THERMODYNAMIC MODEL AND STRUCTURE OF As_2S_3–As_2Se_3 GLASSES BASED ON THE MCR ANALYSIS OF RAMAN SPECTRA

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Raman spectra and structure of six glasses with the composition of $xAs_2S_3 \cdot (1 - x)As_2Se_3$ ($x = 1; 0.75; 0.667; 0.50; 0.25; 0$) were studied. In our previous work the Raman spectral data were interpreted on the basis of the Shakhmatkin and Vedishcheva thermodynamic model, where the glass was treated as an ideal solution of five components, namely: As_2S_3, As_2Se_3, As_2S_2, AsSe, and Se. The lack of mixed S–Se compounds in the model does not allow the interpretation of the measured spectra taking into account the existence of mixed trigonal pyramids of the type $As_2S_{3-x}Se_x$. In the present work an alternative simple thermodynamic model was proposed based on two equilibrium reactions leading to formation of two types of mixed $As_2S_{3-x}Se_x$ ($x = 1, 2$) pyramids. The results of multivariate curve resolution (MCR) analysis of the measured spectra were interpreted as proportional to the molar fractions of four system components: As_2S_3, As_2Se_3, As_2SSe_2, and As_2S_2Se. Using the nonlinear regression treatment the reaction Gibbs energies were optimized by minimization of the sum of squares of deviation between the MCR data and the equilibrium amounts of the systems components. The equilibrium system composition was calculated at experimentally determined glass transition temperature assuming the ideal behavior. It was found that the optimized values of reaction Gibbs energies fit the MCR data with acceptable accuracy.

INTRODUCTION

Due to high transmittance in infrared region, low phonon energies, and significant nonlinearity of optical properties the chalcogenide glasses were subjected to intense fundamental and applied research for a long time [1, 2]. Especially the ternary system As–S–Se acquired enormous significance due to the extremely large extent of the glass-forming region.

The structure of the above mentioned glasses was studied mainly by the Raman spectroscopy, X-ray photoelectron spectroscopy and X-ray absorption spectroscopy (namely EXAFS). In last two decades the importance of structural studies performed by molecular dynamics method (MD) significantly increased. It concerns both the classical MD with empirical pair-potential functions [3, 4] as well as the quantum MD based on the density functional theory [5].

In the previous work [6] the Raman spectral data were interpreted on the basis of the Shakhmatkin and Vedishcheva thermodynamic model [7-11], where the glass was treated as an ideal solution of five components, namely: As_2S_3, As_2Se_3, As_2S_2, AsSe, and Se. The lack of mixed S-Se compounds in the model does not allow the interpretation of the measured spectra taking into account the experimentally proved [1, 12, 13] existence of mixed trigonal pyramids of the type $AsS_{3-x}Se_x$. Therefore an alternative simple thermodynamic model was proposed in the present work based on two equilibrium reactions leading to formation of two types of mixed $AsS_{3-x}Se_x$ ($x = 1, 2$) pyramids. The results of multivariate curve resolution (MCR) analysis of the measured spectra were interpreted as proportional to the molar fractions of four components As_2S_3, As_2Se_3, As_2SSe_2, and As_2S_2Se and the reaction Gibbs energies were calculated by the non/linear least squares analysis of the MCR data.

EXPERIMENTAL

Method

The objective of Multivariate Curve Resolution method (also been referred to as End Member Extraction or Self Modeling Curve Resolution) is to extract concentration profiles and pure component spectra from a set of spectral data. The MCR analysis [14-17] was performed on the baseline subtracted Raman spectra using the Solo_PLS software package of Eigenvector [17]. The obtained scores were interpreted as proportional to the molar fractions of four components As_2S_3, As_2Se_3, As_2SSe_2, and As_2S_2Se.

Two equilibrium reactions of formation of mixed pyramids were considered:

$$2/3\ As_2S_3 + 1/3\ As_2Se_3 = As_2S_2Se \quad\quad (1)$$

$$1/3\ As_2S_3 + 2/3\ As_2Se_3 = As_2SSe_2 \quad\quad (2)$$

The equilibrium constants were related to the temperature independent reaction Gibbs energy, $\Delta_r G$, at the glass transition temperature T_g:

$$K(As_2S_2Se) = \frac{x(As_2S_2Se)}{x(As_2S_3)^{2/3}\,x(As_2Se_3)^{1/3}} =$$
$$= \exp\left(\frac{-\Delta_r G(As_2S_2Se)}{RT_g}\right) \quad\quad (3)$$

$$K(As_2SSe_2) = \frac{x(As_2SSe_2)}{x(As_2S_3)^{1/3}\,x(As_2Se_3)^{2/3}} =$$
$$= \exp\left(\frac{-\Delta_r G(As_2SSe_2)}{RT_g}\right) \qu\quad (4)$$

where $x(i)$ is the equilibrium mol fraction of the i-th system component, and R is the molar gas constant. For given glass composition expressed by molar amounts of As_2S_3 and As_2Se_3 (abbreviated as $x_g(As_2S_3)$ and $x_g(As_2Se_3)$) the minimization of the systems Gibbs energy constrained by the overall system composition has to be performed with respect to the molar amount of each system species to reach the equilibrium system composition [18]. The equilibrium system composition was considered as the function of reaction Gibbs energies. Using the nonlinear least squares method the estimates of reaction Gibbs energies were found by minimization of the sum of squares of deviations between the MCR obtained system composition, $x^{MCR}(i)$, and the system equilibrium composition calculated from thermodynamic model given by the Equations (1-4):

$$U[\Delta_r G(As_2S_2Se), \Delta_r G(As_2SSe_2)] = \sum_{i=1}^{N_g}\{\Delta x_i(As_2S_3)^2 +$$
$$+ \Delta x_i(As_2Se_3)^2 + \Delta x_i(As_2S_2Se)^2 + \Delta x_i(As_2SSe_2)^2\} = min. \qu\quad (5)$$

where

$$\Delta x_i(p) = x_i^{MCR}(p) - x_i(p) \qu\quad (6)$$

is the difference between MCR and calculated molar fractions of the component p for the i-th glass composition, and N_g is the number of glass compositions considered. The numerical minimization of the sum of squares of deviations (5) was performed by the simplex and pitt-mapping methods [19] using the own program written in FORTRAN language.

EXPERIMENTS

Six glass compositions were prepared, i.e. $xAs_2S_3 \cdot (1 - x)As_2Se_3$ (x = 1; 0.75; 0.667; 0.50; 0.25; 0). The studied glasses were prepared by conventional direct synthesis (melt-quenching technique) from elements of 5N purity in evacuated quartz ampoules. The ampoules were exposed to the temperature 850°C for 12 hours in the rocking furnace. The longitudinal rocking motion of furnace is driven by electromotor and tube with quartz ampoule rocks slowly up and down (approx. 0.01 Hz and about ± 20° from horizontal orientation) to homogenize melt during synthesis. The melt was then quenched in cold water. Both homogeneity and composition were controlled using X-ray fluorescence analyzer Eagle II (Roentgen Messtechnik AG).

Raman spectra of 2 cm⁻¹ resolution were taken using FT-IR spectrometer Bruker IFS 55 with Raman accessory FRA 106, with liq. nitrogen cooled Ge detector, Nd:YAG excitation laser (1064 nm; laser power 100 mW). The glass transition temperature was measured by the Step Scan® DSC method (Perkin Elmer, Pyris).

RESULTS AND DISCUSSION

The results of the MCR analysis of baseline subtracted Raman spectra are summarized in Table 1 and Figure 1. It can be seen in Figure 1 that the two-peaks spectra were obtained for the mixed pyramids structural

Table 1. Glass compositions, x_g, glass transition temperature T_g, and compositions (normalized scores), x^{MCR}, obtained by the MCR analysis.

Glass	x_g (As$_2$S$_3$)	x_g (As$_2$Se$_3$)	T_g (K)	x^{MCR} (As$_2$S$_3$)	x^{MCR} (As$_2$Se$_3$)	x^{MCR} (As$_2$SSe$_2$)	x^{MCR} (As$_2$S$_2$Se)
As$_2$S$_3$	1.000	0.000	481	0.9921	0.0079	0.0000	0.0000
S$_{75}$Se$_{25}$	0.750	0.250	472	0.4559	0.0000	0.0000	0.5441
S$_{66}$Se$_{33}$	0.667	0.333	470	0.3173	0.0100	0.1222	0.5505
S$_{50}$Se$_{50}$	0.500	0.500	467	0.1477	0.0000	0.5614	0.2909
S$_{25}$Se$_{75}$	0.250	0.750	461	0.0093	0.1888	0.7189	0.0829
As$_2$Se$_3$	0.000	1.000	457	0.0000	0.9941	0.0000	0.0059

units. Mainly in the low frequency range the significant shift of peak maximum is observed with increasing number of sulfur atoms in the pyramidal structural unit.
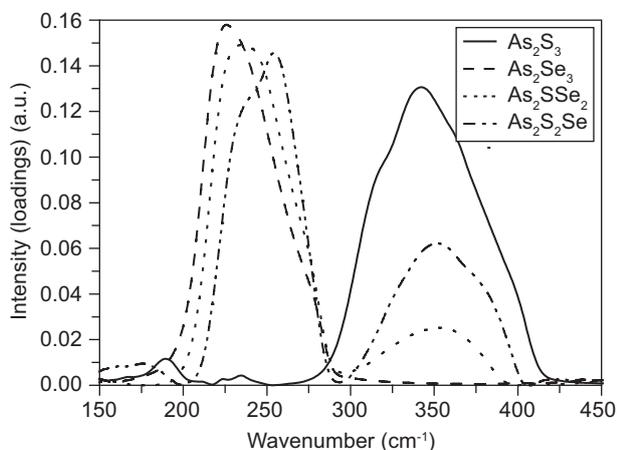

Figure 1. Raman spectra of pure system components (loadings) obtained by the MCR analysis.

On the other hand the low-frequency peak intensity slightly decreases with the increasing number of sulfur atoms while in the high frequency region the peak intensity strongly increases with the increasing number of sulfur atoms. The minimization of the sum of squares of deviations (5) resulted in the following estimates of reaction Gibbs energies:

$$\Delta_r G(As_2S_2Se) = -(10.7 +/- 2.2) \text{ kJ/mol}$$

$$\Delta_r G(As_2SSe_2) = -(15.0 +/- 4.2) \text{ kJ/mol}$$

Thus the standard deviations of obtained estimates are on the relative level of approximately 20 - 25 %. The standard deviation of approximation of x^{MCR} values of 0.06 was obtained corresponding to the value of Fisher *F*-statistics of 32. The comparison between MCR and calculated molar fractions is illustrated in Figure 2. It can be concluded that the calculated values fit the "experimental" (i.e. MCR) ones with acceptable accuracy.
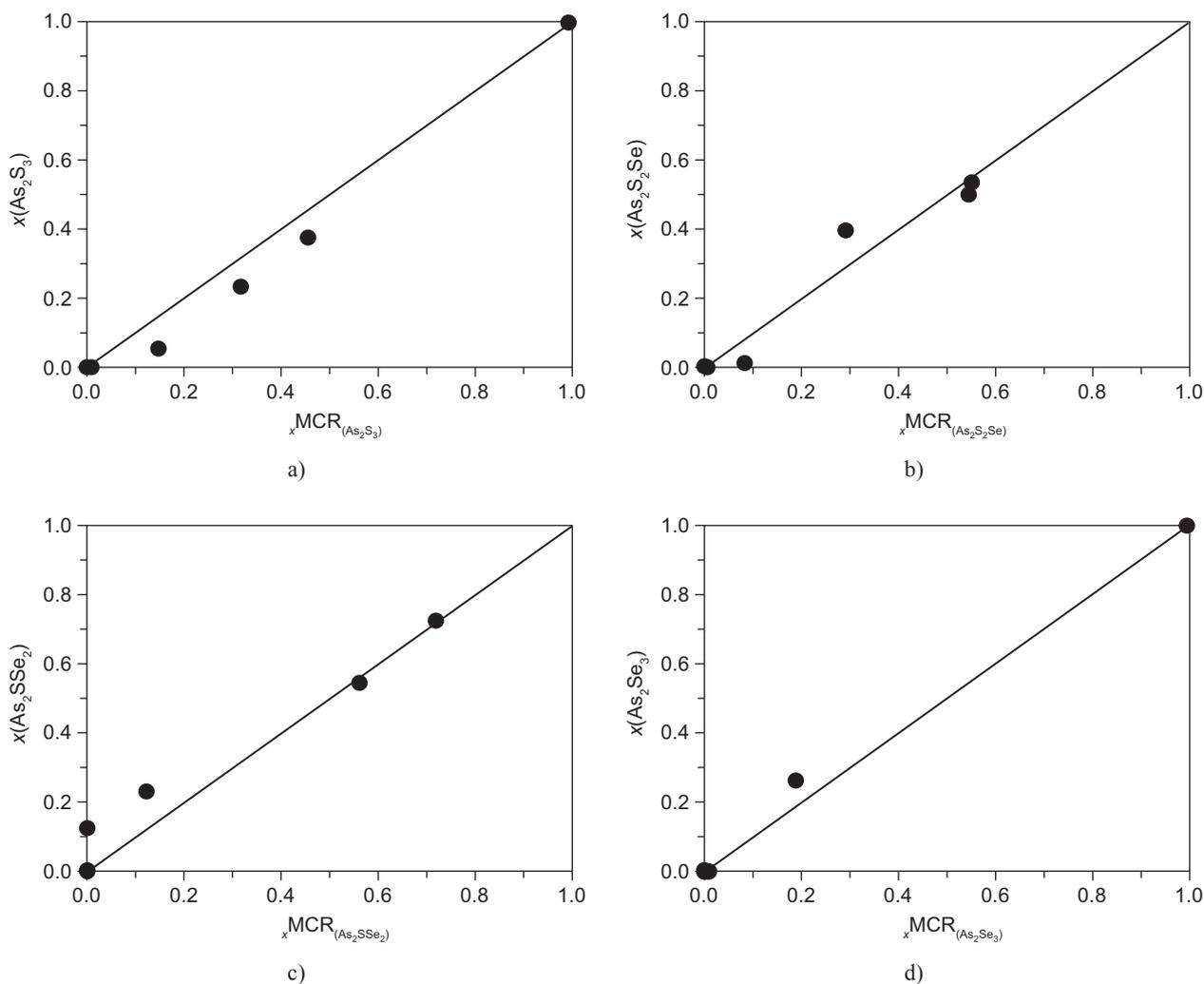

a)

b)

c)

d)

Figure 2. The comparison between MCR and calculated molar fractions.

CONCLUSIONS

The results of MCR analysis of Raman spectra of studied glasses were interpreted in frame of the proposed thermodynamic model of pyramidal structural units $As_2S_xSe_{(3-x)}$ ($x = 0, 1, 2, 3$). The model supposes the ideal behavior and the equilibrium molar amounts of individual structural units were obtained at the experimentally determined glass transition temperatures. The reaction Gibbs energies of formation of mixed S–Se pyramidal structural units were found with the relative accuracy of $20 – 25$ %. The calculated equilibrium molar amounts of pyramidal structural units fit the data obtained by MCR analysis of Raman spectra with acceptable accuracy and such way the validity of the proposed thermodynamic model was confirmed.

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