X-Ray Fluorescence Analysis of Ge–As–Se Glasses Using X-Ray and Electron-Beam Excitation

G. A. Bordovsky, A. V. Marchenko, P. P. Seregin, and K. U. Bobokhuzhaev

Abstract—The quantitative content of germanium, arsenic, and selenium in As$_{1-x}$Se$_x$, Ge$_{1-x}$Se$_x$, and Ge$_{1-x}$As$_x$Se$_x$ (As$_y$(Ge$_{1-y}$Se$_y$)$_{1-y}$) glassy alloys has been determined by X-ray fluorescence analysis with fluorescence excitation by bremsstrahlung X-rays and an electron beam. The use of these techniques has made it possible to determine the quantitative composition of the glasses (x, y, and z) with an accuracy of ±0.0002 in a surface layer 0.1 mm (under X-ray excitation) to 0.1 µm (under electron beam excitation) in thickness.

DOI: 10.1134/S0020168515080063

INTRODUCTION

An important feature of semiconducting chalcogenide glasses is that their composition and, accordingly, properties can be varied continuously over the entire glass-forming region. As a rule, glass compositions are determined from the quantitative glass batch composition, even though glass preparation conditions do not guarantee that the final material will have the same composition as the glass batch. The lack of long-range order in glasses rules out the use of X-ray diffraction as a nondestructive technique for quantitative analysis of glasses. The presence of arsenic in most chalcogenide glasses presents additional difficulties in determining their composition by classic chemical analysis techniques (the need for a certified chemical laboratory, analysis duration, and large uncertainties in analyses for chemical elements). This accounts for the interest in using modern, high-speed, nondestructive techniques for quantitative analysis of glasses.

In this respect, considerable potential is offered by X-ray fluorescence spectroscopy: analysis of characteristic X-rays emitted by a target under excitation with either bremsstrahlung X-rays or a monoenergetic electron beam allows one not only to carry out elemental analysis but also to determine the quantitative composition of the target. However, X-ray fluorescence spectroscopy is relatively rarely used to determine the quantitative composition of chalcogenide glasses [1–6]. Note that, in most studies, characteristic X-rays of a target were only excited by bremsstrahlung X-rays [1, 3–6] and a limited number of materials have been studied to date (As–S, As–Se, As–Se–S [1, 4–6], Cu–As$_x$Se$_y$, and CuI–PbI$_2$–As$_x$Se$_y$ [2] glassy alloys or mechanical arsenic + chalcogen mixtures [3]).

In this paper, we present experimental data on the determination of the composition of As$_{1-x}$Se$_x$, Ge$_{1-x}$Se$_x$, and Ge$_{1-x}$As$_x$Se$_x$ (or As$_y$(Ge$_{1-y}$Se$_y$)$_{1-y}$) glassy alloys, typical chalcogenide semiconductors, by X-ray fluorescence spectroscopy and compare the capabilities of techniques in which fluorescence is excited by bremsstrahlung from an X-ray tube (energy under 30 keV) and a monoenergetic (30 keV) electron beam.

EXPERIMENTAL

We investigated As$_{1-x}$Se$_x$, Ge$_{1-x}$Se$_x$, and Ge$_{1-x}$As$_x$Se$_x$ glassy alloys with the following compositions: As$_{0.6}$Se$_{0.4}$, As$_{0.5}$Se$_{0.5}$, As$_{0.4}$Se$_{0.6}$, As$_{0.3}$Se$_{0.7}$, As$_{0.2}$Se$_{0.8}$, As$_{0.1}$Se$_{0.9}$, Ge$_{0.6}$As$_{0.4}$Se$_{0.5}$, Ge$_{0.5}$As$_{0.5}$Se$_{0.4}$, Ge$_{0.4}$As$_{0.6}$Se$_{0.3}$, Ge$_{0.3}$As$_{0.7}$Se$_{0.2}$, Ge$_{0.2}$As$_{0.8}$Se$_{0.1}$, Ge$_{0.1}$As$_{0.9}$Se$_{0.0}$, Ge$_{0.0}$As$_{1.0}$Se$_{0.0}$, Ge$_{0.9}$As$_{0.1}$Se$_{0.0}$, Ge$_{0.8}$As$_{0.2}$Se$_{0.0}$, Ge$_{0.7}$As$_{0.3}$Se$_{0.0}$, Ge$_{0.6}$As$_{0.4}$Se$_{0.0}$, Ge$_{0.5}$As$_{0.5}$Se$_{0.0}$, Ge$_{0.4}$As$_{0.6}$Se$_{0.0}$, Ge$_{0.3}$As$_{0.7}$Se$_{0.0}$, Ge$_{0.2}$As$_{0.8}$Se$_{0.0}$, Ge$_{0.1}$As$_{0.9}$Se$_{0.0}$, Ge$_{0.0}$As$_{1.0}$Se$_{0.0}$.

The compositions of the samples are given as the glass batch compositions, determined with an uncertainty of ±0.001, which corresponds to a weighing accuracy of 10 mg or better for individual components at a total sample weight of 10 g. The composition of the As$_{0.4}$Se$_{0.6}$, Ge$_{0.333}$As$_{0.667}$, and Ge$_{0.333}$As$_{0.667}$ samples was determined with an uncertainty of ±0.0002. To this end, the weight of those samples was increased to 50 g.

The glassy alloys were prepared by melting elemental mixtures of selenium metal (OSCh 17–3, 99.997% purity), arsenic metal (PM, 99.999% purity), and semiconductor germanium (6N, 99.999+% purity) at a temperature of 700°C (As$_{1-x}$Se$_x$ alloys) or 950°C (Ge$_{1-x}$Se$_x$ and Ge$_{1-x}$As$_x$Se$_x$ alloys) in silica.
ampules pumped down to 0.1 Pa, without additional purification of the starting components. The furnace temperature was raised to the maximum level at a rate of 4 °C/min and the alloys were held there for 6 h and then quenched in air. The glass beads thus obtained had the form of monolithic ingots. No sublimate traces were detected in the top part of the ampules. We considered the following glassy state criteria: conchoidal fracture, the absence of rings in Debye--Scherrer X-ray powder diffraction photographs, and the absence of inclusions and inhomogeneities when polished surfaces are examined under a metallurgical and an infrared microscope.

Before analyses, no mechanical processing (no grinding, polishing, or other processing step) of the glassy alloys was performed, and analyses were carried out on conchoidal fracture surfaces produced by fracturing bulk glass immediately before analyses (that is, the surface to be analyzed was an inner region of the glass).

X-ray fluorescence spectra excited by bremsstrahlung X-rays were measured on an X-Art M spectrometer with a Si(Li) detector at an anode voltage of 30 kV. The analysis area was ≈1 mm². The spectrometer allowed us to determine impurities from Mg to U, with a detection limit of ≈10⁻⁴ at % for light impurities. In none of the glasses studied did we detect impurities.

X-ray fluorescence spectra excited by an electron beam were measured on a Zeiss EVO40 scanning electron microscope equipped with an INCA X-act X-ray spectrometer. The primary electron beam energy was 30 keV, the beam current did not exceed 300 pA, and the analysis area was ≈30 mm². To prevent surface charging, the samples were coated with a carbon layer ≈20 nm in thickness. The spectrometer allowed us to detect and determine impurities from Be to U.

Chemical analysis of the surface of the glasses under such conditions detected no impurities (the detection limit of the spectrometer for light impurities was 10⁻⁴ at %).

RESULTS AND DISCUSSION

The characteristic X-ray spectra of all the glassy alloys contained all of the germanium, arsenic, and selenium K lines. Since the strongest and best resolved lines were a combination of the Kα₁ and Kα₂ components, we restricted our consideration to these Kα₁, 2 lines.

The spectrum of each sample was measured five times at a fixed point on its surface. We determined the areas under the germanium, arsenic, and selenium Kα₁, 2 lines (S_{Ge}, S_{As}, and S_{Se}, respectively). Next, using the relations x_{XFA} = S_{Se}/(S_{Ge} + S_{As} + S_{Se}), y_{XFA} = S_{As}/(S_{Ge} + S_{As} + S_{Se}), and z_{XFA} = S_{Se}/(S_{Ge} + S_{Se}) (for the Ge_{1-x-y}As_{x}Se_{y} or As_{x}(Ge_{1-y}Se_{y}) alloys), we calculated the relative areas of the spectral lines of germanium, arsenic, and selenium. The subscript XFA indicates that x, y, and z were determined from X-ray fluorescence analysis data. The rms deviations of x_{XFA}, y_{XFA}, and z_{XFA} in such series of measurements were within 0.0002.

Using reference data on the fluorescence yields and absorption cross sections of arsenic, germanium, and selenium atoms [7, 8] and the corresponding calculated linear absorption coefficients of the target material for the primary radiation and the Kα₁, 2 lines of these atoms, we found that, for all of the alloys studied, the analysis depth was d = 0.1 mm in the case of exposure to bremsstrahlung X-rays with a maximum energy of 30 keV and d = 0.1 μm in the case of an electron beam of 30-keV energy.

Since the intensity ratio of the Kα₁, 2 lines in the As₁–xSeₓ, Ge₁–xSeₓ, and Ge₁–x–yAsₓSeₓ glasses depends on many factors (fluorescence yields and absorption cross sections of all the constituent atoms for excitation and fluorescence), we used standards to determine the germanium, arsenic, sulfur, and selenium concentrations [5, 6]. To this end, we constructed x = f(x_{XFA}), y = f(y_{XFA}), and z = f(z_{XFA}) calibration plots through three points. As reference alloys, we used germanium, Ge_{0.3333}S_{0.6667}, and selenium for Ge₁–xSeₓ; arsenic, As_{0.4}S_{0.6}, and selenium for As₁–xSeₓ; and germanium, Ge_{0.3333}As_{0.3333}Se_{0.3333}, arsenic, and selenium for Ge₁–x–yAsₓSeₓ. Figures 1–5 show these plots for the As₁–xSeₓ, Ge₁–xSeₓ, and Ge₁–x–yAsₓSeₓ (or Asₓ(Se₁–y) alloys. All of the data were fitted with quadratic polynomials of the form \( t = t_{XFA} + a_{XFA}(1 - t_{XFA}) \), and in all cases the goodness-of-fit index, which quantifies the agreement between the best fit function and raw data, was unity. The polynomials were used as calibration relations for determining the composition of targets (x, y, and z parameters) from the x_{XFA}, y_{XFA}, and z_{XFA} values extracted from X-ray fluorescence spectra.

To demonstrate such a possibility, we plotted the experimentally determined x_{XFA}, y_{XFA}, and z_{XFA}, or all of the synthesized alloys. The choice of the GeSe₂, As₂Se₃, and Ge₃AsSe₃ alloys as references is explained by the fact that they are well-identified compounds in the corresponding systems and can be prepared in a glassy state with high accuracy in determining the quantitative composition from the composition of the glass batch by melting the starting components. As seen in Figs. 1 and 2, the experimental data for the Ge₁–xSeₓ and As₁–xSeₓ binary alloys agree well with the calibration relation between x and x_{XFA}. The deviation of the data points from the calibration plots is caused by differences in composition between the samples and glass batches.

Note that the plots in Figs. 1a, 2a, and 2b for the Ge₁–xSeₓ and As₁–xSeₓ alloys are almost linear.