INTRODUCTION

Advances in materials for tunable transition-metal-doped II–VI semiconductor lasers [1] in combination with achievements in the preparation of glass materials for optical fibers open up new possibilities in fiber laser development for the range 2–6 \( \mu \text{m} \).

There is special interest in new composite materials based on chalcogenide glasses containing nanoparticles of crystalline II–VI compounds doped with transition metals. The potential of using chalcogenide glasses as matrices for active (II–VI) components is determined by the ability to rich low optical losses in the IR spectral region, which makes such glasses attractive for fiber-optic applications [2].

The use of composites in fiber optics involves the problem of minimizing the optical loss, inevitable in such materials because of the light scattering by inclusions of the disperse phase. A key condition for resolving this problem is that the components of the composite be similar in refractive index. This condition is well satisfied for a number of chalcogenide glasses and chromium-doped ZnS and ZnSe, which has led us to focus on these components in the present study.

In recent studies [3, 4], \( \text{As}_2\text{S}_3/\text{ZnS(ZnSe)}:\text{Cr}^{2+} \) composite materials were prepared in the form of both bulk samples and optical fibers and were shown to luminescence in the 2–6 \( \mu \text{m} \) range. This result, obtained for the first time for optical fibers of such composition, suggests that the fabrication of composites in the form of optically active fiber materials is conceptually feasible.

The purpose of this work was to study the dispersion characteristics and optical properties of \( \text{As}_2\text{S}_3/\text{ZnS(ZnSe)}:\text{Cr}^{2+} \) composite materials in relation to the key parameters of the fabrication process: temperature, holding time, and active component concentrations in the melt. Such studies are of interest for both optimizing the technology of composites and gaining new fundamental information about previously unexplored systems.

EXPERIMENTAL

Bulk preforms of the \( \text{As}_2\text{S}_3/\text{ZnS(ZnSe)}:\text{Cr}^{2+} \) composite were prepared according to the following scheme:

1. The individual components \( \text{As}_2\text{S}_3 \) and \( \text{ZnS:Cr}^{2+} \) or \( \text{ZnSe:Cr}^{2+} \) were loaded into separate quartz glass ampules in the form, respectively, of a glass ingot and a polycrystalline \( \text{ZnS(ZnSe):Cr}^{2+} \) material prepared by solid-state reaction of \( \text{ZnS} \) (ZnSe) with CrSe and ball-milled [3].

2. The ampule containing chromium-doped zinc sulfide or selenide was evacuated by a vacuum pump (\( p = 1.3 \times 10^{-2} \) Pa) and held at 500–600 °C for 2 h.

3. Under vacuum (\( p = 1.3 \times 10^{-2} \) Pa) in a closed system, the glass was driven to the ampule containing the II–VI:Cr\(^{2+}\) powder prepared in the preceding step.

4. The ampule containing the components of the system was sealed off under vacuum, placed in a rocking furnace and held at temperatures from 550 to 850 °C for 1–16 h.

5. The composite material was annealed at the glass transition temperature with the furnace turned off.

The composite materials thus prepared were cut and polished for optical measurements. The \( \text{As}_2\text{S}_3/\text{ZnS(ZnSe)}:\text{Cr}^{2+} \) samples were drawn into structureless fibers (with a uniform transverse refractive index profile) 150–200 \( \mu \text{m} \) in diameter.

Figure 1 shows the flow chart of the preparation of optical fibers from \( \text{As}_2\text{S}_3/\text{ZnS(ZnSe)}:\text{Cr}^{2+} \) composites.

The samples prepared as described above were characterized using standard instruments. Transmission spectra of the bulk samples were measured on a Perkin-
INORGANIC MATERIALS  Vol. 49  No. 3  2013

KARAKSINA et al.

Elmer Lambda-900 spectrometer. Transmission spectra of the fibers were taken on a Bruker IFS-113V Fourier transform spectrometer. The luminescence of the fibers was excited by a butt-joined 1.6-µm Er–Yb fiber laser and detected using an LOMO MDR-2 monochromator, SRS SR-830 synchronous detector, and liquid-nitrogen-cooled Hamamatsu InAs photodetector. The luminescence measurement system was calibrated against a certified tungsten lamp.

The particle size composition and concentration in the composite materials were determined by optical 3D microscopy (OM) and laser 3D ultramicroscopy (LUM) [5] using an experimental setup intended for assessing the microhomogeneity of optical materials and built around an Axio Imager 2M optical microscope. The size of micron-sized inclusions was determined by OM. Using LUM, in which laser light scattered by individual inclusions is detected at ~90° to the incident laser beam, we determined the size of submicron inclusions, unresolvable by an optical microscope, from the brightness of diffraction spots by solving the inverse problem of light scattering using the Mie theory [5]. Probing radiation for LUM was provided by a He–Ne laser (λ = 0.63 µm). The particle concentration in the bulk of the samples was determined by counting the particles. The II–VI particle size in the glass matrix was determined by both OM and LUM.

RESULTS AND DISCUSSION

One principal requirement for fiber-optic materials is low scattering and absorption losses. Losses can be caused by both native defects of the material, related to glass crystallization, chemical inhomogeneities, or bubbles, and second-phase inclusions. These include, primarily, II–VI:Cr2+ particles. Typical molecular impurities dissolved in chalcogenide glasses are H2O and oxygen-, hydrogen-, and carbon-containing impurities [2]. As follows from earlier data [2], a range close to the excitation and luminescence region of the materials under consideration contains absorption bands of molecular water and OH and SH groups. However, according to the estimates below, their contribution to the optical loss is not predominant.

A conventional approach for the fabrication of composites of glasses and active-phase inclusions is to dissolve an active phase in molten glass and ensure super-saturated solution decomposition during melt cooling. In the case of composites for fiber-optic applications, almost complete dissolution in the glass bath is critical, and a disperse form of the added compound is preferable. One possible impediment is reduced crystallization stability of the glass in the presence of crystalline inclusions of the active material. There are no data on the solubility of zinc chalcogenides in As2S3 glass and no information about the probability of heterogeneous crystallization on crystalline ZnS(ZnSe):Cr2+ inclusions.

In the fabrication of the As2S3/ZnS(ZnSe):Cr2+ composite, we used polycrystalline ZnS:Cr2+ and ZnSe:Cr2+ materials ground in a Fritsch Pulverisette-7 ball mill. According to OM and atomic force microscopy (AFM) data (Fig. 2), the resultant powder consisted mainly of micron-sized particles: the average particle size was ~1–2 µm. There were also separate aggregates several tens of microns in size and nanoparticles.

To optimize the fabrication process, we examined the effect of the synthesis temperature, concentration of disperse phases, and holding time in the melt on the size composition and concentration of inclusions in the bulk of the composite and on its optical characteristics: light transmission, absorption, and scattering and luminescence properties.

To optimize the synthesis temperature, we assessed the solubility of zinc chalcogenides in molten glass. Their solubility was determined from the weight loss of bulk II–VI samples and the increase in the concentration of zinc as a component of the II–VI compound in the final product relative to the parent glass after holding for a particular time in molten glass. Material bal-