PROPERTIES OF As_2Se_3 CHALCOGENIDE GLASSES MODIFIED BY MANGANESE

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This work is concerned with the study of structural, optical, thermal and magnetic characteristics of the amorphous bulk As_2Se_3 glasses doped with Mn (concentration 2 and 5 wt. %). The studied glasses were synthesized by standard melt-quenched technique in evacuated quarts ampoules with subsequent air quenching.

Structural studies were carried out using Raman and FTIR spectroscopy and X-ray diffraction. The radial distribution functions of doped and undoped bulk glasses were obtained and analyzed. In Raman spectra, main observed effect under the introduction of dopants was the change of relative concentration of main and non-stoichiometric structural unit characteristic for As_2Se_3 glasses. Influence of transition metals on the optical properties of As_2Se_3 glass was studied in mid-IR region. Introduction of transitional and rare-earth elements changes magnetic properties of investigated chalcogenide glasses.

Introduction

Chalcogenide glasses (ChGs) are typical representatives of non-oxide glasses. ChGs due to their unique properties: transparency in IR region, quasistability, numerous photoinduced phenomena, ion-conductivity of doped ChGs serve as a base of their application including integrated and non-linear optics, information technology, etc.

In spite of a wide range of compositions in binary, ternary and more complex systems of ChGs, the problem of modification of parameters still exists. The properties of ChGs can be changed by doping with transitional metals or rare-earth elements resulting in change of thermal, optical, luminescent and magnetic properties [1, 2].

Composite multilayer nanostructures on the base of ChGs are particularly interesting because they enable to realize one-step direct recording of surface relief without selective etching [3-5].

This work is concerned with the study of structural, optical, thermal and magnetic characteristics of the amorphous bulk As_2Se_3 glasses modified by introduction of Mn (concentration 2 and 5 wt. %).

Experimental

The As_2Se_3 glasses with manganese concentration from 0 up to 5 wt. % Mn were prepared by standard melt-quenching technique using constituent elements of 6N purity in vacuum-sealed ampoules.

The amorphous nature of the samples was verified at room temperature by X-ray diffraction (XRD) technique using ARL X'tra (Thermo scientific) diffractometer equipped with a copper tube (λ=0.154 nm).

Room temperature Raman spectra were recorded using Fourier spectrophotometer Bruker IFS-55 Equinox with FRA-106 attachments (measurement resolution – 1 cm^{-1}). Nd:YAG laser light at wavelength of 1,06 μm was used for excitation.

Room temperature transmission spectra in the 700-4000 cm^{-1} region were recorded using an FT spectrometer "Perkin Elmer" Spectrum BXII.

Thermal properties were studied using differential scanning calorimetry (DSC technique), T_g values for undoped and doped glasses were obtained by NETZSCH DSC 404 calorimeter (with accuracy $\pm$0.5K). Calorimetric measurements were carried out using powder samples (m~20 mg) in argon atmosphere under temperature changes within 40–250 °C. Heating rate was q=10 K/min.

Magnetizations of samples were measured with Cryogenic S600 Super-conducting Quantum Interference Device (SQUID) magnetometer in the temperature range of 4-300 K and in magnetic field up to 5T.

Results and discussion

X-ray diffraction

The experimental XRD profiles from glasses of different compositions were similar but showed a systematic variation with composition. Diffraction profiles confirm the amorphous nature of the chalcogenide glass, which is a disordered system without long-range order and three-dimensional periodicity. However, there is short-range order in which the atoms around any system of atoms can be described radial distribution function of the atoms (RDF) [6, 7].

In Fig.1 the calculated RDF profiles for Mn doped As_2Se_3 samples with Mn concentration 0%, 2% and 5 wt. % are shown. The location of the peaks indicates prominent interatomic distances and the area under peaks, after correction for differences in scattering factors, gives a measure of the average coordination number. As can be seen, the addition of manganese slightly affects the structure. The results generally are in agreement with the results of previous researchers on the structure of the As_2Se_3 glasses using X-ray analysis [8, 9].

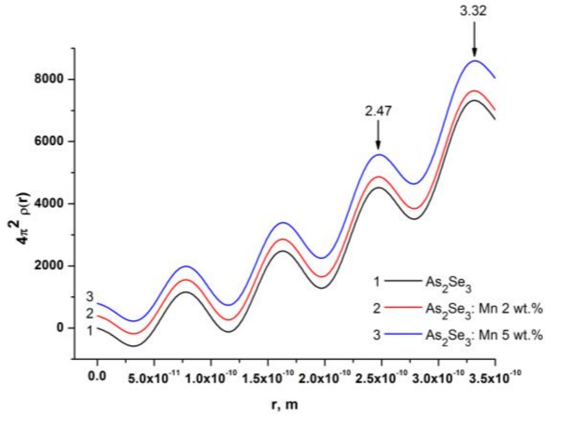

Fig. 1. The RDF profiles for Mn doped As_2Se_3 with Mn concentration (0%, 2% and 5 wt.%) (the plots are shifted along the y-axis for clarity)

Raman spectra

From Fourier Raman spectra information on the structural changes in As–Se glasses doped with transitional metals was obtained (Fig. 2). Analysis of Raman spectra of binary chalcogenide glasses As_2Se_3 have evidenced the presence of nanophase separation effects. Introduction of manganese leads to the intensity increase of 116, 136, 150, 259 cm^{-1} bands corresponding to non-stoichiometric molecular fragments containing homopolar As-As bonds and intensity decrease of 460 cm^{-1} band corresponding to Se-Se bonds [10-12]. The most intense 231 cm^{-1} band of Raman spectra of As_2Se_3 glasses corresponds to symmetric vibrations of $AsSe_{3/2}$ pyramidal units. In the obtained spectra we have detected decrease of this band intensity. The intensity of band at 208 cm^{-1} which is attributed to the vibrations of As-As bonds in As_4Se_4 unit as can be seen Fig. 2 is increasing with growth of Mn concentration.

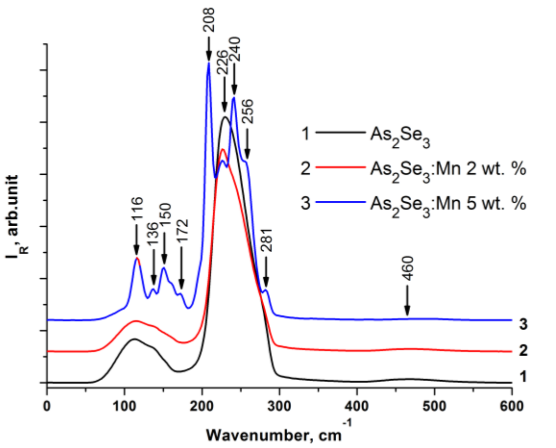

Fig. 2. Raman spectrum of As_2Se_3 manganese doped in different concentrations (the curves are shifted along the y-axis for clarity)

FTIR transmission spectra

The infrared transmission spectra of As_2Se_3:Mn chalcogenide glasses are shown in Fig. 3 and are characterized by several well resolved absorption bands. These bands are observed in the ranges 2.12÷2.9 μm (O-H), 4.23 μm (CO_2), 4.27÷4.28 μm (Se-H), 6.29 μm (O-H), 12.69÷13.09 μm (As-O), 15.34÷15.45 μm (As-O). A comparison of FTIR transmission spectra for chalcogenide glass compositions As_2Se_3, As_2Se_3: Mn 2 wt.% and As_2Se_3: Mn 5 wt.% shows the changes of optical properties [11]. The objective was to determine the effects of manganese doping on IR transparency within the 8-12 μm window. Major observations from the data are:

- manganese doping decreases transmission within the window;
- FTIR transmission spectra for As_2Se_3: Mn 2 wt.% and As_2Se_3: Mn 5 wt.% become rounded between 8-12 μm;
- the most transparent glass from 8-12 μm via FTIR was As_2Se_3. Although arsenic triselenide has the flattest FTIR spectra, it cuts off rather sharply at 11.8 μm, while the As_2Se_3: Mn 2 wt.% and As_2Se_3: Mn 5 wt.% cut off more gradually and are actually more transparent at even slightly higher wavelengths;
- several very weak absorption bands below 8 μm indicate about existence of hydroxyl and oxide complexes.

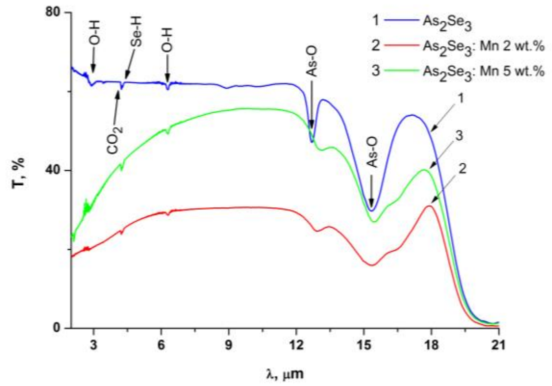

Fig. 3. Mid-infrared transmission spectra of As_2Se_3 doped by Mn

Thermal properties

Thermal properties (T_g values for undoped [13-15] and doped As_2Se_3 glasses) were studied using differential scanning calorimetry. The glass transition temperature T_g was determined for all compositions: As_2Se_3 T_g=185.2 °C, As_2Se_3: Mn 2 wt.% T_g=192.6°C, As_2Se_3: Mn 5 wt.% T_g=191.1°C. Thermograms for As-Se: Mn with different Mn content (heating rate – 10 K/min) is shown in Fig.4. It is necessary to note, that with the increase of heating rate, T_g value is shifted towards the higher temperatures.

Magnetic properties

Pure chalcogenide glasses As_2Se_3 are diamagnetics. Introduction of Mn with concentrations up to 5 wt.% changes magnetic properties of investigated chalcogenide glasses [16-17]. In the fields near 5 T M(T) dependence is observed, which is the characteristic for paramagnetics and ferromagnetics in the paramagnetic range of temperature.

The mass magnetization M (T) in As_2Se_3: Mn 5 wt.% glass (B=0.008 T) shows a sharp increase with decreasing of temperature, which indicates the PM-FM transition at the Curie temperature T_c~14K.

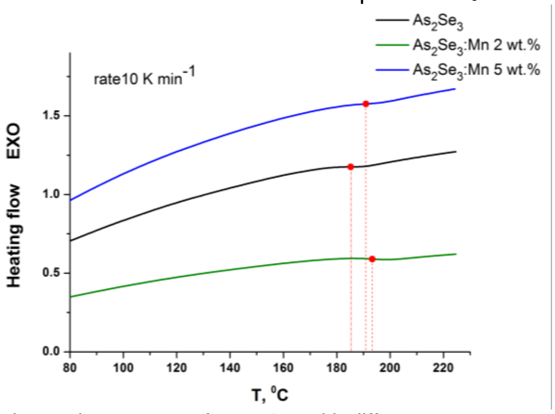

Fig. 4. Thermograms for As_2Se_3 with different Mn content

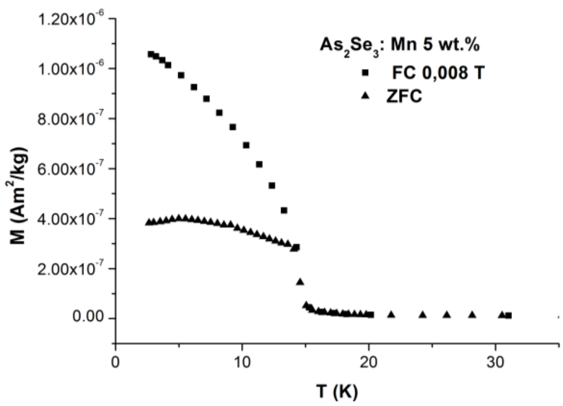

Fig. 5. Dependence of mass magnetization M(T) of As_2Se_3: Mn 5 wt.% in magnetic field 0.008 T

Conclusion

In this paper the results of X-ray diffraction, Raman and mid-IR spectroscopy, DSC technique and magnetic studies for characterization of As_2Se_3 glasses are presented. It was shown that modification of As_2Se_3 glasses by Mn impurity introduction significantly influences the optical, thermal and magnetic properties of chalcogenide glasses. This can be used for the direct recording various surface relief's using composite multilayer nanostructures on the base of chalcogenide glasses and creation optical elements with unique properties [18], optimization of sensitivity, stability improving of registering media on their base, etc.

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