CHEMICAL ORDER OF
SiSe$_2$ GLASS AND CRYSTAL COMPARED

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The local chemistry of Te impurity atoms in SiSe$_2$ glass and crystal is deduced from ^{125}Te and ^{129}I Mossbauer spectroscopy. Evidence for two types of Te sites is observed in the glass but only one type of a Te site in the crystal. Consequences of these observations on the molecular structure of SiSe$_2$ glass are discussed.

INTRODUCTION

Crystalline SiSe$_2$ possesses a quasi one-dimensional molecular structure consisting of infinitely long chains of edge-sharing Si(Se$_{1/2}$)$_4$ tetrahedra (fig 1a). In this structure, adjacent chains have their Si-Se$_2$-Si planes at right angles to each other leading to an out of phase stacking of chains. Peter and Krebs[1] have noted that in this structure the intrachain and interchain non-bonding Se-Se contacts are characterized by nearly the same length.

Crystalline SiSe$_2$ melts at T = 970°C into a rather viscous liquid which yields a bulk glass upon water quenching. The glass transition (T$_g$) and crystallization temperature (T$_x$) have been previously[2] established to be about 460°C and 600°C respectively. Molecular structure of the glass has been the subject of several previous investigations using Raman scattering[3,4] and diffraction[5,6]. A model of this glass consisting of edge-sharing tetrahedral chains cross-linked by corner-sharing tetrahedra (fig 1c),
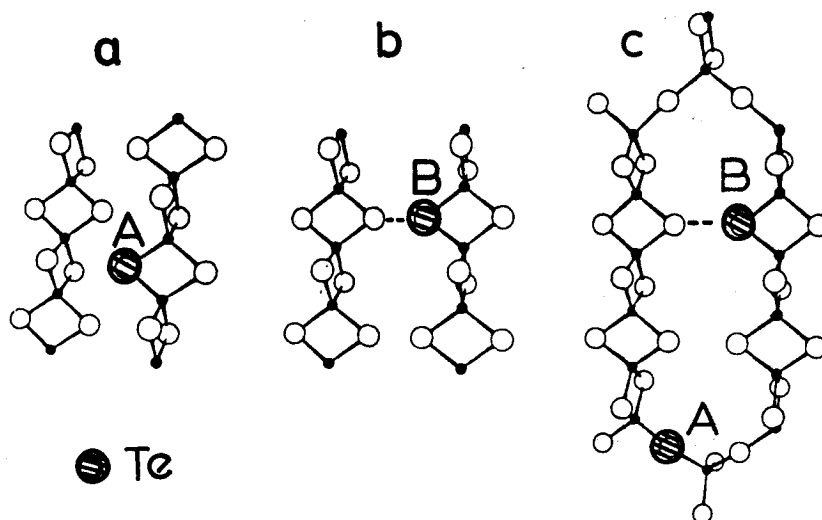
Figure 1a (a) Crystal structure of SiSe$_2$ consisting of edge sharing tetrahedral chains, edges of tetrahedra in neighboring chains are perpendicular; (b) in-phase edge sharing chains of the CLCC cluster modeled by Gladden and Elliott. Note that neighboring chains have tetrahedral edges which are parallel; (c) Fragment of CLCC proposed by Griffiths for structure of SiSe$_2$ glass.

abbreviated as CLCC model[3], provides an attractive basis to understand the vibrational spectra, neutron structure factor, and the magnetic and chemical behavior of this material.

In the present work, we report for the first time on ^{125}Te and ^{129}I Mossbauer spectroscopy of SiSe$_2$ glass and crystal. These experiments permit understanding the molecular structure of the glass by probing the alloying chemistry of the oversized chalcogen probe Te in respective networks. Such experiments have proved to be particularly powerful in decoding the short as well as medium range order in chalcogen based glasses for reasons discussed elsewhere in the literature[7].

EXPERIMENTAL

Glasses of the composition SiSe$_{1.98}$Te$_{0.02}$ were prepared starting with the pure elements including enriched ^{125}Te metal and separately neutron activated ^{128}Te metal. The elements were alloyed in evacuated fused quartz ampule at 1050°C for about a week followed by a water quench. Figures 2, 3, and 4 display Raman scattering, ^{125}Te Mossbauer absorption and ^{129}I emission spectrum of the glass samples. Details of the experimental method and procedure appear elsewhere[7].

The vibrational modes observed in Figure 2 are identical to those reported recently in a previous study[8] and serve to characterize the present samples. We note that the presence of traces of Te in SiSe$_2$ does not alter
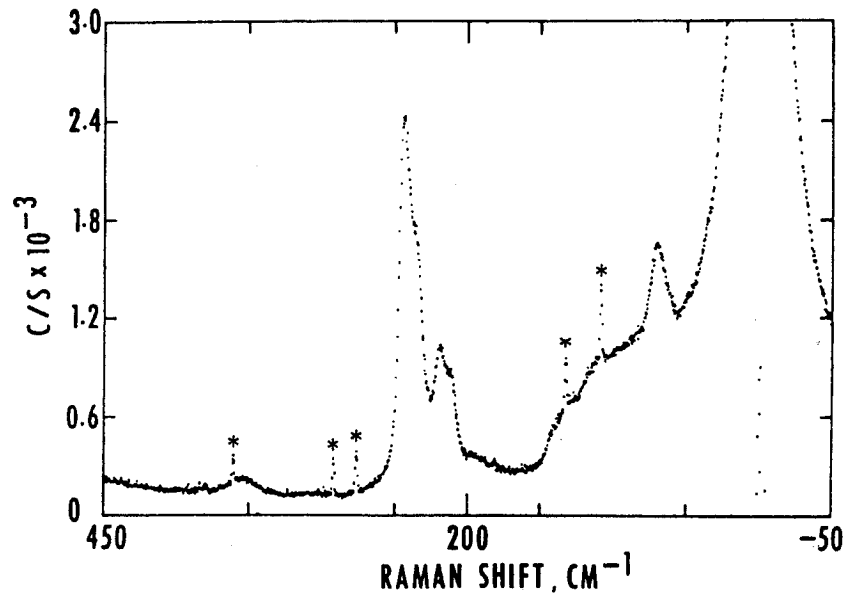
Figure 2 Raman scattering spectrum of g-SiSe$_{1.98}$Te$_{0.02}$ taken using Kr ion laser (same sample was used for ^{125}Te Mossbauer spectroscopy). For mode assignment see References 3 and 8. The asterisks display plasma lines.

the vibrational spectrum in any significant manner. In the glass, the sharp mode seen at 245cm^{-1} and 202cm^{-1} correspond to a symmetric stretch and a scissor mode of SiSe$_4$ units in ES configuration as found in the crystal. On the other hand, the 234cm^{-1} and 218cm^{-1} modes have been attributed to corner-sharing tetrahedra in support of CLCC.

The Mossbauer spectra analyzed[7] in the usual way, demonstrate the high resolution of the emission spectra in relation to the absorption spectra. In particular, we note that the emission spectra are better fit in terms of two sites rather than one site, as illustrated in Figure 4. The relevant ^{129}I Mossbauer parameters are summarized in Table I. Because of extreme reactivity of the glass samples to ambient environment, particularly moisture, the glass samples were transferred from quartz tubing into specially designed cryogenic source and absorber mounts for the two types of Mossbauer experiments, in an high purity Argon environment.

DISCUSSION

The central result to emerge from the present experiments is that predominantly one type of Te site (A) is populated in the glass as in the crystal. We identify this site with a Te impurity atom replacing Se sites at the corner sharing (CS) cross-links (fig 1c) and at edge-sharing (ES) tetrahedral chains (fig 1a) in the glass and crystal networks, respectively. The daughter I-site resulting from such a two-fold coordinated parent Te-site is one-fold coordinated, accounting for the negative sign of the observed nuclear quadrupole coupling[7]. The site A quadrupole coupling of -767(7)Mhz
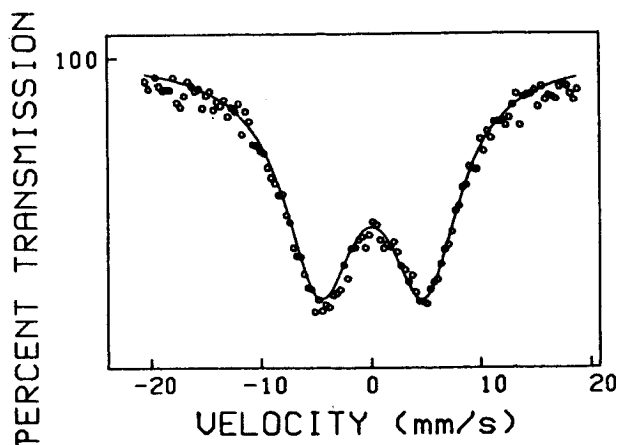
Figure 3 ^{125}Te Mossbauer spectrum of g-SiSe$_{1.98}$Te$_{0.02}$ displaying an average quadrupole splitting of 9.4 ± 0.1 mm/s.

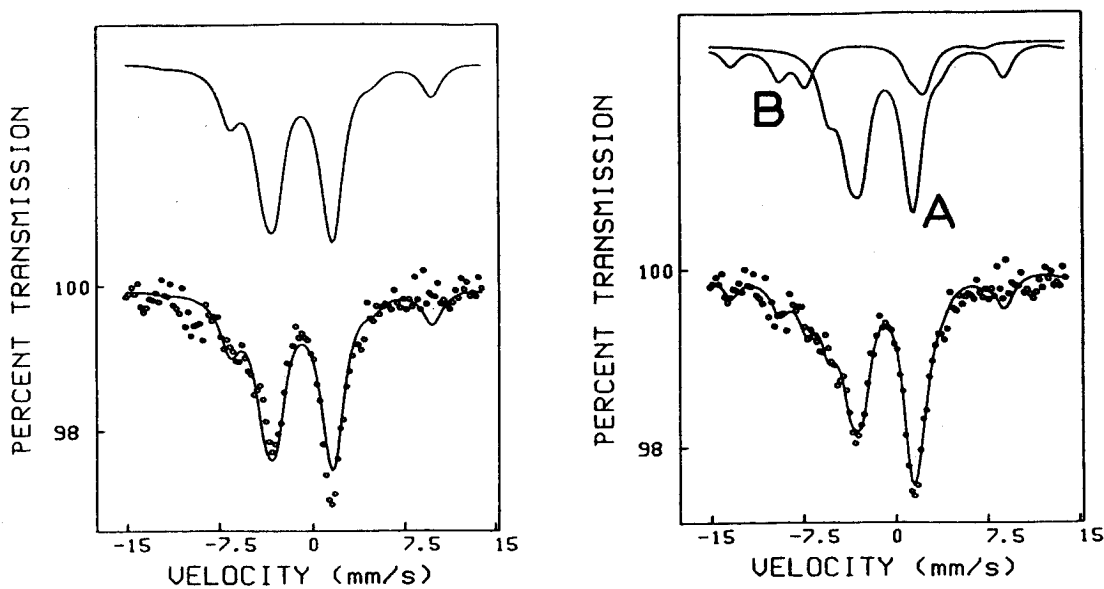**Figure 4** ^{129}I Mossbauer spectrum of g-SiSe$_{1.98}$Te$_{0.02}$ fit to a single site (left) and to two sites (right). Notice how the misfits in the single site fit disappear when two sites are used. Table I lists parameters of the two sites (A, B).

Table I

Host	δ (mm/s)	e^2qQ(Mhz)	η	Comment
g-SiSe$_{2-x}$Te$_x^a$				I_A:I_B = 72:28
Site A	+0.43(4)	-767(7)	0.16(3)	I - Si σ bond
Site B	+2.13(8)	-1694(8)	0.19(4)	I - Se or I - Si σ bond
c-SiSe$_{2-x}$Te$_x$	1.17(5)	-1144(0)	0.10^b	I - Si σ bond
c-Si$_2$Te$_3$				I_1:I_2 = 74:26
Site 1	1.00(3)	+684(4)	0.36(1)	d
Site 2	1.12(5)	-880(4)	0.29(3)	I - Si σ bond

a. x=0.02; b. kept fixed in refinement; d. I-site formed in hcp Te

[129]I Mossbauer parameters of various sites observed in indicated hosts. All measurements taken at 4.2k using a NaI[129] absorber.

is typical of a _relaxed_ I-Si σ-bond observed previously in several binary Si-Te glasses[9] and site 2 in c-Si$_2$Te$_3$ (see Table I). On the other hand, the much higher coupling of -1144(9)Mhz found in the crystal is suggestive of a _strained_ I-Si σ-bond resulting from a Te parent site present in the parallel ES chains of figure 1a. In the crystal, we presume that the interchain non-bonding Van der Waals interactions between a Se atom and its adjacent impurity Te(I) site leads to a compressed or strained I-Si σ bond, resulting in a noticeably larger (60%) quadrupole coupling of -1144(9)Mhz.

The surprising result of the present work is the discovery of a minority site (B site) present in the spectrum of the glass with I_B/I_A=0.4. At the outset, we note that this result is qualitatively different from the one found[7] in the layered glasses (GeSe$_2$, As$_2$Se$_3$) where the site intensity ratio I_B/I_A=1.6. Several interpretations of the B site are possible in the present experiment. This site could represent an I-Si σ bond resulting from a Te parent site present in a highly strained environment of ES chains of the CLCC cluster of figure 1c. As noted recently by Gladden and Elliott[6] in their computer-generated models of the CLCC cluster, adjacent ES chains in this cluster (fig 1b) have their Si-Se$_2$-Si planes parallel to each other with the result that the stacking of adjacent chains is "in phase" with each other. Se replacement by Te impurity atoms in such chains could lead to _highly strained_ I-Si σ-bond, accounting for the unusually large quadrupole coupling of -1694(8)Mhz. An alternate possibility is that the B-site represents an I-Se σ-bond since it is known from previous work[10] that a relaxed I-Se σ-bond

is characterized by a quadrupole coupling of -1385(10)Mhz. Microscopically one can visualize such a site to result from a Te site that cross-links across the "in-phase" ES chains. The two-fold coordination of such a Te site would require that a Si dangling to bond occur, resulting in free spins and leading to paramagnetism upon Te alloying. Clearly, more experiments are suggested to unambiguously decode the microscopic nature of this site.

In summary, the present Mossbauer results on $SiSe_2$ glass provide new information on the nature of various Te sites populated in the present glass. Further experiments are in progress to clarify the nature of the sites populated and the medium range order in $SiSe_2$ glass.

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