Journal of Non-Crystalline Solids 356 (2010) 1288–1293

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Structure-optical property correlations of arsenic sulfide glasses in visible, infrared, and sub-millimeter regions

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ARTICLE INFO

Article history:
Received 7 October 2009
Received in revised form 9 April 2010
Available online 10 May 2010

Keywords:
Absorption;
Amorphous semiconductors;
Chalcogenide glasses;
Coordination;
Rigidity percolation;
Refractive index;
Short range order

ABSTRACT

Optical properties and structural aspects of As_xS_{100-x} glasses from visible to terahertz wavelengths were explored. A series of annealed, bulk As_xS_{100-x} glasses ($x = 30$ to 42) were made and their refractive indices determined at terahertz, infrared, and visible frequencies using a quasi-optical backwards wave oscillator spectrometer for terahertz measurements combined with a prism coupler for visible and infrared measurements. It was found that the refractive index at all frequencies increases with arsenic composition up to 40 at.% arsenic and then decreases with additional arsenic. The structure in X-ray diffraction patterns supports the notion of a minimum volume at 40 at.%, while the average covalent coordination number indicates that the rigidity percolation threshold is reached there. At arsenic concentrations >40 at.%, the network becomes over-constrained, and the molar volume increases.

1. Introduction

Since the infrared (IR) transmission of arsenic trisulfide (As_2S_3 or $As_{40}S_{60}$) glass first was reported in 1870 [1], As_xS_{100-x} and other chalcogenide glasses have been the subject of extensive research, [2,3] particularly due to their exhibition of novel photo-induced phenomena [4]. Many of these glasses have high optical non-linearities [5] that make them attractive for all optical switching and telecommunications [6]. In spite of having a large glass-forming region, small compositional changes can give rise to drastic structural changes near stoichiometry of $x = 40$ in the As–S system, especially at the glass transition temperature [7,8] (T_g) and optical gaps [9,10]. For example, a recent study has shown that the thermodynamic parameters T_g, ΔH, C_p, and ΔC_p, obtained from modulated-temperature differential scanning calorimetry (MTDSC), revealed extrema when the As–S glass system reached the stoichiometric composition at 40 at.% arsenic (i.e., As_2S_3) [11]. It is generally understood that glasses on the sulfur-rich side of stoichiometry ($x<40$ at.%) have similar local structure to crystalline As_2S_3 (orpiment), but with some As–S–As bonds replaced by As–S–S, while glasses on the As-rich side of stoichiometry ($x>40$ at.%) have a significant fraction of nanoclusters of As–As bonds due to As_4S_4 (realgar) type structures [12–15]. The structure-property correlations of this family of glasses in the terahertz (THz) region have not been explored to our knowledge. It was proposed that optical data from the sub-millimeter/THz region would reinforce and complement data obtained in the visible and infrared. In the present paper, refractive index measurements from the visible (0.633-μm wavelength) through the THz region (1.3-cm wavelength) are presented as well as the inherent transparency of As_xS_{100-x} glasses out to at least 0.5 THz. Correlations are drawn between the compositional variations and structure as shown by X-ray diffraction as well as the observance that all of the index data have a maximum at $x = 40$ at.% where the molar volume is minimum.

2. Methods

Five As–S chemistries of chalcogenide glass were studied ($As_x S_{100-x}$, where $x = 30$, 33, 36, 40, and 42) and were synthesized in the Non-Oxide Materials Synthesis Laboratory (NOMSL) at the Pacific Northwest National Laboratory (PNNL) [16,17]. All samples were processed by melting high-purity elements (99.999+% sulfur from ASARCO and 99.99999% arsenic from Alfa Aesar) in evacuated (10^{-4} Pa or 10^{-6} Torr) fused quartz ampoules while homogenizing in a Deltech rocking furnace (Deltech, Inc., Denver, CO). Sample processing conditions are shown in Table 1. All samples were annealed at 140 °C for ~2 h and prepared as windows ~2 to 3 mm thick with parallel sides with an optical quality polish (1-μm diamond suspension). Sample densities were measured using the Archimedes method with deionized water using a Sartorius A200S analytical balance (Sartorius, Goettingen, Germany), and estimated error is 0.3% according to calibration with a copper standard.

Sample transmission was measured using a THz quasi-optical spectrometer (Microtech Instruments, Eugene, Oregon, USA) in the

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doi:10.1016/j.jnoncrysol.2010.04.018

Table 1
Summary of chemistries tested and some basic physical properties. The glass chemistry is also presented as As_2S_x for comparison with previously published data. Error in density measurement is 0.3%. Error in thickness measurements is ±0.01 mm.

Chemistry	Chemistry	Processing Temperature/ time	A (g/mol)	Archimedes ρ (g/cm^3)	<r>	Sample thickness (mm)
$As_{30}S_{70}$	$As_2S_{4.67}$	500 °C/24 h	44.92	2.823	2.30	2.25
$As_{33}S_{67}$	$As_2S_{4.06}$	450 °C/24 h	46.21	2.927	2.33	2.82
$As_{36}S_{64}$	$As_2S_{3.56}$	475 °C/16 h	47.49	3.042	2.36	2.09
$As_{40}S_{60}$	$As_2S_{3.00}$	450 °C/21 h	49.21	3.166	2.40	2.15
$As_{42}S_{58}$	$As_2S_{2.76}$	525 °C/20 h	50.07	3.203	2.42	2.04

frequency range of 172 to 506 GHz (λ = 0.6–1.7 mm) and an ultraviolet-visible-near infrared (UV–Vis-Near IR) dispersive spectrometer (Cary 500, Varian, Palo Alto, California, USA) in the frequency range of 100 to 1000 THz (λ = 3.0 μm to 0.3 μm, respectively). Optical constants were extracted from the THz transmission data and the band gap was extracted from the visible transmission data.

The refractive index at visible and infrared frequencies was obtained at five discrete wavelengths with a modified prism coupler setup (Metricon 2010, Pennington, New Jersey, USA). Laser wavelengths included 0.6328 μm (HeNe), 1.5473 μm (Er-doped telecom), 3.391 μm (HeNe), 5.348 μm (quantum cascade laser), and 10.591 μm (CO_2). Prisms used were rutile (0.6328 and 1.5473 μm) or gallium phosphide (all wavelengths). A germanium detector was used for 0.6328 and 1.5473 μm, and a Hg–Cd–Zn–Te detector was used for 3.391, 5.348, and 10.591 μm. Precision in the measurement of bulk samples was 0.0005, provided that the prism index was known as a function of temperature and the knee in the curve due to the onset of total internal reflection was resolvable.

A Scintag Pad V X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5406 Å, 45 kV, and 40 mA) and a Peltier-cooled Si(Li) solid-state detector was used for diffraction analysis. The measurements were done using θ to 2θ geometry in a step-scan approach from 5° to 110° 2θ using a step size of 0.04° 2θ and a dwell time of 4 s per step. Each sample was rotated in the *X–Y* plane during data collection to minimize preferred orientation in that plane in the event that a crystalline phase(s) was identified. All samples were found to be amorphous.

3. Results

Table 1 shows a summary of the chemistries tested along with the average atomic weight (*A*), the measured Archimedes measured density (*ρ*) in g/cm^3, and the average covalent coordination number (<*r*>). These calculations are reviewed in the Appendix. The density increases linearly with arsenic content and agrees well with previously published data [18].

3.1. Refractive index

A set of backward wave oscillators was used to generate the 170- to 500-GHz frequencies by tuning the voltage applied to the cathode to sweep the frequency of the monochromatic radiation [19]. Refractive indices were determined from the transmission measurements by using the parallel sides of the window as an etalon and fitting complex Fresnel expressions to the fringe maxima (see Fig. 1) [20]. In analyzing the Terahertz transmission data from the oscillation period, the refractive index (*n*) was determined as

$$n = m\lambda / 2d \tag{1}$$

where *m* is the interference maximum number, λ is the wavelength, and *d* is the sample thickness. The oscillating transmittance was then

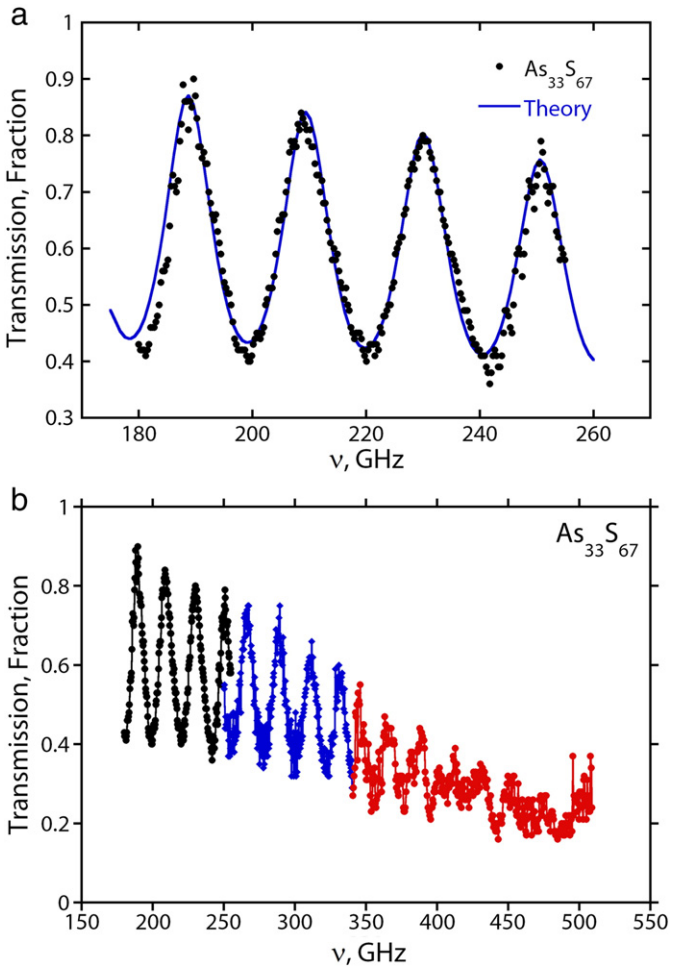

Fig. 1. Example BWO transmission data as a function of frequency, *ν* (GHz). (a) shows the 180 to 255 GHz transmission raw data (points) and fit (line) using Eq. (2), (b) shows raw transmission data from three different BWOs covering a broad frequency range, where the lines here are guides to the eye only.

numerically fit assuming second- or third-degree polynomial variation in the optical constants *n* and *k* as a function of frequency to

$$T = e^{-\alpha d}\frac{(1-R)^2 + 4R\sin^2\psi}{(1-Re^{-\alpha d})^2 + 4Re^{-\alpha d}\sin^2\left(\frac{2\pi nd}{\lambda} + \psi\right)} \tag{2}$$

where the absorption coefficient *α* is

$$\alpha = 4\pi k / \lambda \tag{3}$$

the reflectance *R* is

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{4}$$

and the reflected wave phase shift *ψ* is

$$\psi = \tan^{-1}\left(\frac{2k}{n^2 + k^2 - 1}\right). \tag{5}$$

The real refractive index was described very well with a linear model for the frequency range sampled, as

$$n(\nu) = a\nu + b \tag{6}$$