with a detection threshold of $\sim 10^{-4}\%$. The size of the analyzed surface (adjustable) is from 1 to 10 mm. It is possible to scan the surface of a sample of any size using an external analytical unit. The time of one measurement is from 15 seconds to 24 hours (depending on the task). Operating temperatures range from $-35$ to $35\ ^\circ\mathrm{C}$. Continuous operation time is at least 30 days.

X-ray fluorescence spectra were measured at anode voltage $U$ values from 12 to 50 kV.

The presence of arsenic in the most important from a practical point of view alloys leads to significant difficulties in determining their composition of classical methods of chemical analysis (presence of a special chemical laboratory, analysis time and large errors in determining the content of chemical elements). All this stimulates the development of new methods.

That is why in order to determine the quantitative composition of the glasses used in the study we applied the method of X-ray fluorescence analysis (XRF). The dependence of the fine structure of the spectra on the installation parameters (anode voltage and cathode current) was studied so that the ratio of the lines of arsenic atoms and chalcogens in the X-ray spectra corresponded to the ratio of atoms of arsenic and chalcogens in glasses. Since the intensity ratio of the $K_{\alpha}$ lines of arsenic and selenium for the studied samples depended on many factors (fluorescence yields, absorption cross sections for both primary and fluorescent radiation by all atoms), it was impossible for quantitative analysis to directly use theoretical ratios for line intensities in X-ray fluorescence spectra.

In order to determine the concentrations of arsenic and selenium $\text{As}_x\text{Se}_{1-x}$ alloys, we used the standard method.

The standard method is a traditional X-ray phase analysis method, where the ratios of the intensities of the lines of two atoms for a known compound are first calibrated, and then these calibration ratios are used to determine the composition of the unknown alloy.

If the anode voltages, cathode current, the distance between the detector and the irradiated surface, as well as the detector loading, are fixed, the relative intensity of the arsenic $K_{\alpha}$-line increases with the $x$ index in $\text{As}_x\text{Se}_{1-x}$ alloys, and this confirms the possibility of using the X-ray fluorescence method to determine the composition of these alloys.

For this purpose, X-ray fluorescence spectra of standards were measured - $\text{As}_{0.4}\text{Se}_{0.6}$ glass (at $U = 40\ \text{kV}$, cathode current $5\ \mu\text{A}$, distance between the detector and the irradiated surface $5\ \text{mm}$, detector loading $3800\ \text{counts/s}$). The choice of $\text{As}_x\text{Se}_{1-x}$ alloys as standards is explained by the fact that they are reliably established compounds in $\text{As}_x\text{Se}_{1-x}$ systems, which can be obtained in stoichiometric composition by the method of fusion of the initial components.

For a given alloy composition, the spectrum was measured at an arbitrarily selected point on the surface five times (to calculate the average value and determination error).

The characteristic X-ray spectra of glassy and crystalline alloys $\text{As}_x\text{Se}_{1-x}$ films contained all lines of the $K$-series of arsenic, sulfur and selenium, the most intense lines being the superposition of their $K_{\alpha1}$ and $K_{\alpha2}$ components.

For the spectra of standards, the areas under the $K_{\alpha1,2}$ lines of arsenic and selenium $S_{\text{As}}$ were determined and according to the ratios

$$x_{\text{RFA}}=S_{\text{As}}/(S_{\text{As}}+S_{\text{Se}}),$$

(1)

The atomic fractions of arsenic were determined (here, the “$x_{\text{RFA}}$” index means that the $x_{\text{RFA}}$ values are determined from X-ray fluorescence analysis data with an error of $\pm \ 0.0002$). Then, the calibration dependences of $x_{\text{RFA}} = f(x)$ were built on three points: for $x = 0$ (for it $x_{\text{PFA}} = 0$ was taken), for $x = 1$ (for $x_{\text{RFA}} = 1$ was taken) and for $x$ standard.

The indicated calibration dependences for the $\text{As}_x\text{Se}_{1-x}$ systems are presented in Fig. 1. These dependences can be approximated by polynomials of the second degree. These polynomials and their
graphs can serve as calibration ratios for determining the composition of targets from the \(x_{RFA}\) value obtained from the spectra.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Dependence \(x = f(x_{RFA})\) for \(As_xSe_{1-x}\) glasses. The dots show the value of \(x\) and \(x_{RFA}\) used to construct the calibration dependence (it is drawn with a solid line). Square symbols show \(x\) and \(x_{RFA}\) values for \(As_xSe_{1-x}\) binary compositions. The spectra were measured at \(U = 40\) kV.

In order to demonstrate this feature, in Figure 1 there are additional experimental \(x_{RFA}\) values for \(As_xSe_{1-x}\) glasses (\(As_{0.02}Se_{0.98}\), \(As_{0.1}Se_{0.9}\), \(As_{0.28}Se_{0.72}\), \(As_{0.4}Se_{0.6}\), \(As_{0.47}Se_{0.53}\), \(As_{0.5}Se_{0.5}\), \(As_{0.6}Se_{0.4}\)). In Figure 2 it is possible to see typical X-ray fluorescence spectra of the corresponding alloys. It can be seen that the experimental data fit well the calibration relations between the values of \(x\) and \(x_{RFA}\). Some scatter of data is explained by the greater error in determining \(x\) from the composition of the initial charge (not better than \(± 0.0005\)) as compared to the error in determining \(x_{RFA}\) (not worse than \(±0.0002\)).

Similar measurements for the \(As_xSe_{1-x}\) system were carried out at an anode voltage of 40 kV.

### 3. Results and discussion

Let us calculate the errors in determining the composition of \(As_{1-x}Se_x\) alloys using the calibration ratios. We denote the \(x_{RFA}\) letter \(y\). This parameter is measured experimentally and it is necessary to determine the parameter \(x\) for it.

The approximation will be represented as a parabolic function

\[
y = x + \alpha x (1 - x)
\]

This parabola has only one parameter \(\alpha\), its ends are fixed at the points \((0,0)\) and \((1,1)\):

\[
\alpha = (y_0 - x_0)/x_0(1 - x_0)
\]

Calibration for the case of \(U = 40\) kV has the values \(x_0 = 0.60\) and \(y_0 = 0.61\), the value of the parameter \(\alpha = 0.041\).
Figure 2. X-ray fluorescence spectra of As$_x$Se$_{1-x}$ glasses measured at an anodic voltage of 40 kV

The value of $x_0$ is considered to have no error and, therefore,

$$\Delta \alpha = \Delta y / x_0 (1 - x_0) = 4.1 \times 10^{-4}.$$

The relative error $\delta \alpha = \Delta \alpha / \alpha = 0.01$.

The composition parameter $x$ is extracted from a quadratic equation:

$$\alpha x^2 - (1 + \alpha) x + y = 0,$$

thus,

$$x = (1/2\alpha) (1 + \alpha - (1 + \alpha)^2 - 4\alpha y)^{1/2}$$

We decompose this expression in a row:

$$x \approx y/(1 + \alpha) + \alpha y^2/(1 + \alpha)^3$$

Calculations using this formula give:

| $y$  | $x$   |
|------|-------|
| 0    | 0     |
| 1    | 0.997 |
| 0.61 | 0.599 |

In this formula, the approximate values are $y$ and $\alpha$, and according to the formulas for the errors:

$$\Delta x = \sqrt{((y/(1+\alpha))^2((\Delta y/y)^2 + (\Delta \alpha/(1+\alpha))^2) + (\alpha y^3/(1+\alpha)^6)((\Delta \alpha/\alpha)^2 + 4(\Delta y/y)^2 + 9(\Delta \alpha/(1+\alpha))^2)}$$

The calculated errors do not exceed $5.10^{-4}$ (see table)

| $y$  | $\Delta x$     |
|------|----------------|
| 0.1  | $1.03 \times 10^{-4}$ |
| 0.5  | $1.9 \times 10^{-4}$ |
| 0.9  | $4.5 \times 10^{-4}$ |

The increase in the relative intensity of the line of the light component (arsenic) (compared to the content of this component in the alloy) in the region of small values of the anode voltage $U$ and to its
decrease with increasing U is demonstrated. This is explained by the shift of the X-ray tube bremsstrahlung spectrum to high energies. It was concluded that it is most appropriate to measure X-ray fluorescence spectra of As<sub>x</sub>Se<sub>1-x</sub> alloys at an anode voltage of ~ 30–50 kV.

4. Conclusion

The relative intensities of the lines related to the two components of the alloy also depend on the cathode current of the x-ray tube (which controls the cathode temperature and, consequently, the intensity of the bremsstrahlung of the x-ray tube) – the increase in the cathode current (at a fixed anode voltage) increases the relative intensity in the spectrum light components for As<sub>x</sub>Se<sub>1-x</sub> alloys and an increase in the relative intensity of the heavy components for As<sub>x</sub>Se<sub>1-x</sub> alloys. This is explained by the peculiarities of the shift of the spectrum of bremsstrahlung radiation of the x-ray tube to the high energy region [2].

The above-mentioned data scatter for As<sub>x</sub>Se<sub>1-x</sub> glasses is explained not only by the greater error in determining x in the composition of the initial mixture compared to the error in determining x<sub>RFA</sub>, but also by the uneven distribution of components over the volume of glass. It turned out that the spread of x<sub>RFA</sub> for three arbitrarily selected points is ± 0.001 for As<sub>0.5</sub>Se<sub>0.5</sub>, ± 0.0015 for As<sub>0.6</sub>Se<sub>0.4</sub> glasses and ± 0.004 for As<sub>0.6</sub>Se<sub>0.4</sub>, which significantly exceeds the value of the mean-square measurement errors ± 0.0002. In other words, all As<sub>x</sub>Se<sub>1-x</sub> glasses turn out to be heterogeneous in composition, and the heterogeneity noticeably increases with increasing selenium content in the glass.

Thus, we have demonstrated the high efficiency of the x<sub>RFA</sub> method for determining the quantitative composition of glassy arsenic selenides.

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