Journal of Non-Crystalline Solids 457 (2017) 164–168

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Investigation of structure of $GeS_{1.35}$ glasses with the use of isotopically enriched germanium and Raman scattering spectroscopy

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ARTICLE INFO

Article history:
Received 12 October 2016
Received in revised form 23 November 2016
Accepted 28 November 2016
Available online 9 December 2016

Keywords:
Chalcogenide glasses
Monoisotopic glasses
Raman scattering spectroscopy
Structure of glasses

ABSTRACT

The samples of $GeS_{1.35}$ glasses were synthesized with germanium and sulfur of natural isotopic composition and with isotopically enriched germanium (^{72}Ge, ^{74}Ge, ^{76}Ge). The glasses were investigated by the method of Raman scattering spectroscopy (RSS). It was shown that $GeS_{4/2}$ tetrahedrons and structural units containing Ge—Ge homobonds are present in glasses. The quantum-mechanical calculation of the frequency of fundamental vibrational modes in glass network was carried out. Their dependencies on the atomic mass of germanium were used for identification of bands in RS (Raman scattering) spectra.

1. Introduction

The glasses on the basis of germanium sulfides are the promising materials for fiber, integral and non-linear optics in the near and middle IR range. Quite a lot of papers are cited in literature devoted to investigation of composition, properties and methods of preparation of high-purity chalcogenide glasses of Ge–S system. However, some details in composition of these glasses should be discussed. The use of isotopically enriched elements alongside with the method of Raman scattering spectroscopy makes it possible to increase the reliability in interpretation of vibrational spectra and to specify the composition of glass network. Variation in atomic mass of elements opens the possibility to investigate the effect of isotopic composition of material on its optical properties as well as to obtain new data on the behavior of optically active impurities in glass. Besides, it was assumed that the increase in isotopic purity of material will assist in the lowering of optical losses [1].

The aim of the work is to prepare and investigate the composition of $GeS_{1.35}$ glasses with isotopically enriched germanium by the method of Raman scattering spectroscopy. $GeS_{1.35}$ glasses are suitable objects for such investigations since they have a simple composition and are relatively well studied. The selected composition of glasses is distinguished by the excess of germanium in comparison with stoichiometric compound GeS_2 which predetermines the presence of Ge—Ge homobonds in these glasses. The vibrational frequency of exactly these bonds will have the maximum isotopic shift.

The number of papers on synthesis and investigation of the properties of chalcogenide glasses with the use of monoisotopic elements is limited. In paper [2] the $GeSe_2$ glasses were prepared with monoisotopic germanium and selenium (^{70}Ge, ^{73}Ge, ^{76}Se) and their structure was investigated by the method of neutron diffraction. Some optical properties of the glasses of As–S, Ge–S, Ge–Se systems with isotopically enriched elements are given in paper [3].

2. Experimental

The glasses with the given elemental composition were synthesized by traditional method with the use of melting simple substances. The weighted amounts of sulfur and germanium for preparation of 2 g of glass were loaded into annealed quartz ampoule with internal diameter of 5 mm preliminarily washed with the solution of hydrofluoric acid. The ampoule with charge was evacuated and the charge was melted in the muffle furnace. The preparation of glass-forming melt and annealing of glasses were carried out at 850 and 370 °C, respectively.

In this work the germanium of natural isotopic composition ^{nat}Ge and isotopically enriched germanium ^{72}Ge, ^{74}Ge, ^{76}Ge were used. Table 1 gives the isotopic composition and atomic mass of the used

Table 1
Isotopic composition of the used samples of germanium.

Germanium sample	Content of isotope, at.%					Atomic mass, a.e.m.
	70	72	73	74	76	
^{72}Ge	27.83	51.96	8.63	11.58	0.01	71.69
natGe	21.2	27.66	7.73	35.94	7.44	72.57
^{74}Ge	0.01	2.37	11.02	86.12	0.49	73.78
^{76}Ge	0.06	0.09	0.05	11.59	88.21	75.68

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http://dx.doi.org/10.1016/j.jnoncrysol.2016.11.038
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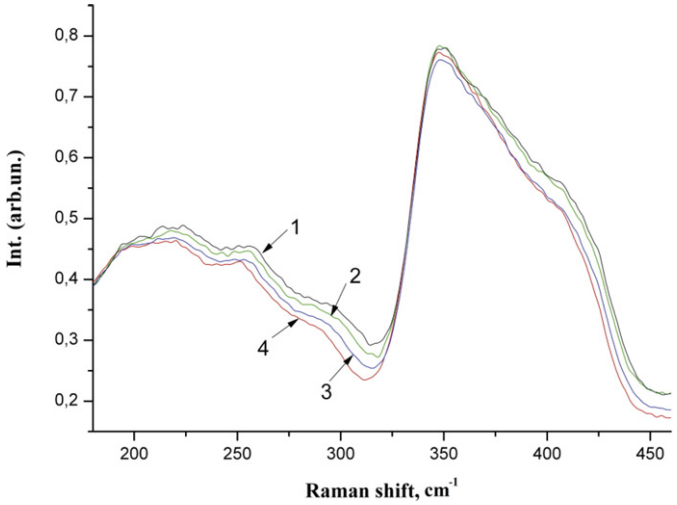

Fig. 1. RS spectra of glass: 1 – $^{72}GeS_{1.35}$, 2 – $^{nat}GeS_{1.35}$, 3 – $^{74}GeS_{1.35}$, 4 – $^{76}GeS_{1.35}$.

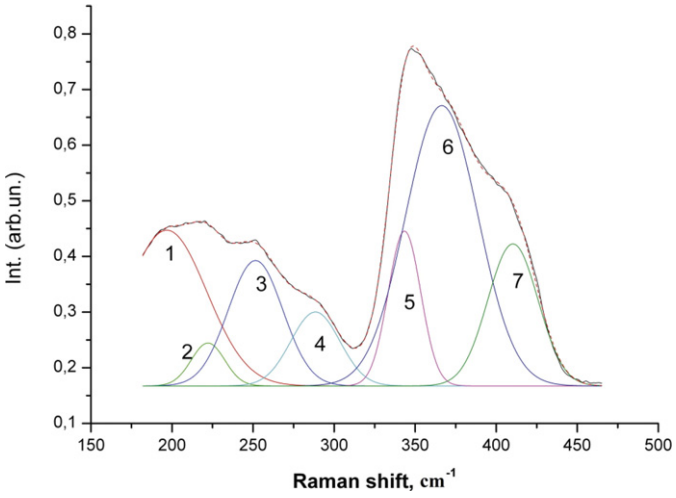

Fig. 3. Results of mathematical decomposition of RS spectra of $^{76}GeS_{1.35}$ glass. Numeric symbols indicate the numbers of bands (identification of bands is given below). The dotted line shows their superposition.

samples of germanium. The atomic mass of sulfur with natural isotopic composition was taken as equal to 32.061 a.e.m.

For RS-spectroscopic investigations the synthesized samples were cut into discs with thickness of 1.5–2 mm and subjected to polishing. The RS spectra were measured on the Senterra instrument and normalized. The emission wavelength is 785 nm which is deeply inside the transparency range of the studied glass. The correction for the temperature population of vibrational states using the coefficient of Bose-Einstein temperature population was taken into account. The experimental temperature was 300 K. The obtained spectra are given in Fig. 1. All spectra were recorded at similar conditions with the same resolution of 3–5 cm^{-1}. The accuracy in determination of wavelength was 0.1 cm^{-1}.

A quantum-mechanical calculation of the frequency of phonons was carried out for different vibrational modes of four structural units (Fig. 2): $GeS_{4/2}$ tetrahedrals, edge-sharing tetrahedrals, corner-sharing tetrahedrals and ethane-like structures $S_{3/2}Ge\text{-}GeS_{3/2}$. The calculation was carried out by the method of density functional B3LYP with the basic set 3-21G** in Gaussian G03W program for ^{72}Ge, ^{74}Ge and ^{76}Ge (the atomic weights of other elements were not changed).

3. Results

On the basis of the results of analysis of literature data [4–10] and of the shape of the obtained spectra the seven bands were selected for their decomposition on the constituent bands in the studied frequency range (Fig. 3). The results of decomposition are given in Table 2. The results, obtained for peak 1, cannot be considered to be correct since partially they are beyond the studied frequency range. However, they are given in this work since they are in good agreement with general regularity.

As an example, Fig. 3 gives the result of Gaussian decomposition of RS spectrum of $^{76}GeS_{1.35}$ glass. A part of these seven peaks is most likely the overlapping of several vibrational modes. In the first place it refers to peaks 1 and 6 with larger half-width. Further detailization does not make any sense since the result of approximation (Fig. 3) actually does not differ from the experimental spectrum.

At the quantum-mechanical simulation the dangling bonds of sulfur on the boundary of structural units were saturated with the atoms of hydrogen. It was done with the aim to decrease the redistribution of

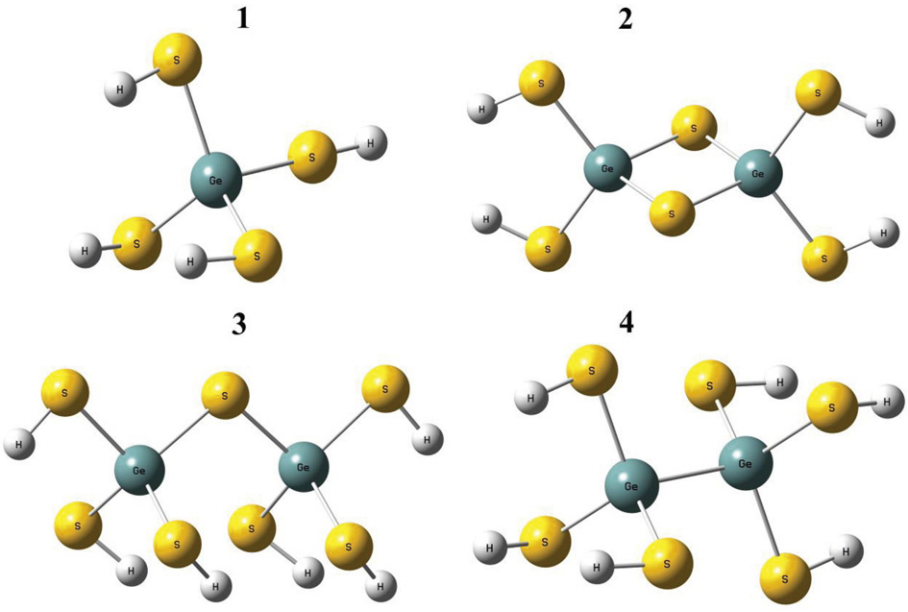

Fig. 2. Structural units with quantum-mechanical calculations: 1 – tetrahedron, 2 – edge-sharing tetrahedral, 3 – corner-sharing tetrahedral, 4 – ethane-like structure.