Extended X-ray Absorption Fine Structure Study on $Ge_{28.33}$ In_6 $Se_{65.67}$ Glass

طيف الامتصاص السيني الدقيق الممتد للتركيبة الزجاجية $Ge_{28.33}$ In_6 $Se_{65.67}$

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Abstract

The local environment of indium atoms in the chalcogenide glass with the stoichiometric composition $Ge_{28.33}$ In_6 $Se_{65.67}$ has been investigated using extended X-ray absorption fine structure (EXAFS) technique. It is found that indium is only coordinated with selenium atoms with a value of three for its coordination number.

تمت دراسة المحيط المحلي لذرات الانديوم في التركيبة الزجاجية النقية ذات التركيب الكيميائي $Ge_{28.33}$ In_6 $Se_{65.67}$ وذلك باستعمال تقنية طيف الامتصاص الدقيق الممتد للإشعاع السيني.

وجد أن ذرات الانديوم متناسقة مع ذرات السيلينيوم ومقدار عدد التنسيق يساوي ثلاثة.

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1. Introduction

Studies on the variation with the average coordination number, Z, of various optical [1-3], mechanical [4-6], electrical [7,8], and physiochemical [9-14] properties of chalcogenide glasses have increased in the past few years because of their potential technological applications in solid state devices [15-18].

The average coordination number of an alloy can only be calculated if the coordination numbers of its constituent elements are known [19,20]. This is not a problem for Ge and Se, which conform with the so-called "8-N"

rule, with N being the number of outer shell electrons [21]. However, the coordination of In is still a subject of considerable debate and controversy where coordination numbers of 1 [22], 3 [23,24], 4 [11, 25, 26], and 5 [27] have been proposed or used.

In order to obtain a value of the coordination number of In, and hence contribute to resolving the controversy regarding it, EXAFS measurements were performed, from the In K-edge, on the glass with the stoichiometric composition $Ge_{28.33}$ In_6 $Se_{65.67}$. For this investigation such stoichiometric composition was chosen because it only consists of heteropolar bonds [28, 29]. In this paper the results of these EXAFS measurements are reported.

2. Experimental

The bulk sample of the glassy alloy $Ge_{28.33}$ In_6 $Se_{65.67}$ was prepared from high purity (5 N, Johnson-Mathey) constituent elements using the classical melt-quenching method. The method consisted of vacuum sealing (10^{-5} mbar) the appropriate amounts (total 3 g) of Ge, In and Se into cylindrical quartz ampoule. The ampoule was then heated in a furnace to a temperature of 850 °C. At this temperature, melting of the sample was homogenized by continuous shaking of the ampoule. Subsequently, the glass was obtained by quenching the ampoule to 0 °C in iced-water.

The EXAFS measurements from the In K-edge (27940 eV), in the transmission mode, were performed at L.U.R.E (Orsay, the French synchrotron radiation facility) using DCI storage ring operated at an energy of 1.85 GeV with a 250 mA average beam current. Energy selection was made using a double-crystal Ge(400) monochromator. The glassy sample was ground to powder, with a grain size of less than 20 μm, and uniformly spread between Kapton tapes. The thickness of the sample was chosen so that the signal-to-noise ratio is optimized. The data were obtained at room temperature with an energy step of 2 eV and using ionization chambers, filled with krypton, acting as detectors.

Five spectra for the sample were collected and added. Despite the small indium concentration in that sample, it produced a good EXAFS signal.

3. Results and Discussion

The EXAFS data analysis was performed using the single scattering theory and the plane-wave approximation where the EXAFS signal, X(k), expressed as a function of the wave vector of the photoelectron, k, is given by [30-33].

$$X(k)=\sum_i \frac{N_i A_i(\pi,k)}{kR_i^2}\exp\left(-2\sigma_i^2 k^2\right)\exp\left[-2R_i/\lambda_i(k)\right]\sin\left[-2kR_i+\psi_i(k)\right]$$

where N_i is the number of atoms in the *i* th shell, R_i is the distance form the central absorbing atom to atoms in the *i th* shell, $A_i(\pi, K)$ is the back-scattering amplitude from each of the N_i neighboring atoms of the *i* th type and σ_i is the Debye-Waller factor which takes into account both thermal and static disorders inside the *i* th shell. The damping factor $\exp[-2R_i / \lambda_i (k)]$ is due to inelastic losses in the process and Ψ_i (k) is the total phase shift experienced by the photoelectron which includes central atom and backscatterer contributions.

In order to extract the structural parameters N_i, R_i, σ_i, about the absorbing atoms the available program on VAX computers at L.U.R.E [34] was used. The pre- and post-edge background subtraction and the Fourier transform (uncorrected for phase shift) were performed using the above mentioned program. The edge energy, E_o, is taken at the inflection point of the absorption spectrum. To suppress an important source of noise for high values of k, a filtering in the k space conserves k-values between 4.2 and 10.4 A^{o-1}. Low frequency oscillations were removed from the pseudo-radial distribution function (RDF) by using a selection criteria to keep R greater than 1.1A^o.

Comparison between the theoretical and experimental k^2 weighted EXAFS spectra are depicted in Figure 1. The filtered EXAFS signals are then Fourier transformed through a Kaiser window ($\tau = 2.5$). Comparison between the experimental and theoretical Fourier transforms has been carried out and is presented in Fig. 2. The transforms shown in this figure are uncorrected for the phase shift and so the R distances appearing in the pseudo-radial distribution functions have to be increased by 0.4 A^o

approximately. As can be seen from Figure 2, only one coordination shell in the pseudo-RDF is observed. This coordination shell is attributed to a shell of nearest-neighbour Se atoms. No evidence of a peak at a higher R value, which could be associated with In-Ge bonds, has been observed.

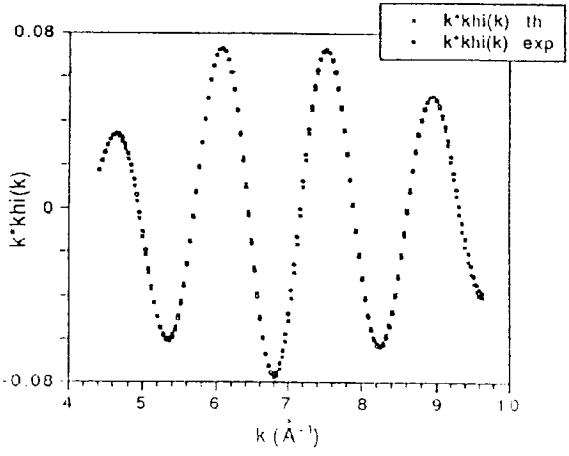

Figure (1): Comparison between Experimental (0) and theoretical (x) EXAFS oscillations extracted at the In K-edge.

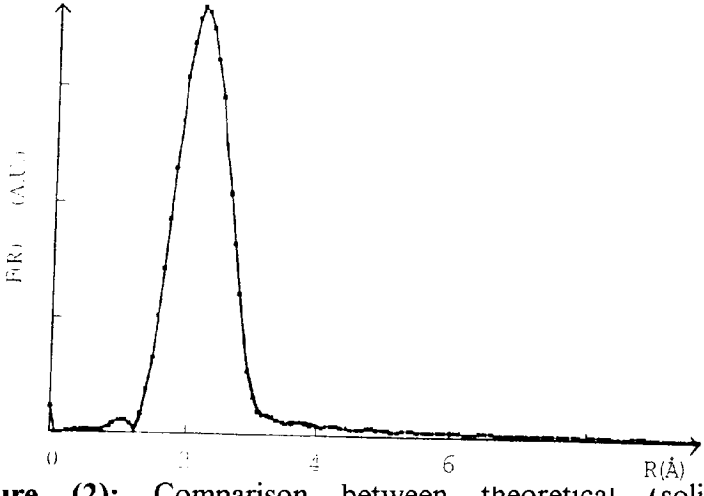

Figure (2): Comparison between theoretical (solid line) and experimental (full symbols) pseudo radial distribution functions around the In atom in the glass.

During the fitting procedure theoretical phases and amplitude functions from [35] were used. In this case it is necessary to determine the correction term, ΔE_o , of the absorption edge threshold relative to the different atomic pairs considered. It is also important to determine the Γ parameter of the photoelectron, that is related to the mean free path via the relation $\Gamma = k/\lambda$. The structural parameters N, R, σ, ΔE and Γ, obtained from the best fit of the first shell EXAFS signal, are listed in table 1. The fitting results show that the In atom is uniquely coordinated by three Se atoms and that the mean bond length R(In-Se) is shown to have the value of 2.57A°.

Table (1): Fit results concerning the Se shell around In atoms in the glass.

N ± 0.1	R(A°) ± 0.02	σ (A°)	ΔE (eV)	Γ (A°$^{-2}$)
3.07	2.57	0.074	-13.2	0.70

4. Conclusions

It is concluded that In atoms in this chalcogenide glass are only coordinated with Se atoms. The value for the coordination number of In in this glass that was obtained in this investigation has been determined to be equal to three. These conclusions confirm the previous results [24] that were obtained from the compositional dependence of the glass transition temperature for glasses in the Ge-In-Se system.

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