Chem. Mater. **1993,** *5,* 377–380 377

Two New Polymorphs of $SiSe_2$: Structural Investigation by Raman and ^{29}Si MAS NMR Spectroscopies and Relationship with the Structure of Vitreous $SiSe_2$

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Received September 18, 1992. Revised Manuscript Received December 14, 1992

Two new polymorphs of $SiSe_2$ can be synthesized by low-temperature reaction of the elements at 400 and 500–600 °C, respectively. Their characterization by X-ray powder diffraction, Raman and ^{29}Si MAS NMR spectroscopies is described. In contrast to the known phase of $SiSe_2$, whose structure consists of infinite chains of edge-sharing tetrahedra, these new polymorphs contain certain amounts of corner-sharing tetrahedra as well. The latter feature illustrates a rather uncommon case for a non-oxide system, where the local structures in the crystalline and glassy states closely resemble each other.

Introduction

During the past decade, the elucidation and modeling of glass structures has received growing interest.[1] Spurred by progress in the power and potency of experimental techniques, such studies have produced intricate detail and structural insights which frequently contradict long-held traditional views and concepts of glass structure, such as the continuous random network or the random close-packing models.[2] A case in point are the chalcogenide glasses, whose intense structural study has revealed substantial intermediate-range order on the one hand, and chemical disorder (differences in local structure between glasses and compositionally identical crystalline compounds) on the other.

For example, infrared, Raman[3–9] and NMR experiments,[10,11] as well as computer-modeling studies[12–16] based on neutron-scattering data[17,18] have revealed that the structure of glassy $SiSe_2$ consists of $SiSe_{4/2}$ tetrahedra that are interconnected both via common edges and corners. This finding contrasts with the hitherto only known crystalline form, which contains infinite chains of edge-sharing tetrahedra, and no corner-sharing.[19–21] However, low-temperature crystallization studies carried out during our previous work on $Li_2Se–SiSe_2$ glasses,[22,23] hinted at the presence of two low-temperature polymorphs. Here, we describe the synthesis procedure of these polymorphs, and their structural characterization by Raman and ^{29}Si MAS NMR spectroscopies. As will become evident, the structures of these new polymorphs are possibly closely related to that of glassy $SiSe_2$.

Experimental Section

Sample Preparation. Stoichiometric quantities of reagent grade Si and Se were thoroughly mixed and placed into a silica glass ampoule sealed under vacuum. Reaction temperatures of 400, 500, 600, 700, and 850 °C were chosen. The mixtures were slowly heated to their reaction temperature at a rate of 10 °C/h, held there for 1 day to 6 weeks (depending on the temperature), and subsequently air-quenched to room temperature. The reaction kinetics were monitored by differential scanning calorimetry. Reaction was considered complete, when the endotherm at 220 °C indicating the melting of Se had completely disappeared. While a reaction time of 4 days was found to be sufficient to complete the reaction at 700 and 850 °C, the required reaction times were 10 days at 500 and 600 °C, and up to 6 weeks at 400 °C.

Similar experiments were carried out with silicon–sulfur mixtures and with two substoichiometric compositions "Si_2Se_3" and "SiSe".

Characterization. X-ray powder diffraction analysis was carried out on a SEIFERT diffractometer using CuKα radiation. Raman spectra were recorded on an OMAR 89 DILOR spec-

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Table I. Observed Distances (Å) between Crystallographic Planes (*hkl*) and Relative Intensities of X-ray Diffraction Lines in the Three $SiSe_2$ Polymorphs

$SiSe_2$-400		$SiSe_2$-500		$SiSe_2$-700	
d_{obs}	I_{rel}	d_{obs}	I_{rel}	d_{obs}	I_{rel}
5.824	10	6.365	5	5.075	80
5.006	15	5.570	100	4.828	10
4.935	15	3.385	20	3.160	100
4.623	5	3.343	20	2.990	20
3.182	75	3.133	50	2.923	15
3.095	100	3.116	50	2.568	5
3.025	50	3.066	15	2.415	10
2.900	40	3.025	20	2.094	5
2.574	5	2.985	20	1.878	20
2.401	25	2.910	25	1.863	10
2.124	15	2.829	20	1.759	10
1.984	15	2.782	20	1.729	5
1.865	20	2.744	15	1.695	5
1.834	25	2.540	15	1.620	5
1.751	5	2.021	10		
1.739	5	1.886	15		
1.696	20	1.857	15		
1.672	20				
1.638	5				
1.566	5				

trometer coupled with a SPECTRA PHYSICS 164 laser (Ar, 514.5 nm, 100 mW). The samples were examined in the form of crystalline powders within sealed evacuated silica ampoules. ^{29}Si MAS NMR experiments were carried out at 59.7 MHz on a General Electric GN-300 spectrometer, equipped with a 7-mm multinuclear MAS NMR probe from Doty Scientific. The following typical experimental conditions were used: spinning speeds 3–6 kHz, 90° pulses of 8–10 μs length, relaxation delay 1 h. Experiments with variable relaxation delays (up to 3 h) showed that these conditions resulted in representative peak area ratios.

Results and Discussion

While all of the silicon–sulfur mixtures result in the formation of the previously known phase of SiS_2,[21,24] three different X-ray diffraction patterns were obtained for the silicon–selenium mixtures, depending on the reaction temperature (see Table I). While the previously known phase of $SiSe_2$ (SiSe2-700) is observed at reaction temperatures of 700 °C and above, two new X-ray patterns corresponding to the new polymorphs were obtained at the lower temperatures, $SiSe_2$-400 (at 400 °C) and $SiSe_2$-500 (at $500 \leq T \leq 600$ °C). Replicate sample preparation showed X-ray and solid-state NMR patterns with reproducible intensity ratios and absence of common lines, hence confirming that both materials are single phase. Both $SiSe_2$-400 and the high-temperature phase are reddish brown in color, whereas both $SiSe_2$-500 and glassy $SiSe_2$- are light yellow. The polymorphs were stable at room temperature for a period of 1 year. However, when the reaction time at 400 °C was extended to 3 months, the form $SiSe_2$-500 was obtained, which is probably a good indication that the polymorphs are metastable. Studies on the reversibility of transitions between these phases yielded irreproducible results, presumably due to very sluggish kinetics. However, both low-temperature polymorphs convert to the known form of $SiSe_2$ when heated to 850 °C. We note that previous DTA studies by Hillel and Cueilleron[20] indicate that the reaction between Si and Se is initiated between 400 and 550 °C, the range of stability found here for these new polymorphs. These authors also carried out some isothermal annealing experiments in this temperature range, but did not report on the existence of new polymorphs. Finally, all attempts to produce compounds with compositions Si_2Se_3 and SiSe, the latter previously claimed to exist,[25] resulted only in $SiSe_2$–Si mixtures.

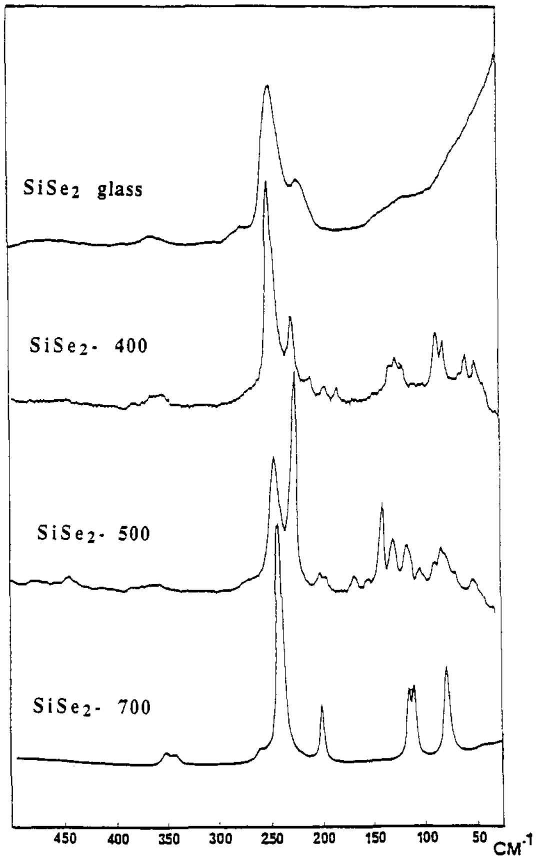

Figure 1. Raman spectra of the $SiSe_2$ polymorphs and of $SiSe_2$ glass.

Attempts to grow single crystals of the $SiSe_2$ low-temperature polymorphs for structure determination have to date remained unsuccessful. Therefore, Raman and ^{29}Si NMR experiments were carried out in order to obtain structural insights. Figure 1 shows the Raman spectra of the three $SiSe_2$ polymorphs along with the spectrum of glassy $SiSe_2$. In agreement with the X-ray results, the Raman spectrum of the high-temperature (labeled here $SiSe_2$-700) form corresponds to that already reported in the literature and discussed in detail by several authors.[3–5,7] The lines at 240 and 350 cm^{-1} are respectively assigned to the A_1 and F_2 modes characterizing the symmetric and nonsymmetric stretching motion of the Se atoms about the central Si atoms in edge sharing $SiSe_{4/2}$ tetrahedra, while those at 80 and 117 cm^{-1} are assigned to the E and F_2 modes characterizing symmetric and nonsymmetric bending motion. The line at 202 cm^{-1} was attributed to the $A_1{}^B$ companion line characterizing the symmetric stretching motion of the Se atoms outside of the bitetrahedral unit.

The Raman spectra of the two new $SiSe_2$ polymorphs are dominated by two intense peaks at 242 and 222 cm^{-1} which correspond to the main peaks observed in the Raman spectrum of glassy $SiSe_2$. The latter spectrum has already been discussed in detail in the literature. The line at 243 cm^{-1} is assigned to the symmetric stretching vibration of

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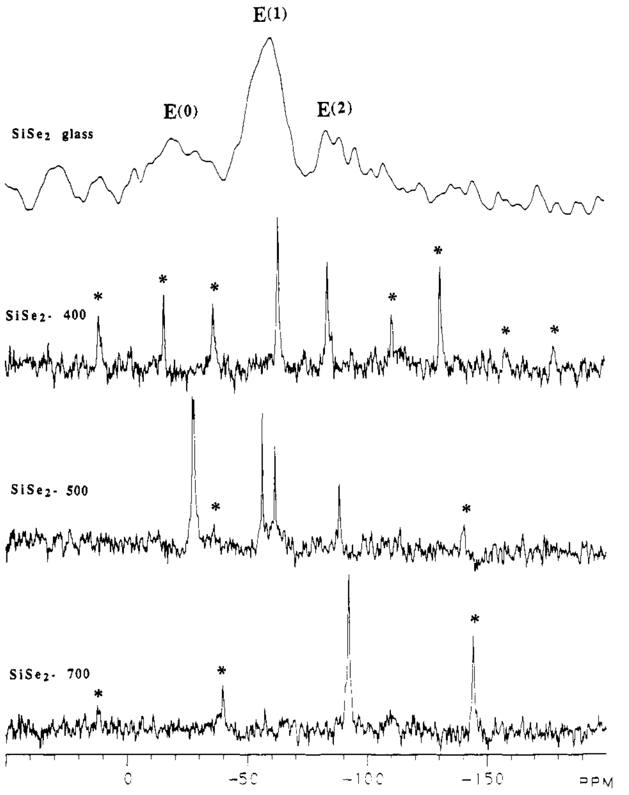

Figure 2. ^{29}Si MAS NMR spectra of the SiSe$_2$ polymorphs and SiSe$_2$ glass. Spinning sidebands are indicated by asterisks.

the Si-Se bonds involved in edge-sharing tetrahedra, while the line at 222 cm^{-1} was attributed by Tenhover[3–5] to the A_1^B companion line, and by Sugai[9] and Griffiths[7] to the A_1 vibrations of Si–Se bonds involved in corner-sharing. Intensity arguments and the comparison with the NMR data discussed below suggest the latter assignment both for glassy SiSe$_2$ and the two new crystalline polymorphs. It can thus be concluded, from the Raman study that both new polymorphs contain, along with edge-sharing tetrahedra, a certain amount of corner-sharing tetrahedra, giving rise to the new line at 222 cm^{-1}. The relative intensities of the main lines at 242 and 222 cm^{-1} suggest that the fraction of corner-sharing tetrahedra is larger in SiSe$_2$-500 than in SiSe$_2$-400. We also note that the much reduced intensity of the A_1^B companion line at 202 cm^{-1}, indicates a lower number of bitetrahedral units compared to SiSe$_2$-700.

Figure 2 shows the ^{29}Si MAS-NMR spectra of the three SiSe$_2$ polymorphs along with that of glassy SiSe$_2$. As expected from the X-ray and Raman data presented here, the NMR spectrum of the high-temperature form corresponds to that already discussed in the literature.[10] The single peak at −92.6 ppm is assigned to the crystallographically unique Si atom sharing two edges with adjacent silicon tetrahedra, in the following referred to as an $E^{(2)}$ unit.

The NMR spectra of the new SiSe$_2$ polymorphs reveal considerably more complexity. SiSe$_2$-400 shows a spectrum with two peaks at −83.5 and −63.0 ppm in a 1:1 ratio, which can be attributed to $E^{(2)}$ and $E^{(1)}$ units, respectively. Here, the denomination $E^{(1)}$ characterizes a SiSe$_{4/2}$ unit sharing one common edge with an adjacent unit, and being linked to two SiSe$_{4/2}$ units by corner-sharing. Since in NMR spectroscopy, the signal intensity is directly related to the number of nuclei giving rise to this signal, we can conclude that the ratio of $E^{(2)}$ to $E^{(1)}$ sites is 1:1. Figure 3 shows a plausible model that is consistent with this information. In this hypothetical structure, the infinite chains of the high-temperature form is broken up into edge-shared tetramers, linked to each other in two dimensions via corner-sharing.

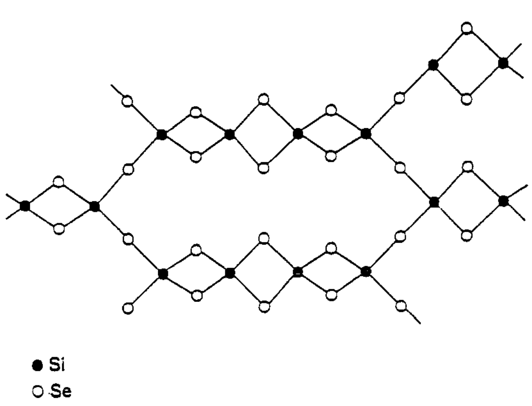

Figure 3. Proposed structural model for the SiSe$_2$-400 polymorph.

The spectrum of SiSe$_2$-500 shows five resonances at −27.3, −28.0, −56.3, −61.6, and −88.4 ppm. These peak positions are rather close to those found previously in glassy SiSe$_2$. In accord with the Raman spectra and the NMR peak assignments for the other SiSe$_2$ polymorphs, and the previous interpretation of the NMR spectrum of glassy SiSe$_2$, the −88.4 ppm peak is assigned to $E^{(2)}$ species, the −61.6 and −56.3 ppm peaks to $E^{(1)}$ species, while the −27.3 and −28.0 resonances are attributed to $E^{(0)}$ species, i.e., SiSe$_{4/2}$ tetrahedra that are interconnected to others exclusively by corner-sharing. The intensity ratio of the $E^{(2)}$:$E^{(1)}$:$E^{(0)}$ species is 1:2:2. This result agrees qualitatively with the Raman result discussed above, that SiSe$_2$-500 has a larger fraction of corner-sharing SiSe$_{4/2}$ units than SiSe$_2$-400. Figure 4 shows two structural proposals that are consistent with all of the above information. The starting point for these models is the structure of GeSe$_2$, which consists of corner-sharing GeSe$_{4/2}$ tetrahedra forming infinite chains that are crosslinked by two edge-sharing tetrahedra.[26] This arrangement results in equal numbers of $E^{(0)}$ and $E^{(1)}$ species. If we modify this structure by replacing the dimeric crosslinks in GeSe$_2$ by trimeric ($E^{(1)}$–$E^{(2)}$–$E^{(1)}$) cross-links, we obtain the structure shown in Figure 4a. The asymmetric unit of such a proposed structure is indicated by dashed lines; it is consistent with the observation of five distinct ^{29}Si NMR peaks. Due to the geometry of the trimeric crosslinks, a three-dimensional network with infinite [SiSe$_{4/2}$]$_n$ chains in two dimensions results. A second possibility is shown in Figure 4b. Here, the structure contains a mixture of dimeric ($E^{(1)}$–$E^{(1)}$) and tetrameric ($E^{(1)}$–$E^{(2)}$–$E^{(2)}$–$E^{(1)}$) edge-sharing cross-links, resulting in a two-dimensional structure that is even more closely related to GeSe$_2$.

Both structures have the same $E^{(0)}$:$E^{(1)}$:$E^{(2)}$ ratio as indicated by the NMR spectrum. However, the structure shown in Figure 4b provides a more satisfactory explanation for the large chemical shift difference between the two $E^{(1)}$ units. Of course many other arrangements resulting in the same $E^{(n)}$ ratios may be possible. More insights into the connectivities of these $E^{(n)}$ species in SiSe$_2$-500 can be obtained in principle by structural modelling

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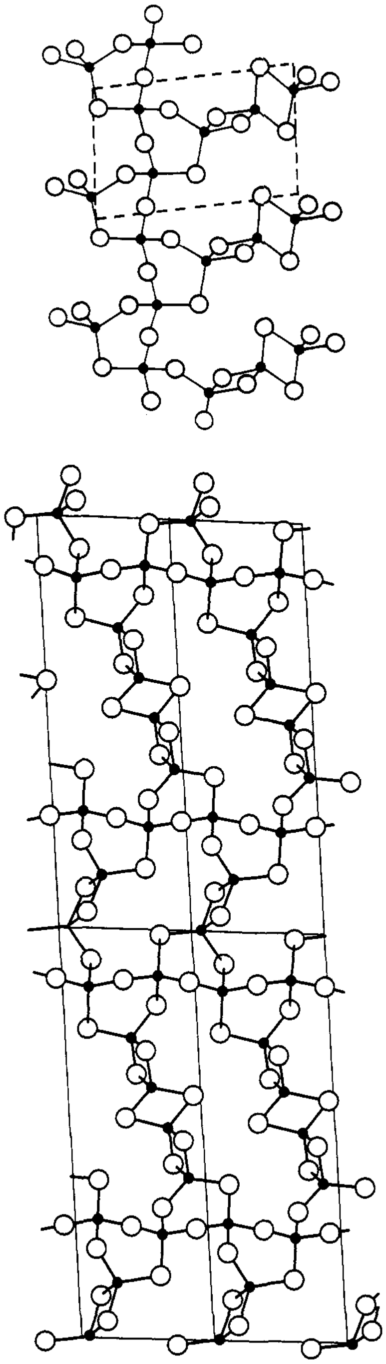

Figure 4. Two proposed structural models for the $SiSe_2$-500 polymorph (see text). The dashed lines shown in part a indicate the proposed asymmetric unit; the solid lines in part b show the proposed unit cell.

from X-ray powder diffraction patterns. Furthermore, two-dimensional ^{29}Si–^{29}Si correlation spectroscopy and/or spin-diffusion experiments on isotopically enriched material are expected to provide further connectivity information. Specifically, these experiments could decide between the two structural models shown in figure 4a,b. If the model in Figure 4a is correct, both $E^{(1)}$ species would show fast coherence transfer with the $E^{(2)}$ unit, whereas in the case of model 4b, an order-of-magnitude difference between the two $E^{(1)}$–$E^{(2)}$ coherence transfer rates would be observed.

The structural characterization of the new crystalline $SiSe_2$ polymorphs may also shed new light on the structure of glassy $SiSe_2$. While existing models for the structure of glassy $SiSe_2$ generally agree with respect to the coexistence of $E^{(0)}$, $E^{(1)}$, and $E^{(2)}$ units, their relative amounts and the way in which these entities are linked to each other are still a matter of controversy in the literature. On the basis of Raman experiments, Griffiths[7] proposed the CLCC model, where chain fragments containing $E^{(2)}$ units are interconnected by $E^{(1)}$ and $E^{(0)}$ $SiSe_{4/2}$ tetrahedra. This model was further refined in subsequent modeling studies of neutron diffraction data.[12–15] The best agreement was obtained for a mixture of 85% random chains, each containing an average of seven $E^{(2)}$ units and 15% cross-linked chain clusters, consisting of rings with two $E^{(0)}$ and four $E^{(1)}$ units each. However, such a model does not meet the quantitative constraints imposed by the NMR results, because it greatly underestimates the relative fractions of both the $E^{(1)}$ and the $E^{(0)}$ units. Thus, a structural model that accounts for all experimental data is still missing.

Perhaps the most striking result of the present study is the close structural relationship between $SiSe_2$-500 and glassy $SiSe_2$ evident both in the NMR and the Raman data. There is only a minor remaining discrepancy with respect to the $E^{(2)}$:$E^{(1)}$:$E^{(0)}$ ratios, which are 2:2:1 and 1:2:1 for $SiSe_2$-500 and glassy $SiSe_2$, respectively. Better agreement in these peak ratios can be obtained, if one assumes glassy $SiSe_2$ to be comprised of a mixture of the structural units present in $SiSe_2$-400 and $SiSe_2$-500. The idea is particularly appealing because the glass transition temperature, i.e., the temperature at which the vitreous structure is frozen in lies around 450 °C, close to the regions of stability of both of these two polymorphs. It would also agree with the suggestion of the modelling study that the glass is a mixture of several different intermediate-range order building blocks. The results on $SiSe_2$-500 presented here show that structures containing large fractions (40%) of $E^{(0)}$ units have intrinsic stability in this system. They should thus be considered in future modelling studies of glassy $SiSe_2$.

Acknowledgment. This work was supported by CNRS and the National Science Foundation (grants DMR 89-13738 and INT-9115972). A.P. thanks the CNRS for sponsoring a four-month research stay at UCSB.