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## Spectral dimensions and free volume in $As_xS_{1-x}$ glasses

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A low-frequency (LF) Raman spectra of  $As_2S_3$  glasses, prepared at different temperatures of melts ( $T_i$ ) and different rates of cooling ( $V_j$ ) and Raman spectra of binary glasses  $As_xS_{1-x}$ , prepared at optimal conditions are given. A relation between reduced intensity of LF maxims and slope of high-frequency part of LF spectra of  $As_2S_3$  glasses on temperature of melt and rate of cooling are revealed. In framework of fractal approximation a spectral dimension ( $d_f$ ) was calculated. It is sensitive to the conditions of preparing of  $As_2S_3$  glasses. A spectral dimension of fractals was determined by independent way from concentration dependence of ultrasound velocity of  $As_xS_{1-x}$  glasses. A dependence of intensity of density of states and free volume on average coordination number of  $As_xS_{1-x}$  glasses are revealed.

**Key words:** Raman spectra, temperature, glasses, concentration.

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Low-frequency (LF) Raman scattering spectroscopy is an efficient method for the investigation of structural properties of non-crystalline solids. There is especially a great interest in the analysis of Raman spectra where middle range order is manifested through frequency position of boson peak. The frequency dependence of the light as a function of vibration coupling coefficient  $C(\omega) \sim \omega$  in the region of boson peak ( $\omega_B$ ) mainly in stoichiometric glasses is known by comparing the Raman scattering with the neutron ones and specific heat data [1-5].

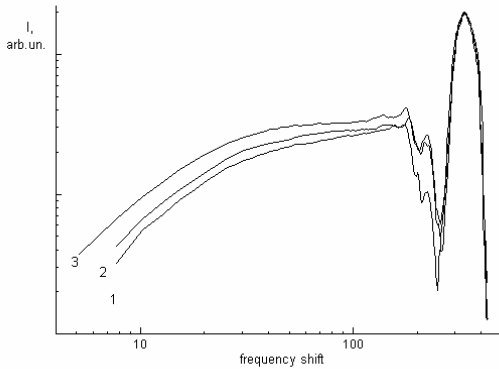
In [6] the model that connects a linear law of coefficient  $C(\omega)$  with the vibration correlation function was proposed. The similar relation for describing the correlation in fractal structures was used [7]. For the latter the correlation length  $\xi$  and spectral dimension  $d_f$  of fractals are included in equation. One of the methods for determining  $d_f$  of non-crystalline materials in the fracton approximation is LF Raman

spectroscopy [7]. The second simple independent way to determine  $d_f$  is calculations carried out with the relation between sound velocity  $v_s$  and density  $\rho$  [7]. In accordance with the constrain counting model and its subsequent modification, the change in mechanical properties with the composition (average coordination number  $z$ ) reflects structural compactness of glasses [9,10]. The relation connecting microhardness  $H$ , softening temperature  $T_g$ , density  $\rho$  and free volume  $V_h$  of binary glasses are given in [11]. The aim of these notes is to determine  $d_f$  for glassy  $g-As_2S_3$  by different methods and to determine  $d_f, V_h$  in  $As_yS_{1-y}$  when varying the composition (or  $z$ ).

When preparing glassy (g)  $g-As_2S_3$  different temperature of melt ( $T_{mi}$ ),  $T_{m1}=870$  K and cooling rate  $V_j$  ( $V_1=10^{-2}$ ,  $V_2=1,5$ ,  $V_3=1,5 \times 10^2$  K/s) were used. The non stoichiometric glasses  $As_xS_{1-x}$  ( $x \neq 0.4$ ) for investigations were prepared from melt ( $T_m=870$  K) with cooling rate  $V_2=1,5$  K/s. Ultrasound velocity  $v_s$  was

measured by echo-method.

At first we shall consider the influence of temperature-time conditions of preparing g-As<sub>2</sub>S<sub>3</sub> on LF Raman spectra. As we can see from reduced Raman spectrum,  $I_R = I/(n(\omega)+1)$  (Fig.1), at constant rate of cooling ( $V_1=10^{-2}$  K/c), the intensities  $I_R$  of maxim near  $\omega_B$  increase with the temperature varied from  $T_1=870$  K up to  $T_3=1370$  K, and maximum shift in depolarized Raman spectra from  $\omega_B(T_1V_1)=26$  up to  $\omega_B(T_1V_3)=22$  cm<sup>-1</sup>.



**Fig.1.** Reduced Raman spectra of As<sub>2</sub>S<sub>3</sub> prepared at different conditions  $T_1V_1$  ( $T_1=870$ ,  $T_2=1120$ ,  $T_3=1370$  K,  $V_1=10^{-1}$  K/s).

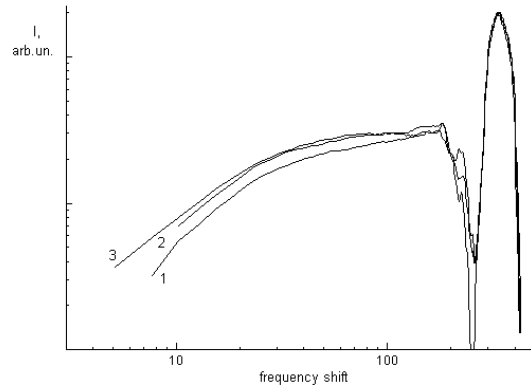
The reduced Raman spectrum  $I_R$  is proportional to density of states  $g(\omega)$  [7]:

$$I/(n(\omega)+1)=C(\omega)g(\omega)/\omega \quad (1)$$

As it was mentioned above  $C(\omega)\sim\omega$  [6] and  $I_R=\rho(\omega)$  are obtained from (1). Therefore within the framework of this approximation the increase in  $I_R$  and the shift of low-frequency maximum  $\omega_B$  ( $T_{mi}V_1$ ) reflects the change in function  $\rho(\omega)$  with increasing  $T_{mi}$  ( $i=1-3$ ).

In fig.2 Raman spectra of g-As<sub>2</sub>S<sub>3</sub>, which were prepared at cooling from  $T_1=870$  K with various rate of cooling  $V_j$  ( $j=1-3$ ), are given. The minimum of intensity and the highest-frequency maximum  $\omega_{max}(T_{m1}V_2)=27$  cm<sup>-1</sup> correspond to  $T_{m1}V_2$  conditions of preparing. According to direct electron-microscopic researches of glass plates, these conditions of preparing g-As<sub>2</sub>S<sub>3</sub> provide the most homogeneous structure of a glass [12].

Within the framework of fractal approximation the dependence  $I_R$  for the frequency region  $\omega_{max}<\omega<60$  cm<sup>-1</sup> may be extrapolate by function  $I_R \sim \omega^p$ , where



**Fig.2.** Reduced Raman spectra of As<sub>2</sub>S<sub>3</sub> prepared at different conditions  $T_1V_j$  ( $T_1=870$ K,  $V_1=10^{-2}$ ,  $V_2=1,5$ ,  $V_3=1,5 \times 10^2$  K/s).

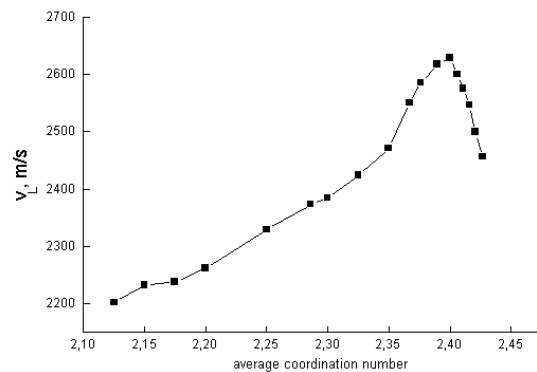
$$p=-2[(d_f/D)(D-d-\sigma)+1/2] \quad (2)$$

Taking into account that fracton dimension  $D=2.5$ , the scaling factor  $\sigma=1.1$  and the dimension of Euclidean space  $d = 3$  [7, 8], the values of  $d_f$  were estimated. The calculations have shown that received experimental values  $d_f$  are a little bit higher than that of  $d_f = 4/3$  calculated for percolating systems.

In the fracton approximation [7] the reduced LF Raman spectrum  $d_f$  is connected with density of states by relation  $g \sim \omega^{d_f-1}$  and

$$C(\omega)\sim\omega^{2d_f/D} \quad (3)$$

Therefore the changes in intensity and position of a maximum  $g(\omega)$  can be logically



**Fig. 3.** Dependence of ultrasound velocity  $v_s$  on average coordination number.

connected with the changes of spectral dimension  $d_f$  (see Table). Substituting calculated values of  $d_f$  into (3) we shall obtain  $C=1.4-1.6$  for the frequency region  $\omega_{max}<\omega<60$

Table

Calculations of spectral dimensions  $d_f$  and free volume  $V_h$  in g-As<sub>2</sub>S<sub>3</sub> prepared under different conditions and in glasses As-S system

Composition / T <sub>i</sub> V <sub>j</sub> As <sub>2</sub> S <sub>3</sub> (T <sub>1m</sub> V <sub>1</sub> )	$d_f$ from Raman spectra	$d_f$ from sound velocity	$V_h, \text{\AA}^3$
As <sub>2</sub> S <sub>3</sub> (T <sub>m2</sub> V <sub>1</sub> )	1.85	-	-
As <sub>2</sub> S <sub>3</sub> (T <sub>m3</sub> V <sub>1</sub> )	1.76	1.55	-
As <sub>2</sub> S <sub>3</sub> (T <sub>m1</sub> V <sub>2</sub> )	1.65	-	19,7
As <sub>2</sub> S <sub>3</sub> (T <sub>m1</sub> V <sub>3</sub> )	1.78	-	-
As <sub>29,6</sub> S <sub>70,4</sub> (T <sub>m2</sub> V <sub>1</sub> )	1.93	1,75	39,3
As <sub>26,1</sub> S <sub>73,9</sub> (T <sub>m2</sub> V <sub>1</sub> )	2,14	1,77	54,1

cm<sup>-1</sup>. These values are a little bit higher than those ones obtained for other glasses by the neutron spectroscopy method [3]. Therefore to determine  $d_f$  by independent way we shall use the data of measurements of ultrasound velocity (Fig.3) for glasses of As-S system.

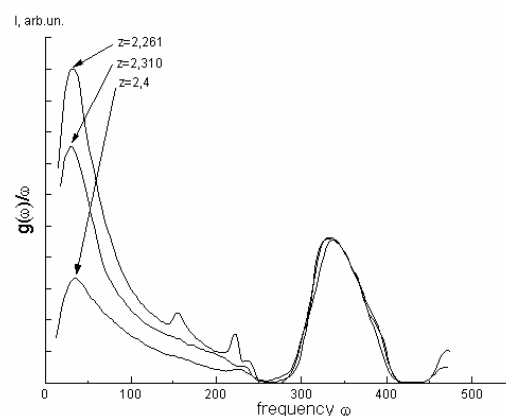
Within the framework of fractal approximation [7] the spectral dimension connects ultrasound velocity and density of states by relation

$$v_s \sim \rho^{(D/d_f - 1)/(d_f - D)} \quad (4)$$

The measured values of longitudinal sound velocity are presented depending on the average coordination number  $z=3y+2(1-y)$  (Fig. 3) calculated for As-S binary glasses by relation based on Mott rule of 8-N valence chemical bond [14]. It is easy to approximate part of curve  $V=V(z)$  (Fig. 3) at  $z=2,1-2,4$  by three linear intervals  $2,1 < z < 2,2$ ,  $2,2 \leq z < 2,3$  and  $2,3 \leq z \leq 2,4$ . Based on ratio (4) for these intervals the following values of  $d_f$  were obtained:  $d_f(z_1)=1,77$ ,  $d_f(z_2)=1,75$  and  $d_f(z_3)=1,55$  (see Table 1). Substituting the results of an estimation  $d_f(z_3)=1,55$  for g-As<sub>2</sub>S<sub>3</sub> from ultrasound velocity into (4), we obtain  $C(\omega) \approx 1,03$  that coincides with the data of theoretical and experimental investigations [6, 13]. For nonstoichiometric glasses As<sub>x</sub>S<sub>1-x</sub> the estimations give the greater values of  $C(\omega)=1,18$ .

In fig. 4 the reduced Raman spectra of some glasses of As-S system from the three mentioned regions are given. We found compositional (an average coordination number  $z$ ) dependencies of  $I_R$  for As<sub>x</sub>S<sub>1-x</sub> glasses. The minimum of intensity and maximum of frequency shift in depolarized spectra at  $\omega_B=26$

cm<sup>-1</sup> correspond to stoichiometric g-As<sub>2</sub>S<sub>3</sub> whose constrain matrix structure is formed by AsS<sub>3/2</sub> trigonal structural elements. The frequency minimum  $\omega_B=18$  cm<sup>-1</sup> and maximum  $I_R$  are observed for g-As<sub>10</sub>S<sub>90</sub>. The rigidity percolates when the number of constraints per atom exceeds the number of degrees of freedom per atom [9,10]. For a three-dimensional structure the threshold is at average coordination number 2.4. For less content of As concentration the dominant S-S bonds have additional degrees of freedom (floppy modes) that results in the growth of  $I_R$  [9].



**Fig. 4.** The density of states divided by the frequency,  $g(\omega)/\omega$ , for various values of the average coordination of As<sub>x</sub>S<sub>1-x</sub> glasses.

Within the fracton approximation we found values  $d_f$  for the region of a spectrum  $\omega_{\max} < \omega < 60$  cm<sup>-1</sup>. The values of  $d_f$  calculated from LF spectra are a little bit higher than those ones calculated from the measurements of ultrasound velocity (see Table 1).

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## Спектральні розмірності та вільний об'єм в $As_xS_{1-x}$ склах

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В роботі розглянуті низькочастотні (НЧ) спектри комбінаційного розсіювання (КР) стекол  $As_2S_3$ , одержаних загартуванням від різних температур розплаву ( $T_i$ ) і з різною швидкістю ( $V_j$ ) гартування та бінарних стекол  $As_xS_{1-x}$ , одержаних при оптимальних умовах. Виявлена залежність приведеної інтенсивності НЧ максимуму та нахилу високочастотної частини НЧ спектру стекол  $As_2S_3$  від температури розплаву і швидкості його гартування. В рамках фрактального наближення розрахована спектральна розмірність ( $d_f$ ) виявилася чутливою до умов одержання стекол  $As_2S_3$ . Незалежно від оптичних вимірювань, розрахована спектральна розмірність фракталів із концентраційної залежності швидкості звуку в стеклах  $As_xS_{1-x}$ . Виявлена залежність інтенсивності густини станів і вільного об'єму в стеклах  $As_xS_{1-x}$  від середнього координаційного числа.