JOURNAL OF MATERIALS SCIENCE **39** (2004) 1065–1069

Extended X-ray absorption fine structure spectroscopy of amorphous IR transmitting optical materials

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Extended X-ray absorption fine structure (EXAFS) spectroscopic analysis of As-containing amorphous materials transmitting IR radiation with the potential for use as optical materials for night vision (FLIR) systems has been investigated. The materials, obtained from Amorphous Materials Inc., Garland, TX [1], consist of As-Se-Te, GaAs, As_2S_3, $Ge_{28}As_{12}Se_{60}$, and $Ge_{33}As_{12}Se_{55}$. These amorphous materials were prepared via rapid quenching of melts via a proprietary process. The local structure of materials, such as GaAs and As_2S_3, prepared via various methods has been studied in the past [2, 3]. In addition amorphous optical materials such as GeSbTe and GeTe have also been investigated by EXAFS techniques and compared with their crystalline counterparts [4]. However, the local structure of these novel materials produced by Amorphous Materials Inc., has not been analyzed. The results of the investigation of these new kinds of amorphous glassy materials using EXAFS are presented in this paper.

The absorption vs. energy spectra were obtained at the National Synchrotron Light Source facility of the Brookhaven National Laboratories (beamline X 18B and X 19A). The EXAFS interference function was extracted from the absorption spectra and its Fourier transformation was performed [5] using the WinXAS code. The analysis procedure is given only briefly here. The raw data were processed to remove the background absorption using a Victoreen formula and the resultant data were subjected to normalization. The normalized EXAFS interference function was fitted to an advanced cubic spline expression. A Fourier transformation was applied to the obtained signal. The EXAFS oscillations obtained were multiplied by a Hamming window function and amplified with a k^2 weight to reduce the ripples in the Fourier-transformed spectra in r-space. The k-range for the Fourier transform is from 0 to 8 Å^{-1}. The Fourier peak of interest was filtered by multiplying by a similar window function followed by an inverse Fourier transformation into the k-space again. The ranges of the inverse Fourier transforms were about 1–3 Å including the main peaks. In order to obtain the structural parameter of the inter-atomic distance, the coordination number and the Debye–Waller factor, the experimental spectrum was fitted by a non-linear least-squares method to the theoretical expression of the EXAFS oscillations using FEFF 7 [5]. Figs 1–5 are the EXAFS spectra of the amorphous materials and the Fourier transformation of the EXAFS spectra. The summary of the structural parameters of the amorphous materials is provided in Table I. The following is a discussion of analysis of the EXAFS spectra obtained for each material at the corresponding K-edges.

1. *$Ge_{33}As_{12}Se_{55}$*: Fig. 1A (i)–(iii) are the EXAFS spectra of the $Ge_{28}As_{12}Se_{60}$ at the As, Ge and Se K-edges, respectively. The major peak observed at 11.87 keV is that of the As K-edge while the Ge and Se K-edges are found at 11.11 and 12.65 keV, respectively. Fig. 1B (i)–(iii) are the Fourier transformation of the data in Fig. 1A. In Fig. 1B (i), the peaks observed at around 1.54 and 2.85 Å correspond to the nearest-neighbor atoms around As. The peak at about 2 Å in Fig. 1B (ii) corresponds to the nearest neighbor around the Ge atom while the one at approximately 2 Å in Fig. 1B (iii) corresponds to the nearest neighbor

TABLE I Summary of EXAFS analysis of IR transmitting amorphous alloys

Bonds	Coordination number (N)	Bond length R (Å)	σ^2
GaAs			
Ga-Ga	6.05	2.644	0.03
Ga-As	3.41	2.407	0.011
As-As	11.41	3.992	0.026
$Ge_{33}As_{12}Se_{55}$			
As-As	7.19	3.532	0.014
As-Se	2.36	2.552	0.0019
Ge-Se/As	2.48	2.833	0.002
Se-Se	3.31	1.842	0.01
As-Se-Te			
As-As	5.79	3.951	0.002
As-Te/Se	1.34	2.668	0.028
Se-Se	2.83	2.463	0.0065
$Ge_{28}As_{12}Se_{60}$			
As-As	7.09	4.182	0.019
As-Se	2.32	2.552	0.0019
As_2S_3			
As-As	1.13	2.76	0.047
As-S	1.96	2.24	0.005

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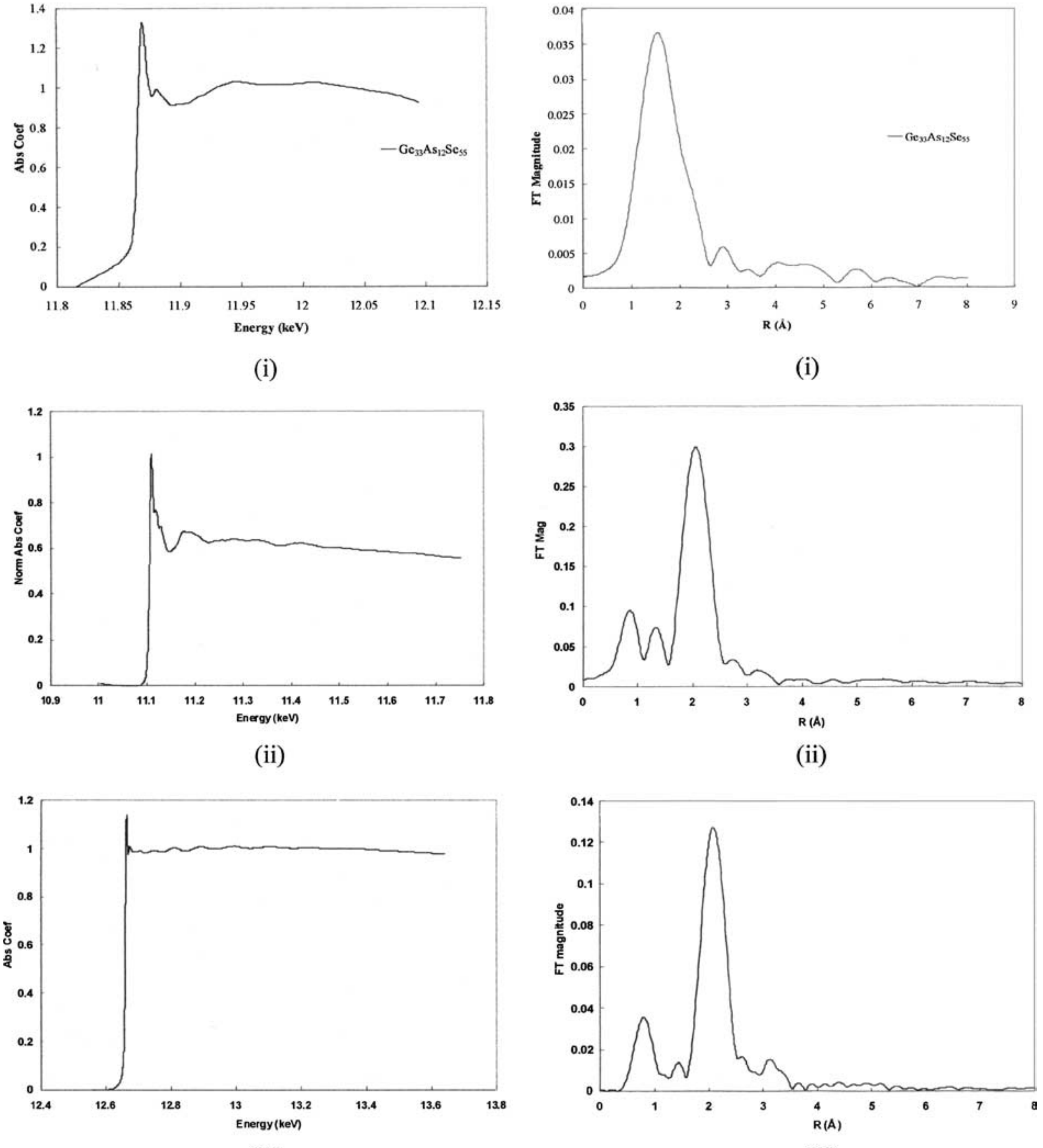

(i) (i)

(ii) (ii)

(iii) (iii)

A B

Figure 1 (A) EXAFS spectra and (B) Fourier transformation of EXAFS spectrum of $Ge_{33}As_{12}Se_{55}$ film; (i) As K-edge, (ii) Ge K-edge, and (iii) Se K-edge.

around the Se atom. The data obtained from the fitting show that the Ge atoms in the amorphous state are 2.5 fold coordinated by As (and/or Se) atoms. It must be noted that EXAFS measurements cannot distinguish between As and Se atoms in backscattering mode since the atomic number of As is very close to Se. Similarly, EXAFS measurements cannot distinguish between As and Ge atoms in backscattering mode. The results obtained from fitting As and Se K absorption edges show that there are no Ge atoms in the first coordination shell of the As atom. The nearest neighbors to the Se central atom are very likely Se atoms at a distance of 1.84 Å. An analysis of the absorption spectra also shows that the coordination number for the Se atom is 8.

2. *$Ge_{28}As_{12}Se_{60}$*: Fig. 2A (i)–(iii) show the EXAFS spectrum of the $Ge_{28}As_{12}Se_{60}$ at the As, Ge and Se K-edges, respectively. The major peaks at 11.87, 11.11 and 12.65 keV correspond to the As, Ge and Se K-edges, respectively. Fig. 2B (i)–(iii) are the Fourier

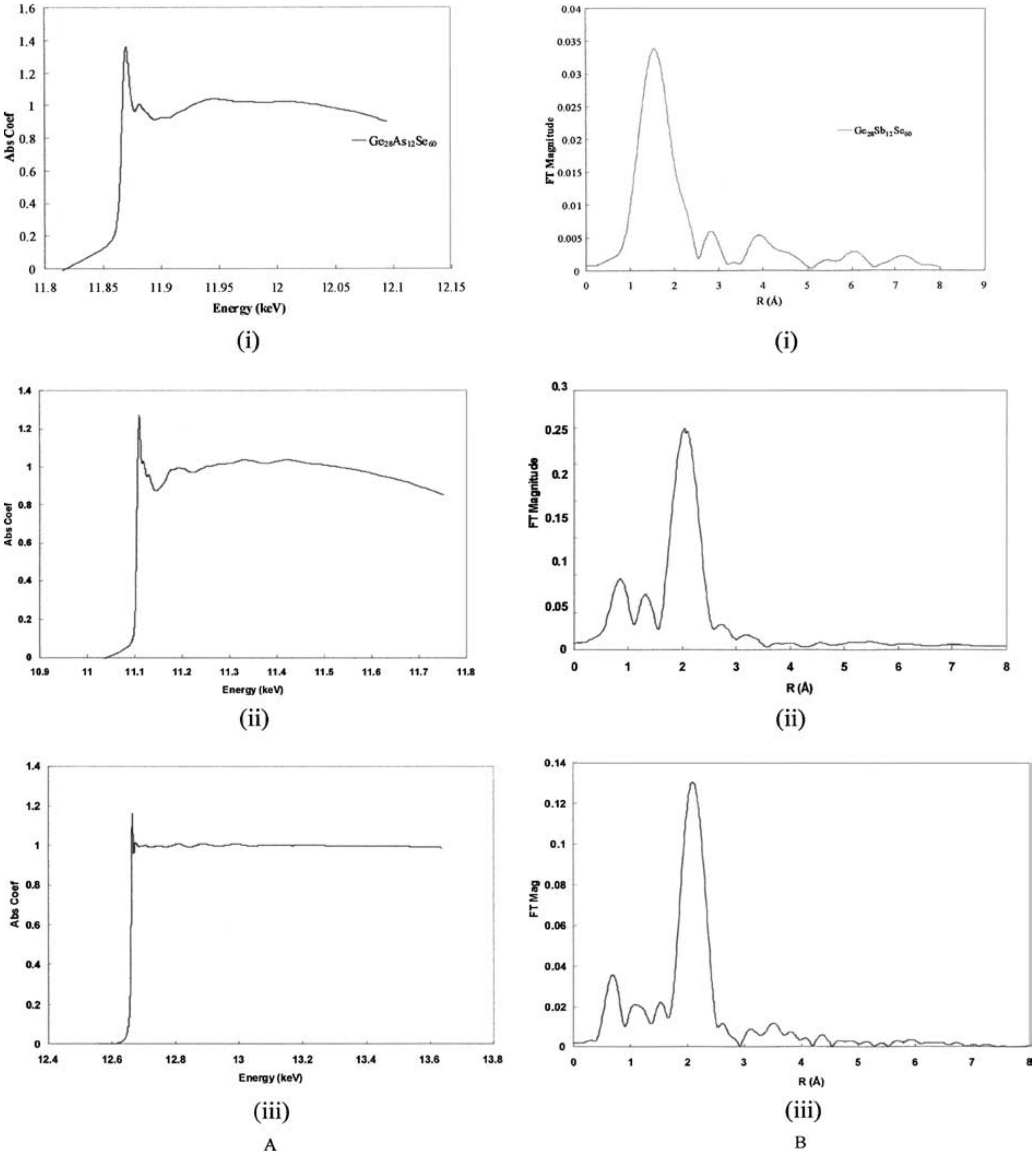

Figure 2 (A) EXAFS spectra and (B) Fourier transformation of EXAFS spectrum of $Ge_{28}As_{12}Se_{60}$ film: (i) As K-edge, (ii) Ge K-edge, and (iii) Se K-edge.

transformation of the data in Fig. 2A. In Fig. 2B (i), the peaks around 1–2 Å correspond to the nearest neighbor atoms around As. The peak around 2–3 Å in Fig. 2B (ii) is related to the nearest neighbor for the Ge atom while that around 2 Å in Fig. 2B (iii) is related to the nearest neighbor for the Se atom. The data on the structural parameters obtained from the current analysis were similar to the corresponding data for the $Ge_{33}As_{12}Se_{55}$ sample except for the amplitudes. The change in Ge and Se content in the materials does not appear to affect the local structural parameters.

3. *As-Se-Te*: Fig. 3A (i) and (ii) show the EXAFS spectrum of the As-Se-Te at the As and Se K-edges, respectively. The peaks corresponding to the As and Se K-edges are observed at 11.87 and 12.65 keV, respectively. Fig. 3B (i) and (iii) show the corresponding radial distributions after Fourier transformation at the As and Se K-edges, respectively. The Fourier transformation (real part) of the signal (Fig. 3B (i)) shows the presence of one dominant peak at 1.62 Å thus clearly indicating that the sample is amorphous. A minor peak is also observed at 2.95 Å. The peak at 2 Å in Fig. 3B corresponds to the nearest neighbors for the Se atom. The pertinent structural parameters, as determined by the least-squares fitting of the theoretical expression of the EXAFS oscillations on the experimental spectra,

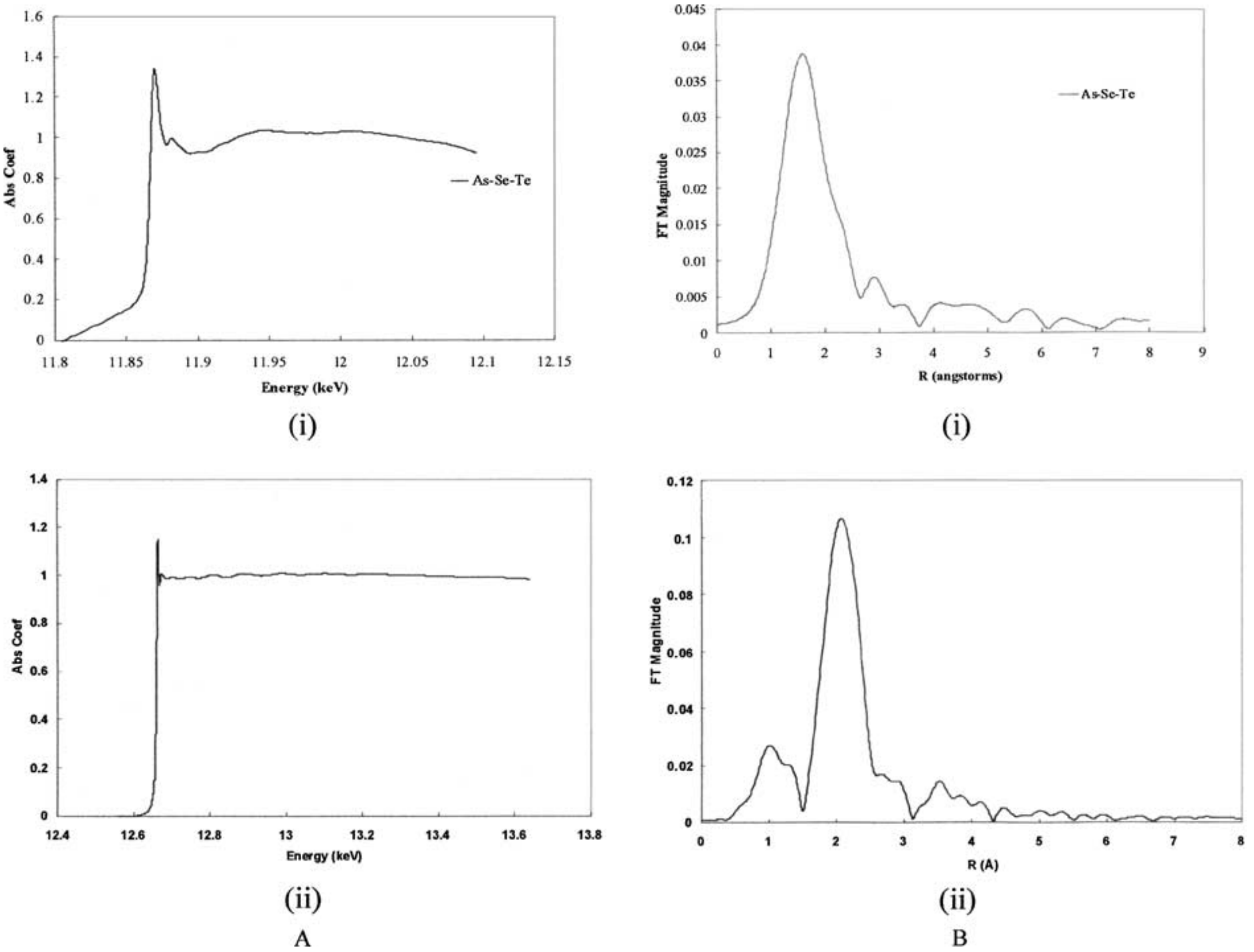

Figure 3 (A) EXAFS spectra and (B) Fourier transformation of EXAFS spectrum of As-Se-Te film: (i) As K-edge and (ii) Se K-edge.

showed that 2 types of bonds must be considered. Both As-As and As-Se or As-Te exist in the nearest neighbor shell of the As atoms. According to the best fit, each As atom is surrounded by 5.8 As atoms at a distance of 3.95 Å and 1.34 Se or Te atoms at a distance of 2.67 Å. The structural parameters extracted from the absorption spectra at the Se K-absorption edges show that there are no As atoms in the first coordination shell of the Se atom. The nearest neighbors are very likely Se atoms at a distance of 2.46 Å. The results obtained at the Se-K edge of As-Se-Te show that the Se central atom has 2.83 nearest neighbors.

4. *GaAs*: The EXAFS spectrum (absorption vs. energy) and Fourier transformation (amplitude vs. distance) of the signal at the As K-edge are shown in Fig. 4A (i) and B (i). For this sample, a peak is observed at an energy level of about 11.87 keV, which gradually decreases over higher energy levels. The peak corresponds to the As-K edge. The Fourier transformation of the absorption spectra shows one major peak at about 1.62 Å. Therefore, it is concluded that only short distance order is possible. Hence, the sample is ascertained to be amorphous or glassy. A broad but minor peak is found beyond 3 Å. The EXAFS spectrum (absorption vs. energy) and Fourier transformation (amplitude vs. distance) of the signal at the Ga K-edge are shown in Fig. 4A (ii) and B (ii) respectively. A peak, corresponding to the Ga K-edge is observed at the energy level of about 10.37 keV, which gradually decreases over higher energy levels. The Fourier transformation of the data in Fig. 4A (ii) shows one major peak between 2–3 Å. Two broad minor peaks are found at distances greater than 3 Å. The non-linear least square fitting of the data show that the coordination numbers for Ga and As were 8.46 and 11.4, respectively. The bond lengths for Ga-Ga and Ga-As were 2.64 and 2.41 Å, respectively. The bond length for As-As was estimated to be 3.99 Å.

5. *As_2S_3*: The EXAFS spectrum (absorption vs. energy) and Fourier transformation (amplitude vs. distance) of the signal at the As K-edge are shown in Fig. 5A and B. A peak, corresponding to the As K-edge is observed at an energy level of about 11.87 keV, which gradually decreases over higher energy levels. The Fourier transformation of the normalized absorption spectra shows one major peak at about 1.65 Å, which is significant in that it indicates the absence of long-range order. A second minor peak is observed at 3 Å. The analysis of the Fourier transform revealed that the As atom had 3 nearest neighbors: ~1 As (the bond length is 2.76 Å) atom and ~2 S atoms (the bond length is 2.24 Å).

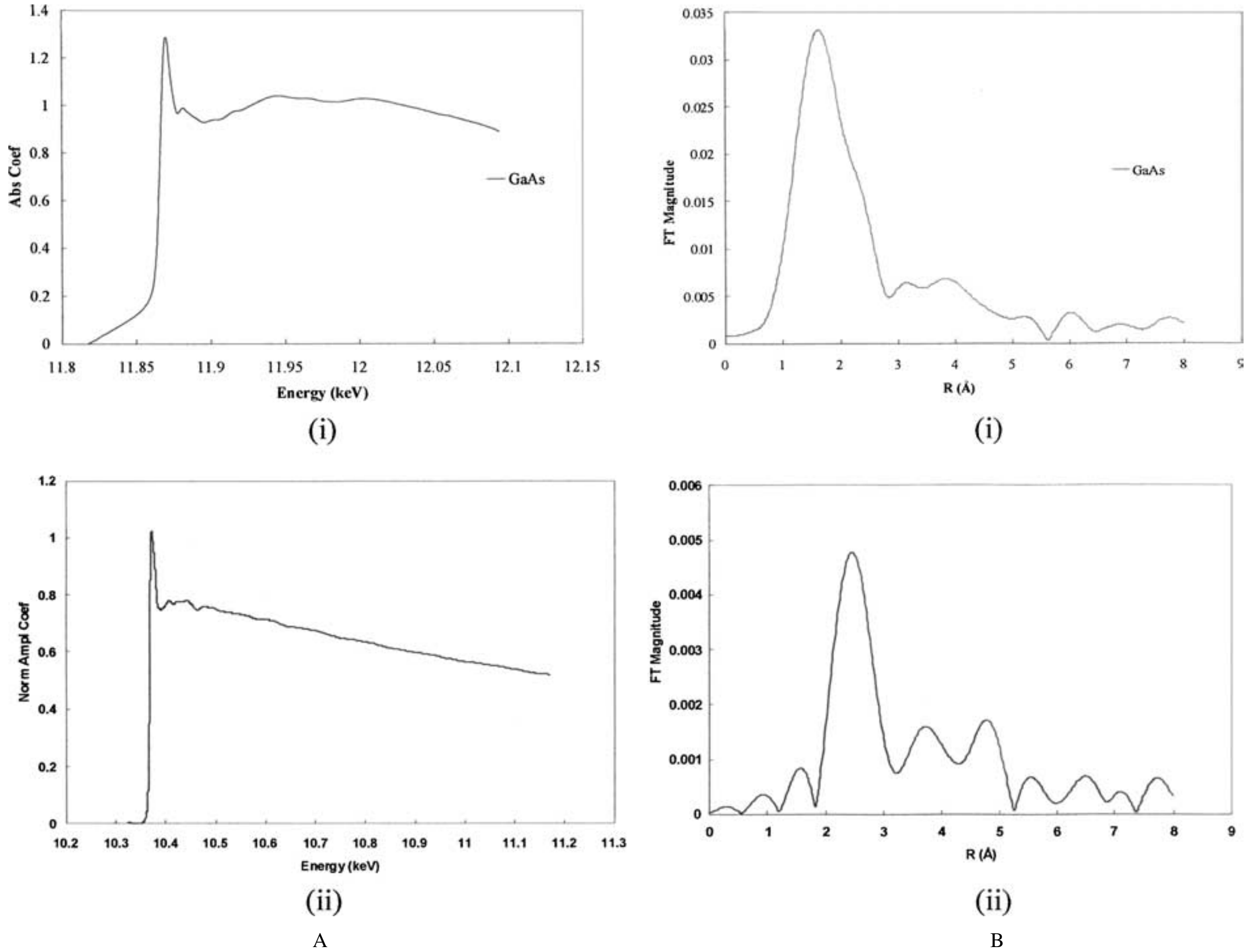

Figure 4 (A) EXAFS spectra and (B) Fourier transformation of EXAFS spectrum of GaAs film: (i) As K-edge and (ii) Ga K-edge.

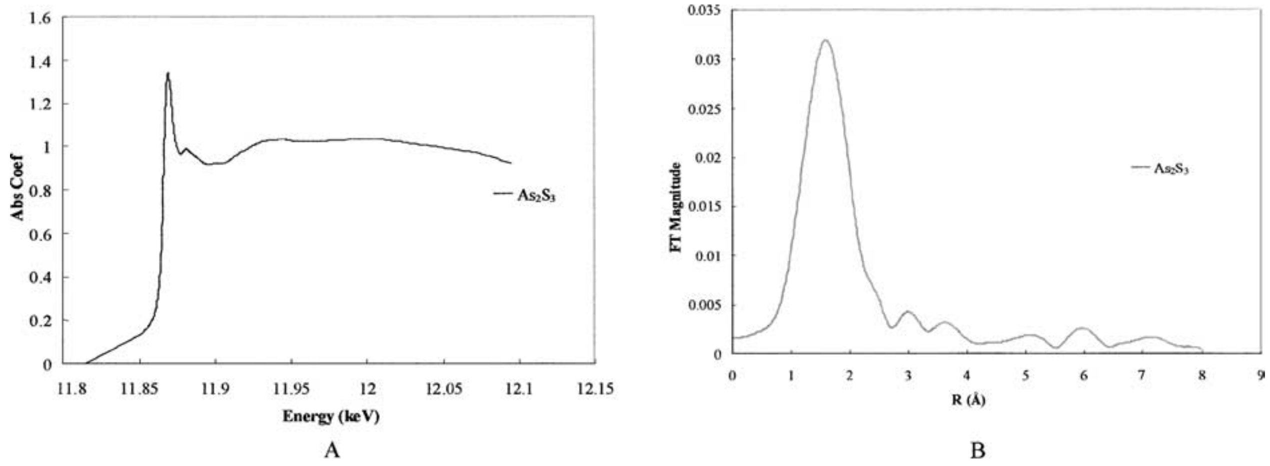

Figure 5 (A) EXAFS spectra and (B) Fourier transformation of EXAFS spectrum of As_2S_3 film at the As-K edge.

Acknowledgments

Support for this research, funded through Southern Illinois University, was provided by CARS, Argonne National Labs.

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Received 26 June
and accepted 28 August 2003