STRUCTURAL ORIGIN OF GLASS FORMATION IN GROUP IV DISELENIDES

P. Boolchand[a]; J. Hernandez[b]

[a] Department of Electrical and Computer Engineering and Department of Physics, University of Cincinnati, Cincinnati, Ohio [b] Energy Conversion Devices Troy, Michigan

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P. BOOLCHAND
Department of Electrical and Computer Engineering and Department of Physics
University of Cincinnati, Cincinnati, Ohio 45221-0030

and

J. HERNANDEZ
Energy Conversion Devices
Troy, Michigan   48084

Abstract $SiSe_2$, $GeSe_2$ and $SnSe_2$ crystallize in a quasi 1-d, quasi 2-d and a quasi 2-d structure with the cations possessing a coordination number (CN) of 4,4 and 6, respectively. $SiSe_2$ and $GeSe_2$ melts readily yield bulk glasses upon water quenching, while non-crystalline $SnSe_2$ can only be prepared by vapor deposition onto room temperature substrates as amorphous thin-films. In the non-crystalline state, a cation CN of 4 is preferred largely because tetrahedral $Si(Se_{1/2})_4$, $Ge(Se_{1/2})_4$ and $Sn(Se_{1/2})_4$ units form the principal building blocks of these networks. Furthermore, tetrahedra share predominantly edges in $SiSe_2$ glass, a combination of both corners and edges in $GeSe_2$ glass and corners in amorphous $SnSe_2$ films. The intermediate range order of these non-crystalline materials has emerged from Raman scattering, Mossbauer spectroscopy and neutron structure-factor measurements.

INTRODUCTION

Most inorganic solids can be made amorphous by vapor deposition onto suitably cooled substrates. However only a select few inorganic melts can be readily supercooled by an air or water quench to yield bulk glasses which solidify at the glass transition temperature. The chalcogenides and oxides of the group IV and V elements represent some of the best-known glass-formers found in nature.

There are growing indications that the origin of glass formation may in general be the consequence of a delicate balance between chemical and mechanical stability of glassy networks[1]. In particular for the binary chalcogenides of the group IV and V elements, the glass forming tendency (GFT) is promoted when anions and cations conform to the 8-N coordination rule of bonding in corresponding crystals. Satisfaction of the 8-N rule in crystals is thought to promote covalently bonded networks in corresponding glasses, and this represents the chemical stability factor. The *lone-pair*

chemistry of chalcogens promotes in general a low average CN $\simeq 2.4$ in such molecular crystals which possess either a chain-like (quasi 1-d) or layer-like (quasi 2-d) morphology. J.C. Phillips and M.F. Thorpe recently recognized[2] that in covalently bonded networks when <CN> $\simeq 2.4$, such networks are optimally constrained in a mechanical sense. The threshold <CN>=2.4 leads to mechanical stability of glassy networks. These considerations permit one to understand why in the $As_x(S$ or $Se)_{1-x}$ binary the mechanical and chemical stability is optimized at x=2/5 leading to an exceptional GFT at this composition even though there exists a crystalline compound of exactly the same stoichiometry.

The origin of GFT has been a subject of several discussions for the past fifty years. Broadly speaking two opposed explanations have attracted wide support: the microcrystalline model based on crystal-like large molecular clusters and a stochastic model based on a random network or random-packing model. Recent experimental evidence[3] in a variety of chalcogenide glasses appears to support models based on molecular clusters. In the present work we shall review some of this evidence particularly for group IV diselenides.

CRYSTAL STRUCTURES OF $SiSe_2$, $GeSe_2$ and $SnSe_2$ and GLASS FORMING TENDENCY

The correlation between crystal morphology and GFT as a function of cation mass in the group IV diselenides provides an interesting trend. Table 1 and Figure 1 lists some of the relevant data.

$SiSe_2$

The ambient pressure polymorph of crystalline $SiSe_2$ possesses a quasi 1-d molecular structure[4] consisting of infinitely long chains of edge-sharing (ES) $Si(Se_{1/2})_4$ 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[4] have noted that in this structure the intrachain and interchain non-bonding Se-Se contacts are characterized by nearly the same length. $SiSe_2$ melts at $970^{\circ}C$ into a rather viscous liquid which readily yields a bulk glass upon water quenching.

β-$GeSe_2$

The high-temperature polymorph of (β-) $GeSe_2$ consists of a layered structure[5]. In a given layer both corner-sharing (CS) and ES tetrahedra occur in

Table I.   Glass (T_g), Crystallization (T_x), and Melting (T_m)
Temperature of Indicated Materials

Group IV diselenide	<CN>	Molecular Structure and Morphology	Glass Forming Tendency
$SiSe_2$	2.66	chains of ES tetrahedra; 1-d	high; T_g=460°C T_x=600°C; T_m=970°C
β-$GeSe_2$	2.66	layers of CS and ES tetrahedra; 2-d	high; T_g=425°C T_x=480°C; T_m=735°C
$SnSe_2$	4.0	layers of octahedral $Sn(Se_{1/3})_6$ units; 2-d	poor $T_x \approx$200°C; T_m=675°C

the ratio 2:1. One may visualize the layers (Fig. 1b) to consist of chains of CS tetrahedra which are laterally cross-linked by a pair of ES tetrahedra, with the arrangement looking much like a step-ladder. The inter-layer separation is determined by the non-bonding Se-Se contacts mediated by Van der Waal's forces. The GFT in binary Ge_xSe_{1-x} melts has been extensively studied and reveals that bulk glasses are readily formed by water quenching over a wide Ge concentration 0<x<0.43 including the stoichiometric composition x=1/3, at which the glass transition temperature $T_g(x)$ exhibits a local maximum[6].

SnSe_2

SnSe_2 is an indirect band gap semiconductor and possesses a close-packed layered structure[7] based on CdI_2. In this structure cations and anions possess a CN=6 and 3 as shown in Figure 1c. $SnSe_2$ melts at 675°C and attempts to supercool such melts by a water quench have invariably produced the crystal rather than a glass. However, we have succeeded[8] in preparing amorphous thin-films of $SnSe_2$ by RF diode sputtering onto Al substrates held near room temperature. Molecular structure of such films has been probed[8] in optical absorption edge, Raman scattering and Mossbauer spectroscopy experiments. Results of some of these experiments will be discussed in the next section.

MOLECULAR STRUCTURE OF GROUP IV DISELENIDES

SiSe_2

Gladden and Elliot[9] have recently generated computer models of $SiSe_2$ glass to explain the structure factor recorded by R.W. Johnson[10] et al. in inelastic neutron scattering experiments. The algorithm for computer generating

FIGURE 1a taken from ref. 9 shows a fragment of ES $Si(Se_{1/2})_4$ units in the crystal (left) and fragment of cross-linked chain cluster (right). The filled circles represent Si atoms.

(a)

(b)
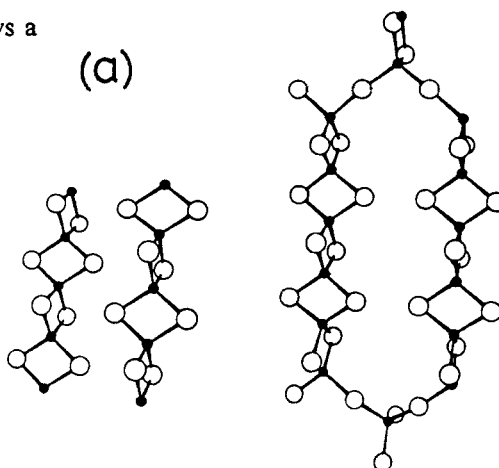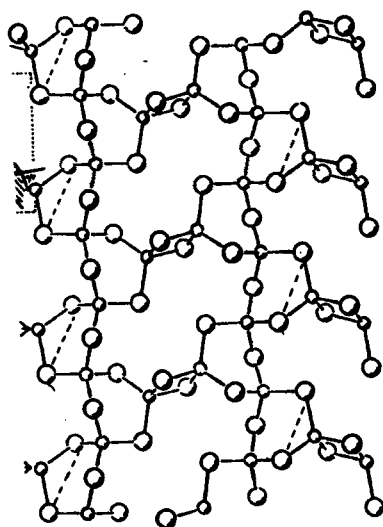
FIGURE 1b shows a layer of β-$GeSe_2$. It consists of chains of CS $(GeSe_{1/2})_4$ units crosslinked by a pair of ES units. In the glass the edges of this fragment are reconstructed to have Se-Se dimers as shown by the broken lines.
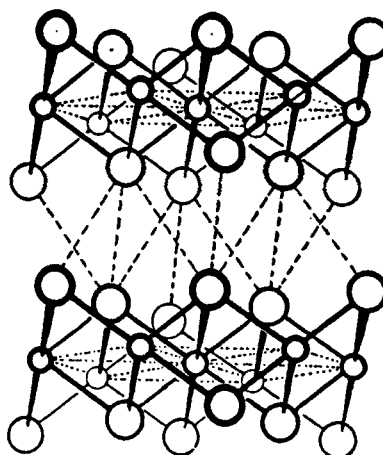
(c)

FIGURE 1c shows closed-packed structure of $SnSe_2$ in which Sn (small atom) possesses a CN=6 while Se (large atom) a CN=3.

specific models of $SiSe_2$ glass consisted of starting from various seeds such as random chain seeds, locally parallel seeds and microcyrstalline seeds. A 1200 atom assembly packed at the observed glass density was generated. The structure factor of various computer generated models was compared to the neutron structure factor. This analysis clearly reveals that a purely continuous random network or a purely microcrystallite based model is inappropriate to describe the structure of $SiSe_2$ glass. On the other hand molecular fragments based on ES chains of $Si(Se_{1/2})_4$ tetrahedra some of which are present in a configuration as found in the crystal and others as found in a cross-linked chain cluster[11] (CLCC) can account for the principal features of the neutron structure factor rather well.

Historically, Raman scattering experiments of Tenhover et al.[12] and independently Griffiths et al.[11] were one of the first to probe the molecular structure of $SiSe_2$ glass. Upon contrasting the glass and crystal vibrational modes in the bond-stretching regime (figure 2), it becomes clear that the sharp modes at $245cm^{-1}$ and $205cm^{-1}$ observed in the crystal spectrum have analogues in the glass spectrum, while modes at $234cm^{-1}$ and $218cm^{-1}$ in the glass have no counterparts in the crystal. These results led Griffiths et al.[11] to propose a CLCC model of $SiSe_2$ glass in which the $234cm^{-1}$ and $218cm^{-1}$ modes are identified with CS tetrahedra that cross-link ES tetrahedral chains.

Recently Enzweiler et al.[13] have performed Mossbauer spectroscopy experiments on $SiSe_2$ using both ^{125}Te and $^{129}Te^m$ as a tracer. In these experiments one probes the anion site chemistry by replacing available Se sites of the network by isovalent Te atoms. The results show that although one type of a Te site is populated in the crystal, two types of Te sites occur in the glass. Comparison of the nuclear hyperfine structure of the majority site in the glass and the crystal site lead to the conclusion that in the glass network, Te dopant prefers replacing Se bridging sites at the more flexible CS tetrahedra in contrast to replacing the more constrained Se bridging sites of ES tetrahedra in the crystal. The picture emerging from all these results appears to be one where the glass network predominantly consists of ES tetrahedral chains which are cross-linked by CS tetrahedra. The latter may be viewed as topological defects of the glass network.

$GeSe_2$

Two recent articles on the molecular structure of $GeSe_2$ glass have

appeared somewhat coincidently in the same book. One of these by Lucovsky[14] emphasizes the stochastic model based largely on a continuous random network of $Ge(Se_{1/2})_4$ tetrahedra. The discussion is largely based on an improved Bethe-Lattice formalism to rationalize the observed Raman vibrational modes. The other article by Boolchand[15] discusses new Mossbauer and Raman scattering results on pseudobinary glasses where the role of composition on the evolution of bond and site distributions is systematically analysed. The latter experimental results decisively favor a model of $GeSe_2$ glass based on the principle of broken chemical order.

Specifically the glass network is pictured as composed of two types (A,B) of molecular clusters: a layer-like large molecular cluster (A) based on β-$GeSe_2$ whose edges are dressed by Se-dimers and a compensating Ge-rich chain-like molecular cluster (B) composed of ethane-like Ge_2Se_6 units. The A and B clusters are easily discriminated in ^{119}Sn Mossbauer spectroscopy largely because of two reasons. First the isovalent Sn atom as a dilute impurity in the glass replaces available Ge sites in the network randomly. Second the local symmetry of cations in the A-cluster is tetrahedral, but becomes trigonal in the B-cluster and this leads to widely different nuclear hyperfine structures for the two sites. Figure 3 depicts the compositional variation of the different molecular clusters (A, B and C) in binary Ge_xSe_{1-x} and Ge_xS_{1-x} glasses deduced from deconvoluting ^{119}Sn Mossbauer spectra of the glasses. The C-cluster is thought to represent a fragment of a distorted rocksalt phase based on the layered structure of c-GeS and c-GeSe as discussed elsewhere[16]. This phase diagram also provides a convenient basis to understand not only the compositional variation of Raman vibrational mode strengths in binary (Ge-S and Ge-Se) and ternary (Ge-Sn-Se_2) glasses, but also the photo- induced reversible reconstruction of $GeSe_2$ glass network documented by Griffiths et al.[17] and the cryobaric Raman measurements on GeS_2 of Weinstein et al.[18] The so called A_1 companion-line observed at $215cm^{-1}$ is identified as a cluster-edge mode of CS tetrahedra associated with broken chemical order as substantiated by Murase[19] and Stevens[21] but not as a mode of chemically ordered ES tetrahedra as suggested by Sugai[19].

An important aspect of the Figure 3 phase diagram[16] is the degree of broken chemical order $I_B/I \simeq 0.16(1)$ for $GeSe_2$ glass which leads to an A
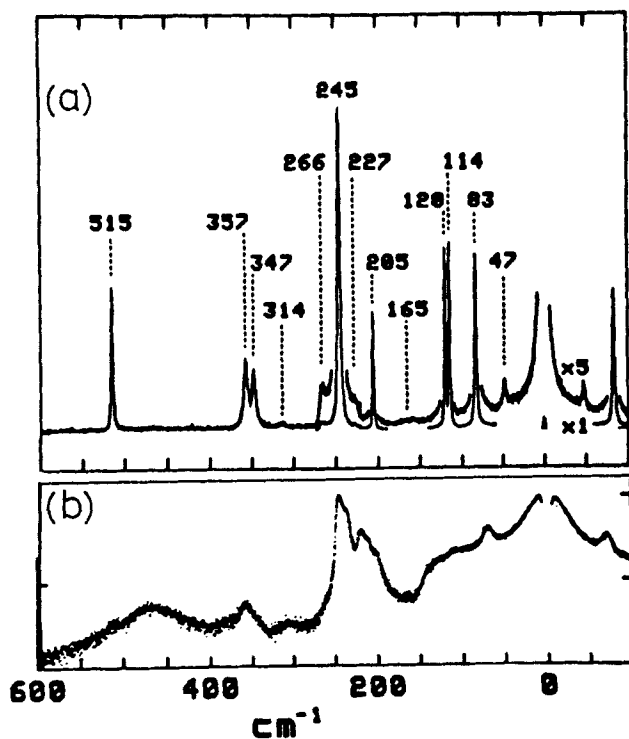
FIGURE 2. Raman scattering in crystalline (a) and glassy (b) $SiSe_2$ taken from ref. 11 shows bond-stretching modes at $245 cm^{-1}$ and $205 cm^{-1}$ in the crystal but modes at $245 cm^{-1}$, $234 cm^{-1}$, $218 cm^{-1}$ and $205 cm^{-1}$ in the glass.

FIGURE 3. Molecular Phase Diagram of binary Ge_xS_{1-x} (top) Ge_xSe_{1-x} (bottom) glasses as a function of Ge concentration x showing presence of A, B and C molecular clusters. This figure is taken from ref. 16.
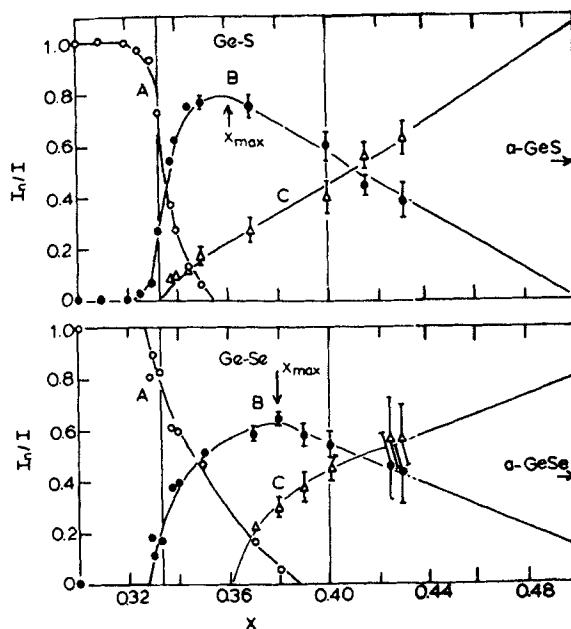
cluster size dimension of 50 to 75Å in lateral width. Remarkably, ^{129}I
Mossbauer emission spectroscopy[20] experiments quantitatively lead to the same
degree of broken anion site chemical order in GeSe$_2$ glass. In the latter
experiments analysis of the results is compounded by the fact that Te site
selectivity for the Se-edge versus Se-interior sites in the A cluster has to be
included[15]. The B-molecular phase is unstable in corresponding crystals. Its
presence in the stoichiometric glass acts to promote GFT by suppressing
crystallization.

SnSe$_2$

RF sputtered amorphous thin-films of SnSe$_2$ crystallize near $T_x \simeq 200^\circ$C
which can be tracked in ^{119}Sn Mossbauer spectroscopy and Raman scattering
experiments as shown in figure 4 and 5. In the Mossbauer spectra (figure 4) the
isomer-shift of the main absorption at $\delta = 1.56$ mm/s suddenly shifts to $\delta = 1.35$
mm/s upon crystallization. We identify this result with a change in Sn CN from
4 in the amorphous film to 6 in the crystalline state. The shift $\delta = 1.56$ mm/s is
characteristic of Sn as an impurity in g-GeSe$_2$ or g-Ge$_{1-x}$Sn$_x$Se$_2$ alloys[21], and
it is identified[15] with a Sn atom present in a tetrahedral Sn(Se$_{1/2}$)$_4$ unit. In
Raman scattering the strong (polarized) band at 182.5cm^{-1} in the amorphous
film represents an A$_1$ symmetric stretch of Sn(Se$_{1/2}$)$_4$ units. This identification
is inferred from our previous work[21] on g- Ge$_{1-x}$Sn$_x$Se$_2$ alloys, where the A$_1$
mode of GeSe$_2$ glass (x=0) at 202cm^{-1} progressively red-shifts as a function of
SnSe$_2$ alloying. The 182.5cm^{-1} band is replaced by a sharp and narrow mode at
186cm^{-1} characteristic of hexagonal SnSe$_2$ when the film crystallizes.

It becomes apparent from these spectroscopic results that amorphous
SnSe$_2$ films largely consist of a tetrahedral network of Sn(Se$_{1/2}$)$_4$ units. In g-
Ge$_{1-x}$Sn$_x$Se$_2$ alloys, we had previously noted[21] that an abrupt red-shift of A$_1$
mode frequency occurs near $x \simeq 0.25$. This shift was interpreted as a network
dimensionality change from 2-d like ($x_- 0.25$) to 3-d like ($x_- 0.25$). This
transition appears as a precursor to the realization of a fully chemically ordered
3-d Zachariasen network[21] at $x \simeq 0.35$. On this basis, we speculate that the
network structure of a-SnSe$_2$ films probably consists of CS Sn(Se$_{1/2}$)$_4$
tetrahedra.

Some degree of broken chemical order into Se-rich and Sn-rich regions
appears to be an intrinsic feature of the as deposited amorphous SnSe$_2$ films.
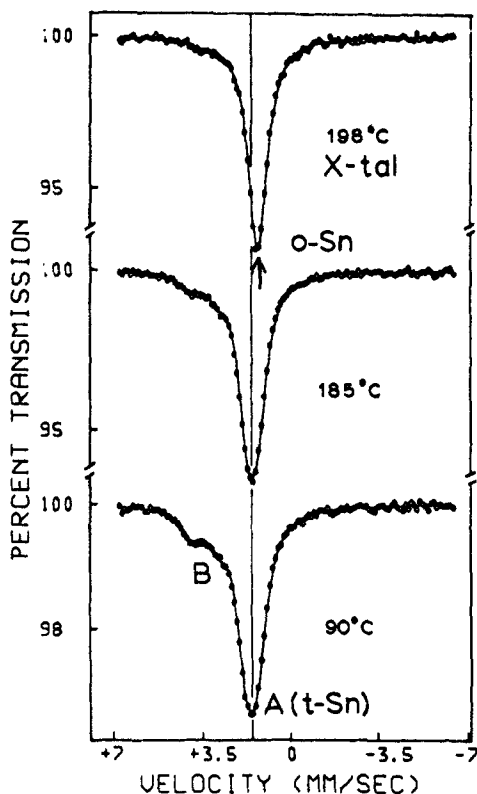The Sn-rich phase probably consists of a microcrystalline SnSe phase and it

FIGURE 4. ^{119}Sn spectra of a-SnSe$_2$
films exhibit a tetrahedral (A)
site and a non-tetrahedral (B) site.
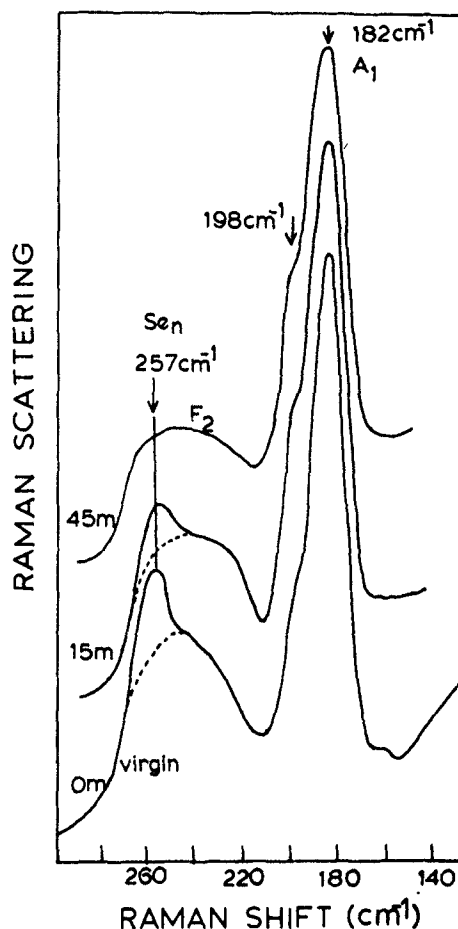Crystallization leads to octahedral
(o) Sn as in c-SnSe$_2$.

FIGURE 5. Room temperature Raman
scattering from a-SnSe$_2$ films
cycled through 180°C show extinc-
tion of the 257cm^{-1} band with
indicated annealing time.

gives rise to a doublet feature having a large positive isomer-shift in the
Mossbauer spectra (Figure 4). The presence of the compensating Se-rich phase
in the films gives rise to additional Raman scattering at 257cm^{-1} which is
usually attributed to a Se-Se stretch in either. Sub-T$_x$ thermal annealing
promotes chemical ordering in the films as the Sn-rich and Se-rich phase
reconstruct. This becomes clear from an increase in the tetrahedral fraction of

the amorphous films upon thermal annealing and a concommitant drop in Raman scattering strength near 257cm^{-1} (Figure 1). Nevertheless a measurable degree of broken chemical order (~10%) persists in the annealed state and appears to act as a barrier against crystallization of the films at $T < T_X$.

CONCLUDING REMARKS

The molecular conformations present in c-SiSe$_2$ and β-GeSe$_2$ and corresponding melt-quenched glasses bear a close relationship to each other and these can be regarded as flexible and low-pressure polymorphs. These molecular clusters are chemically stable and almost optimally constrained and therefore promote glass formation. Hexagonal SnSe$_2$ and amorphous SnSe$_2$ on the other hand, provide examples of two widely different molecular conformations, the former a high-pressure one while the latter a low-pressure one. The high pressure conformation is mechanically rigid and it is the reason why SnSe$_2$ melts are poor glass formers. In the non-crystalline state the tetrahedral networks exhibit a systematic trend consisting predominantly of ES units in a quasi 1-d morphology for SiSe$_2$, a combination of ES and CS units in a quasi 2-d morphology for GeSe$_2$ and primarily of CS units in a quasi 3-d morphology for SnSe$_2$, respectively. The topological defects metastabilizing respective networks appear to be CS tetrahedra in g-SiSe$_2$, homopolar bonds leading to molecular phase separation in g-GeSe$_2$, and Sn-rich and Se-rich nanoclusters dressing the tetrahedral network in a-SnSe$_2$.

ACKNOWLEDGEMENTS

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