The composite materials on the basis of As_2S_3 glass containing crystals ZnS and ZnS doped with Cr(2+)

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The method for preparation of the new composite materials on the basis of As_2S_3:ZnS(ZnSe):Cr(2+) is developed. The parameters of the stages of procedure of synthesis of the composites and the individual ZnS(ZnSe):Cr(2+) compounds are established. The luminescence and optical losses of fibers, drawing from preform of composites are investigated: the maximum emission for both composites corresponds to 1.9 μm (which is close to ZnS(Cr(2+)), the level of losses in the range of 2-3 μm is about 5 dB/m.

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1. Introduction

At present, II-VI compounds, namely ZnS and ZnSe, doped with transition metals, represent a relatively new class of solid state gain media with strong and ultra-broad absorption and emission in the mid-IR range: 1.9-5 μm. This spectral range is very interesting, as it is characterized by the presence of absorption lines of various gases, atmospheric constituents and vapors. Over the last years a great success was achieved in development of solid state laser on the basis of these materials with high quantum efficiency at room temperature (more than 70%), the power >12 W, wide tunable band and narrow spectral line-width (<20 MHz) [1,2].

The idea of using of state-of-the art in the development of solid state laser together with advantages of fiber laser technology opens a new possibility of these materials since now there are no broadly tunable fiber sources for different special applications, such as, medicine, information system, optical communication, environmental monitoring and so on.

The present work is aimed to development and preparation of the new composite materials for fiber optics, consisting of chalcogenide glasses with crystalline particles of II-VI Cr-doped compounds.

2. Experimental

The overall scheme for the process of production of the composite materials As_2S_3-ZnS(ZnSe):Cr(2+), includes a sequence of operations presented in Fig.1. The conditions of the stage of homogenization are the next: temperature is varied in 500-850 ^oC range, duration – 1-16 hours, the initial concentration of II-VI compounds – 0.05-8 wt%. Cr-doped II-VI compounds were prepared by solid phase reaction between ZnS(ZnSe) and CrSe at T=1000 ^oC in high vacuum during 144 h. The conditions in procedure of the fiber drawing by a typical one crucible method were the same for the pure As2S3 glass: T=360-380 ^oC, drawing rate ~ 2 m/min.

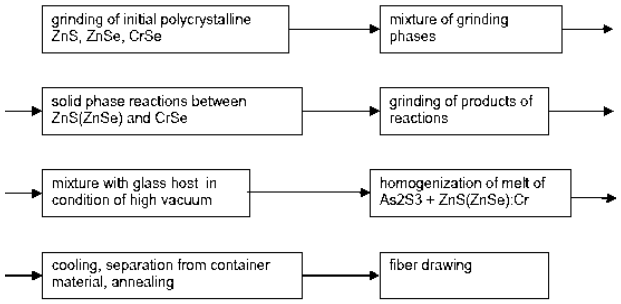

Fig. 1. Scheme of preparation of As_2S_3-ZnS(ZnSe):Cr(2+).

The loading of the components of systems As_2S_3-ZnS(ZnSe):Cr(2+) (before the stage of homogenization) was realized in such manner (Fig. 2)

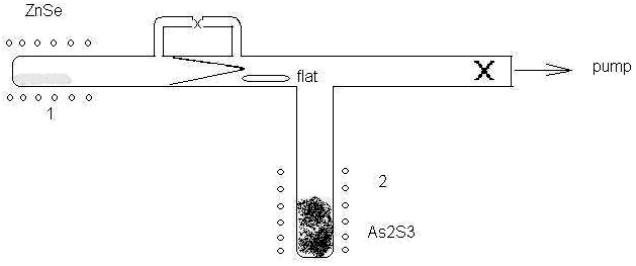

Fig. 2. Scheme of the loading of components (the execution sequence – a-c – in text).

a) The samples of fine-grinded II-VI compounds (average size of particles is about 1 μm) were placed in the 1th tube, evacuated at T= 500-600 °C at P=10^{-4} mm Hg for several hours, and were sealed.(«x» – the points of sealing)

b) The sample of As_2S_3, that was preliminary purified by distillation in vacuum, was placed into the 2nd tube, evacuated and sealed too.

c) The distillation of As_2S_3 from the 2nd into the 1st tube was carried out at P=10^{-4} – 10^{-5} mm Hg, the tube was sealed and placed into rotating furnace where the process of homogenization at high T (700-750 °C) was realized.

3. Results and discussion

One of the main requirements to optical materials, used for fiber optics is the low level of the optical losses on scattering. It is possible when the average size of introduced particles is much less than the wavelength of passed radiation. So the preliminary calculation was carried out using Mi theory to estimate the values for size and concentration (or volume fraction) of particles limited by the required level of optical losses.

In Fig. 3 (top) one can see the results of theoretical calculation in approximation of one scattering particle. One can conclude that the particles of II-VI compounds with size of about 10 nm may be introduced into glass As2S3 at the level of 10^{16} / cm^3. On the whole, it is necessary to decrease the particle size as much as possible in order to achieve their high concentration.

Methods of optical microscopy and laser ultramicroscopy were used to control the particles in glasses [3].

As minimum two phases in the blanks of composites were identified: the particles of II-VI compounds and particles having trigonal structure as a result of crystallization of glass As_2S_3 (Fig.3 (down)). At low level of II-VI (up to 0.1 wt%.) the crystals of As2S3 were still visually absent (in the range of micrometric resolution). As II-VI compounds content is higher, a branched crystal structure of As2S3 was revealed.

Fig. 3 shows a pattern with wide dispersity in size of particles. It is very important to note that one can differentiate the contribution of particle of II-VI compounds from that of crystalline particles of As_2S_3. As one can see on the histogram, the average size (d) of particles of II-VI is about 1 μm that greatly exceeds the size for the required level of optical losses (conditionally – 100 dB/km).

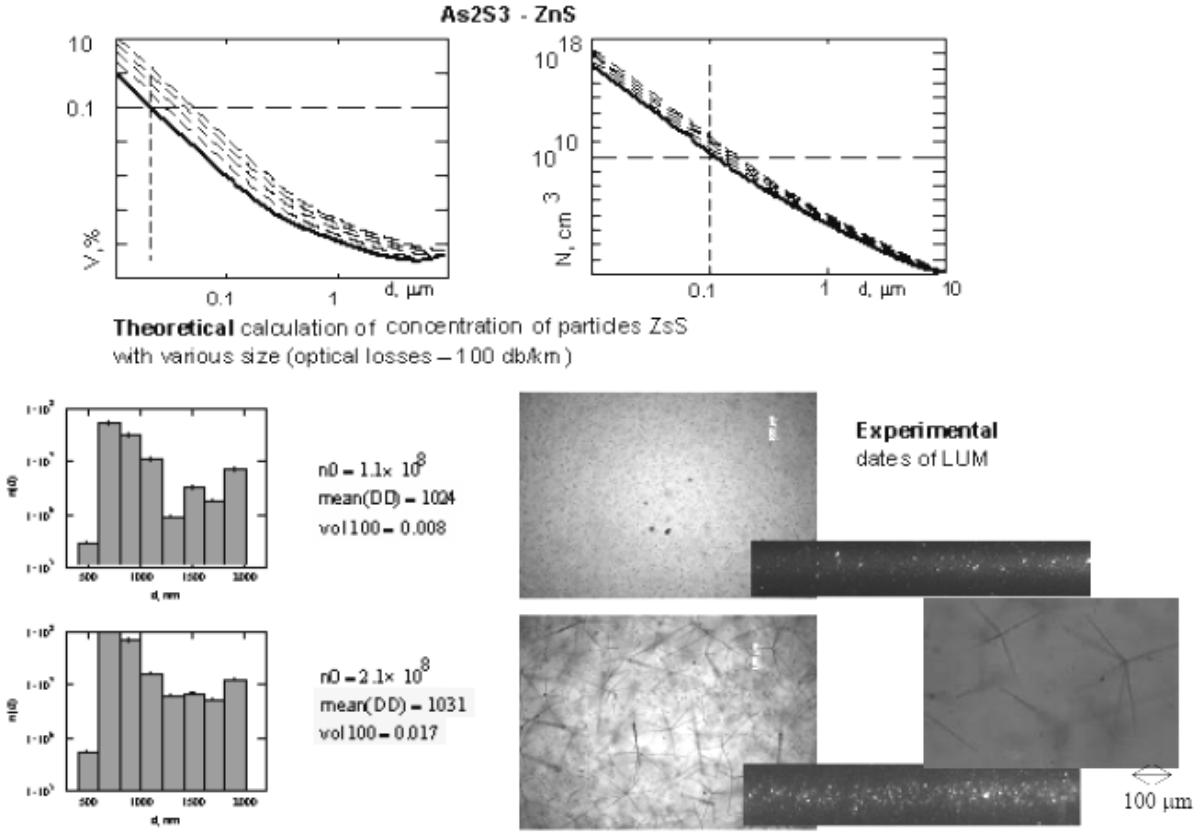

Fig. 3. Theoretical and experimental data of the method of laser ultramicroscopy.

The data of laser ultramicroscopy method correlate with the spectral data for the extinction coefficient (γ) near shortwave spectral range of composites. (Fig. 4) As the concentration of II-VI compounds and duration of synthesis are increased, the extinction is also enlarged.

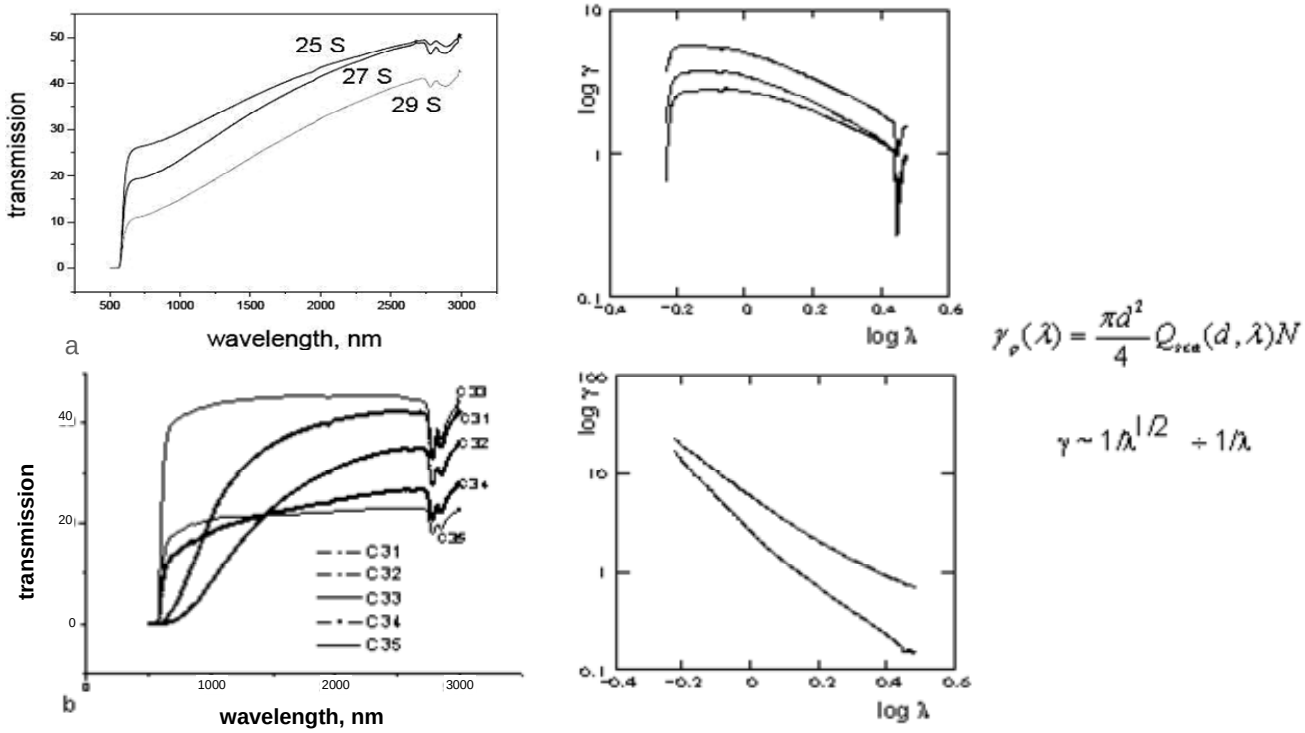

Fig. 4. Transmission spectra of composites on the basis of As_2S_3: a-25-29 – [ZnSe:Cr] – 0.08-0.18 wt%. (t=4 h.), b-31-35 – t = 1-16 h.([ZnSe:Cr]=0.13 wt%.), 33- As2S3; examples of dependences of log γ(λ) (on the right).

The result, presented in logarithmic scale (Fig.4.) demonstrates that none of the dependences can be described by conventional calculation (the exponent is between 0.5-1) for monodispersed systems; thus, we have a polydispersed system and the total losses are determined by superposition of individual mechanisms. The scattering on the large crystal particles (more than 100 μm) of As_2S_3 is the main mechanism of losses.

The luminescence and optical losses of mono-index fibers, 150-300 μm diameter, drawn from bulk preforms, were investigated. Luminescence spectra (Fig.5,a) were obtained by using the Er–Ib fiber laser as a pumping source with wavelength of 1.6 μm. The result demonstrates the nearness of spectral position of the luminescence peak in the range of 2-3 μm in different systems: As_2S_3 with ZnSe(Cr) and As_2S_3 with ZnS(Cr) although the difference between emission peak position related to Cr(2+) for individual ZnS and ZnSe is about 100 nm.

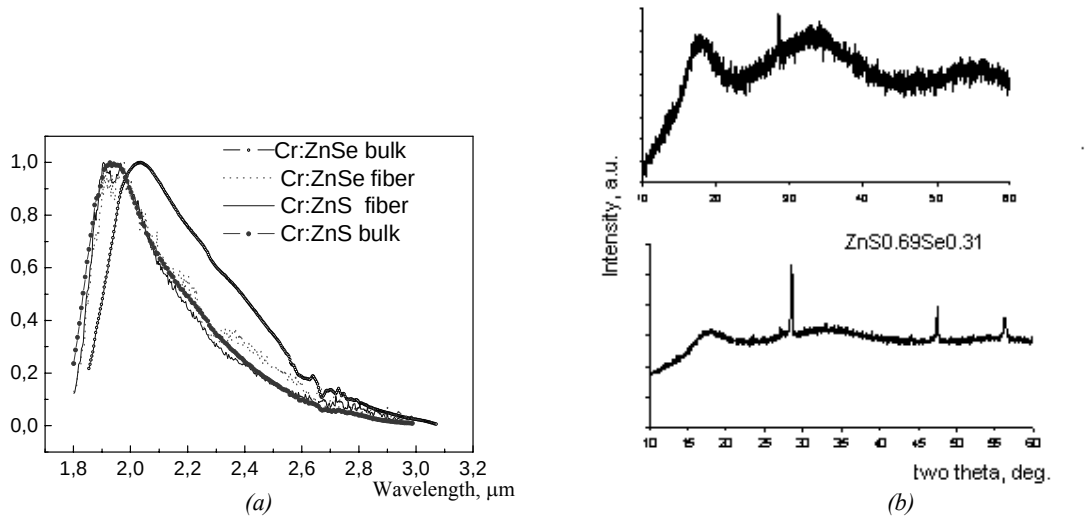

Fig. 5. (a) Luminescence spectra (intensity, n.u.) of bulk samples of ZnS, ZnSe and fibers of As2S3-ZnS(ZnSe): Cr(2+), (b) X-ray diffraction data of composites of As_2S_3-ZnSe:Cr(2+): top - 4wt% of ZnSe, down – 8wt% of ZnSe.

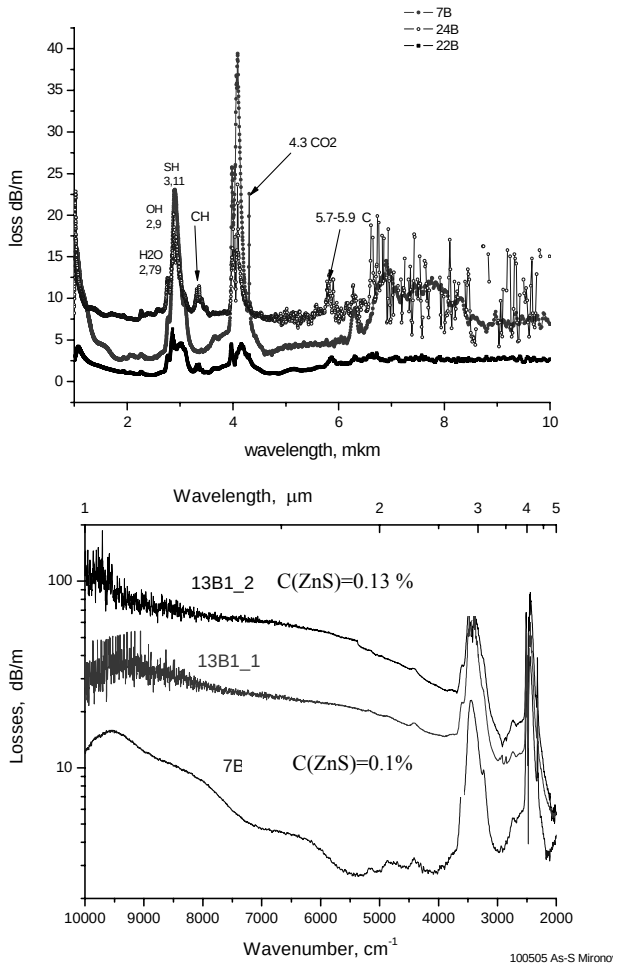

Fig. 6. Optical losses of typical fibers of As_2S_3-ZnS:Cr(2+). 22B –pure As_2S_3, 7B, 24B – the composites,13B1,13B2 – the various pieces of the fiber.

This fact may be explained on the basis of results of X-ray analysis of composites with high content of ZnSe:Cr presented in Fig. 5,b. One can see that composition of crystalline phase is $ZnS_{0.69}Se_{0.31}$ which proves the possibility of reaction between solid phase of ZnSe and liquid phase of As2S3 (replacing Se in lattice of ZnSe by S as a component of glass.). Optical losses (IFS-113V (Bruker)) in the Fig. 6 demonstrate, firstly, the dependence of content of II-VI compounds in As2S3 as a result of crystallization one (Fig. 6, down), and secondly, the negative influence of the impurities in 2-3 μm range, such as H2O, compounds with -OH,-SH,-CH-bond (Fig. 6, top).

The well developed methods of purification [4] will make it possible to suppress their influence and thereby to increase the luminescence intensity. The estimation of the level of optical losses gave the value of about 5 dB/m, which is still far from the required one.

4. Conclusions

1. The first new composite materials on the basis of As_2S_3-ZnS(ZnSe):Cr(2+) have been developed. The ranges of the concentration of ZnS(ZnSe):Cr(2+) compounds, temperature and duration of synthesis, in which the crystallization of As2S3 is minimized, are determined.

2. The mono-index optical fibers with luminescence in 2-3 -μm spectral range have been prepared. The luminescence spectra of fibers of As_2S_3-ZnS(ZnSe):Cr(2+) are close to that of ZnS:Cr(2+).

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