Structure 2

✓ Structure of amorphous chalcogens

✓ Structure of some binary ChGs

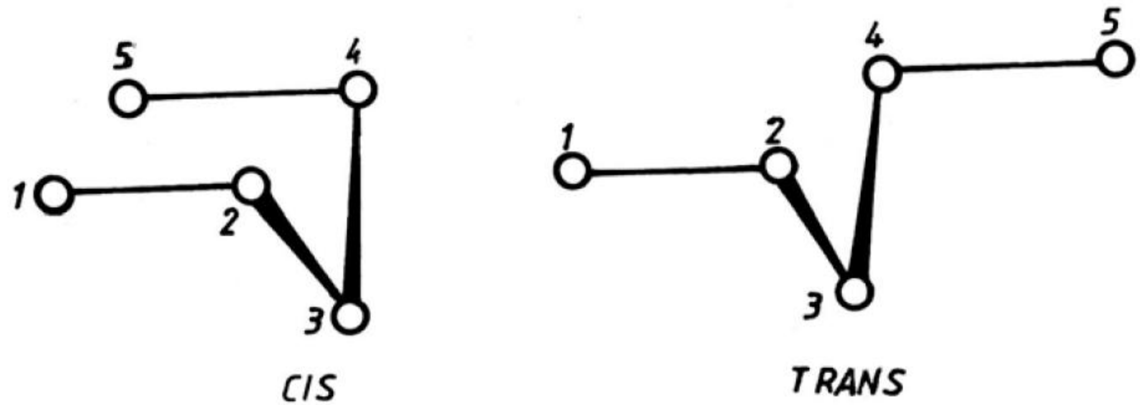
✓ Structure of some ternary ChGs

Sulfur

- The valence electronic shell of sulfur consists of 6 electrons with the disposal $3s^2$, $3p^4$. The sulfur can have the following oxidation states: -2, 0, +2, +3, +4, +5, +6. It is a typical non-metal and its maximum coordination number is 6.

- Sulphur forms di-covalent bonds. It has two unpaired p electrons and can form σ-type bonds. The angle between sulphur bonds is 105°, which is very close to the characteristic angle for the sp^3 hybridization.

- Starting from these bonds it is possible to define two distinct positions in the series of four bonded atoms**: the cis or eclipsed position and the trans or staggered position.**



Popescu book, ch. 1.

Sulfur

- The bonding in the configuration ‘cis’ leads to the formation of ring molecules, i.e., S_6 or S_8, and the ‘trans’ configuration leads to the formation of chain-like molecules.

- The special situation for the two types of configurations appears due to the contribution of the π-bonds between the p-electron pairs on neighboring atoms.

- The ring (crown) molecules S_8 give the most stable structural configuration in the solid state. Other molecules such as S_4 and long chains of atoms can be packed in the solid state of sulfur as well.

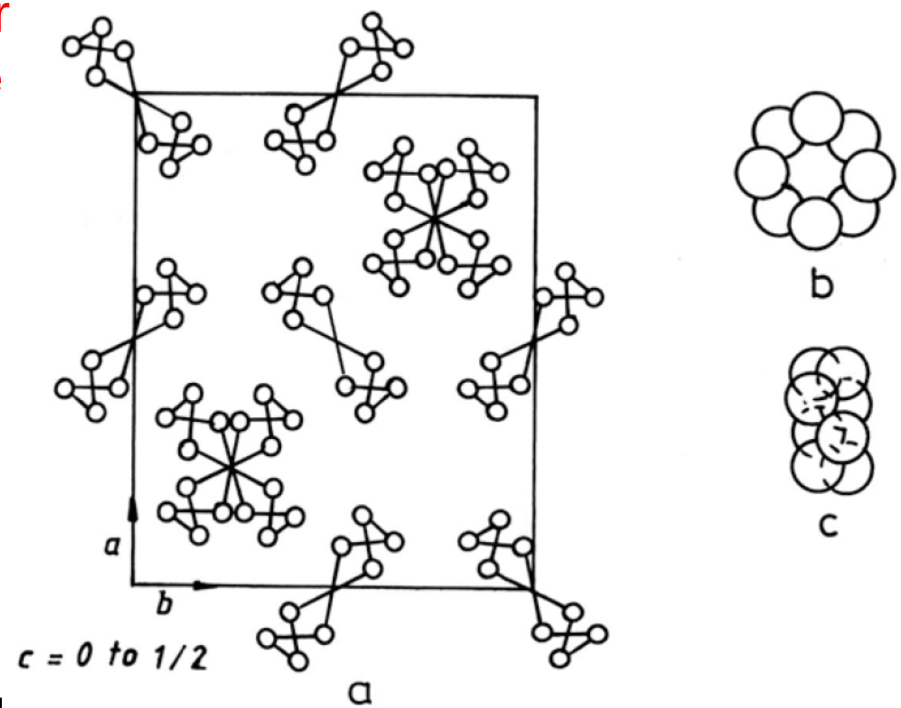


Figure 1.2. The unit cell of the orthorhombic sulphur (S_α).
a the ring packing b, c. front view and side view of the S_8 ring.

Popescu book, ch. 1.

Sulfur

- In liquid and amorphous sulfur the molecules exhibit a tendency towards ordering based on lattice fragments with orthorhombic structure. The molecules interact each other by weak chemical bonds, presumably by Van der Waals bonds.

- Both sulfur rings and chains play an important role for the amorphous state. The rings act as plastifiers in the process of stretching the amorphous plastic sulfur.

- Moreover, they prevent the closer approaching of the chains one to another. On the other hand, the chains prevent the approaching and the ordering of the sulfur rings. In this way, the amorphous, disordered state is stabilized.

Popescu book, ch. 1.

Selenium

- The configuration of the valence electrons of selenium is $4s^4$, $4p^4$. The oxidation states of selenium are -2, 0, +2, +4, +6. The sp^3 hybridization is less stable than in sulfur.

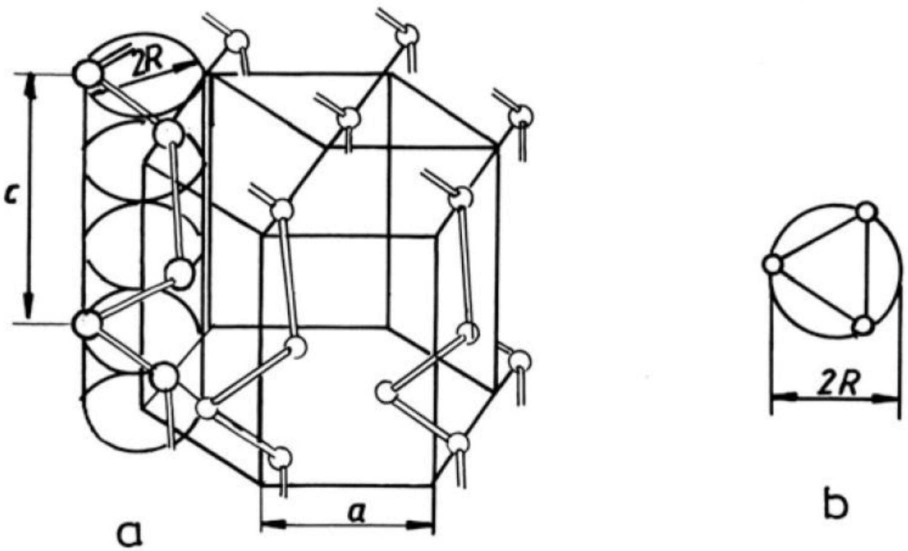


Figure 1.5. The hexagonal selenium **(Se_γ)** a. chain configuration in the unit cell, b. the atom chain (view along the c-axis),

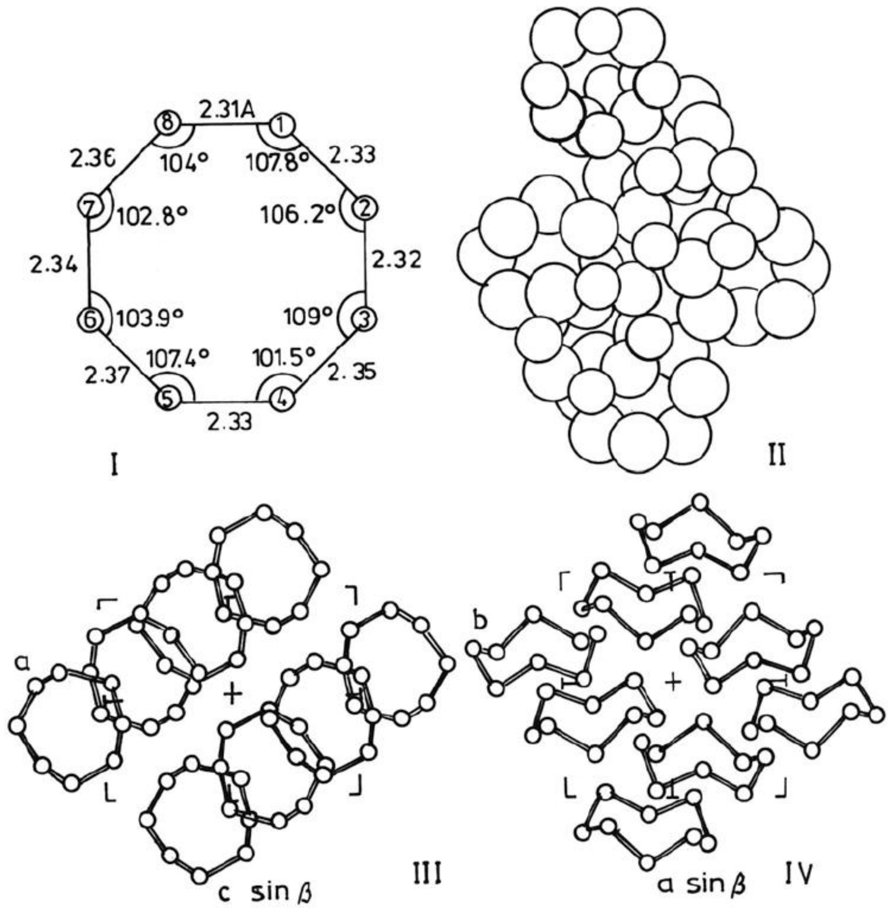


Figure 1.6 a. Monoclinic selenium: **Se_α**. I - **Se_8** ring II - ring packing in the unit cell III – structure projected along the b axis IV - structure projected along the c axis.

Popescu book, ch. 1.

Selenium

- The non-crystalline selenium is a dark-grey solid, which is built from disordered chains and rings of di-covalent selenium atoms.

- The covalent distance, the valence angle, the dihedral angle and the second order distance in non-crystalline selenium seem to be similar to those from the hexagonal selenium crystal.

- The same Van der Waals forces act between the chains. The density deficit of ~10% in the amorphous phases suggests that the packing of the structural units be far from close packing.

- All the amorphous structures of selenium seem to consist of rings and chains, of which ratio is closely dependent on the preparation conditions of the amorphous selenium.

Popescu book, ch. 1.

Tellurium

- The valence shell configuration: $5s^2$, $5s^4$.
- It is a hard solid with metallic character.
- The oxidation states in compounds are +2, +4 and +6.

- Because the cis configuration is not favored in tellurium, it exists as only one crystalline state at normal pressure, called α-tellurium that exhibits hexagonal symmetry and is analogous to the grey selenium.

- The crystal structure of tellurium consists in long spiral atom chains.

- In an ideal molecular crystal with chain structure, the bonds within the chains are purely covalent while those acting between chains are Van der Waals bonds.

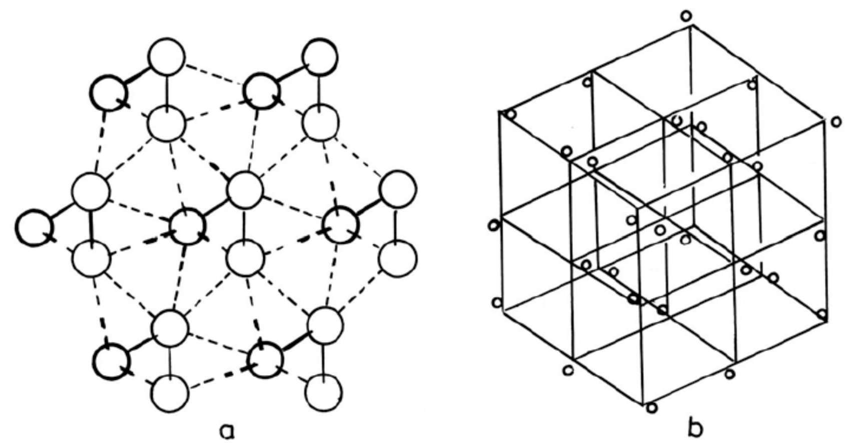


Figure 1.7. a The structure of α-tellurium projected down the c-axis. The bonding distances (solid lines) are 2.834 Å and the interchain distances (dashed lines) are 3.494 Å. b. The same structure shown as a distorted simple cubic structure (after [11]).

Popescu book, ch. 1.

Tellurium

- Tellurium cannot be obtained in glassy state by melt quenching. However, the amorphous state is obtained by evaporation and deposition on solid substrates maintained at very low temperatures.

- In the amorphous state, the inter-atomic bond distance (2.80 A) and the coordination number are lower than in the crystal.

- It was suggested that amorphous tellurium should have a distorted chain structure where the inter-chain bonding is weaker than in the hexagonal tellurium, but the bonds within the chains are longer and nearer to the covalent bond.

Popescu book, ch. 1.

Some structural data of chalcogens

Table 1.2.
Crystallo-chemical data on chalcogens [11,12].

Element	Structure	Average bond length (Å)	Average bond angle (°)	Average dihedral angle (°)	Average intermolecular distance (Å)
Sulphur	S_α	2.039	108.2	90÷100	3.51
	S_β	2.045	107		
	S_ε	2.057	102.2	74.5	3. 515
	S_γ	2.044	106	129	
	Amorphous (plastic)	2.08	106		
	Liquid (supercooled)	2.07			
Selenium	Se_α	2.336±.006	105.7±1.6	101	3.58
	Se_β		105.7±0.3		
	Se_γ	2.373±.005	103.1±0.2	100.6	3.44
	Se-rhombohedral	2.356±.009	101.1±0.3	76.2±0.4	
	Amorphous	2.35	105		3.70
	Liquid	2.38	104		
Tellurium	Te-hexagonal	2.834	103.2±0.1	100	3.494
	Liquid	2.96 2.79±0.1	97		
	Amorphous				

Popescu book, ch. 1.

Physicochemical data of chalcogens

Property	S	Se	Te
Atomic number (Z)	16	34	52
Atomic mass	32.064	78.96	127.60
Electronegativity (Pauling)	2.5	2.4	2.1
Electronic affinity (eV)	2.077	2.022	2
Ionisation energy (eV)	10.360	9.752	9.009
Atomic radius (Å)	0.810	0.918	1.111
Covalent radius (Å)	1.04	1.17	1.37
Ionic radius (ion 2^-) (Å)	1.82	1.93	2.21
Internuclear distance in diatomic molecules (Å)	1.889	2.1659	2.5574
Melting temperature (°C)	112.8 (α) 119.3 (β)	217(α) 429 (β) 494.2 (γ)	449.8 (α)
Boiling temperature (°C)	444.6	685	990±2
Dissociation energy (kJ/mol)	421.33	305.2	259
Electrical conductivity ($\Omega^{-1}cm^{-1}$)	5.26×10^{-18}	$\sim10^{-12}$	~0.02
Thermal conductivity (J/m.s.K)	0.272	0.237	5.85
Density (g/cm^3)	2.069 (α) 1.96 (β) (1.92) (μ)	4.48 (α) 4.46 (β) 4.79 (μ) 4.28; 4.82 (amorph.)	6.22 (hex) 6.00 (amorph.)
Vapour pressure (Torr) at 20 °C	195	354	525.5
Bonding energy (kJ/mol)	266	184	168

Popescu book, ch. 1.

As-S or As-Se

- In the crystalline state As_2S_3 and As_2Se_3 are iso-structural with monoclinic lattice. The structure consists of extended layers of interconnected 12 atom rings. This configuration was proved to be the densest packing possible for the chalcogens atoms linked with arsenic.

- Every arsenic atom has five valence electrons. Three electrons are used for valence bonds with three neighboring chalcogens and the other two electrons form non-bonding orbitals.

- The chalcogen has 6 valence electrons: two are used for bonding with arsenic and the other four electrons form two non-bonding orbitals.

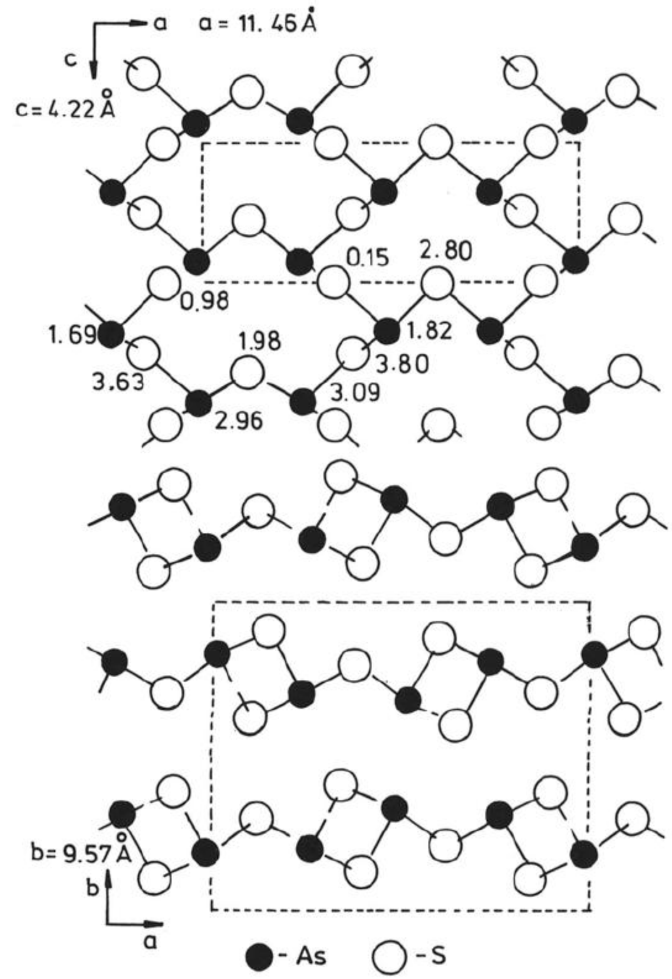


Figure 1.13. The structure of orpiment (As_2S_3) viewed in two projections. (the figures indicate the position of the atoms above the plane of the paper)

Popescu book, ch. 1.

As-S or As-Se

- The arsenic atoms show strong covalent bonds with three chalcogens and the chalcogen with two arsenic atoms.

- The electronegativity difference between arsenic and chalcogens corresponds to a maximum value of the bond ionicity of ~6%.

- The arsenic chalcogenides could be considered as molecular crystals where the molecules are extended to infinite in two spatial directions.

- The interaction forces between layers are hundred times weaker than the binding forces within the layers.

Popescu book, ch. 1.

As-S glass

- As_xS_{1-x} glass is known to form for 0.05 < x < 0.45.
- For low S concentration, the chain fragments and rings are interconnected by As, forming $AsS_{3/2}$ units.
- The higher As content, the shorter the average length of S chains between the $[AsS_3]$ units.

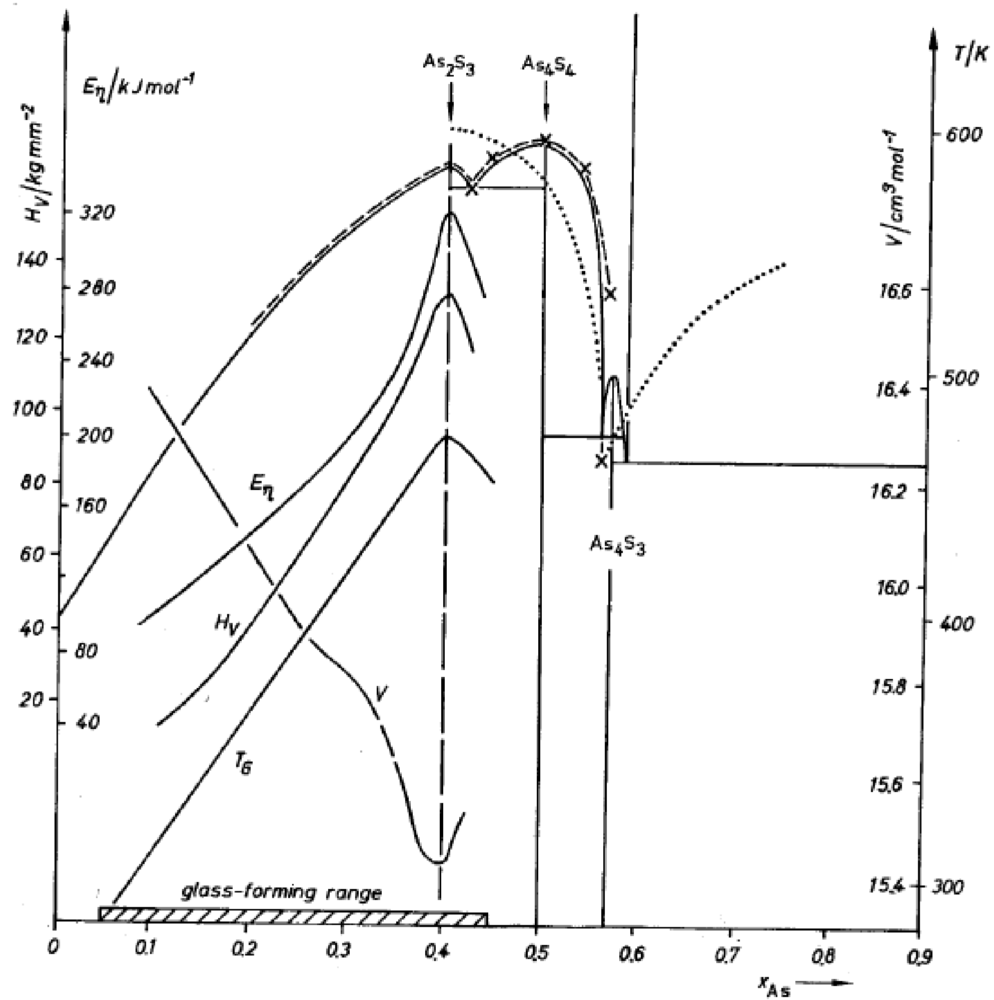


Fig. 3.32. Phase diagram according to [3.363] (full line) and [3.340] (dashed line) showing the range of glass formation in the system As_xS_{1-x}, and dependence of glass transition temperature T_G, activation energy for viscous flow E_η, microhardness H_v, and molar volume V on molar fraction x.

Feltz book, p. 206.

As-S glass

PHYSICAL REVIEW B VOLUME 39, NUMBER 14 15 MAY 1989-I

Chemical order in the glassy As_xS_{1-x} system: An x-ray-absorption spectroscopy study

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(Received 21 October 1988)

We have examined chemical ordering in the glassy As_xS_{1-x} system by determining the effect of composition on the local structure of these chalcogenide glasses using x-ray-absorption spectroscopy. Structural changes associated with composition indicate that with increasing S content, the S-rich glasses on the As site have a similar local structure to crystalline As_2S_3 (orpiment), but the As—S—As linkages are replaced by As—S—S linkages at higher S concentration. In As-rich glasses a breakdown of the local AsS_3 configuration is evident and the formation of As—As bonds is observed. Further comparison between As-rich alloys and crystalline As_4S_4 (realgar) suggests that a significant fraction of disordered As_4S_4 molecular fragments is contained in the As-rich region.

Although As_4S_4 and As_4Se_4 are isostructural, it is remarkable that As_4Se_4 is very stable in the glassy state while As_4S_4 cannot be obtained in the glassy state even by very rapid quenching; only rapid quenching accompanied by high pressure can determine the formation of glass. The domains of glass formation for As-S and As-Se are shown in

* Popescu book, p. 27.

APPLIED PHYSICS LETTERS **91**, 031912 (2007)

AsS: Bulk inorganic molecular-based chalcogenide glass

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(Received 3 May 2007; accepted 22 June 2007; published online 19 July 2007)

The authors have developed a high pressure method to produce bulk chalcogenide glasses of a unique AsS composition. The structure, optical properties, and stability of the obtained glasses have been studied. Glasses have an intrinsic deep-red color, optical pseudogap $E_g \approx 1.75$ eV, a broad Urbach absorption tail $W_U \approx 120$ meV, and high temperature stability up to 130 °C. AsS glasses show photoinduced transformations, including photocrystallization. The glass structure is largely based on the quasimolecular As_4S_4 units with partial polymerization providing an example of an inorganic molecular-based glass. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2759261]

As-Se glass

- Much wider glass forming range of As_xSe_{1-x} glass than the sulfide glass.
- For x < 0.4, glass structure is very similar to that of As-S glass with analogous composition.

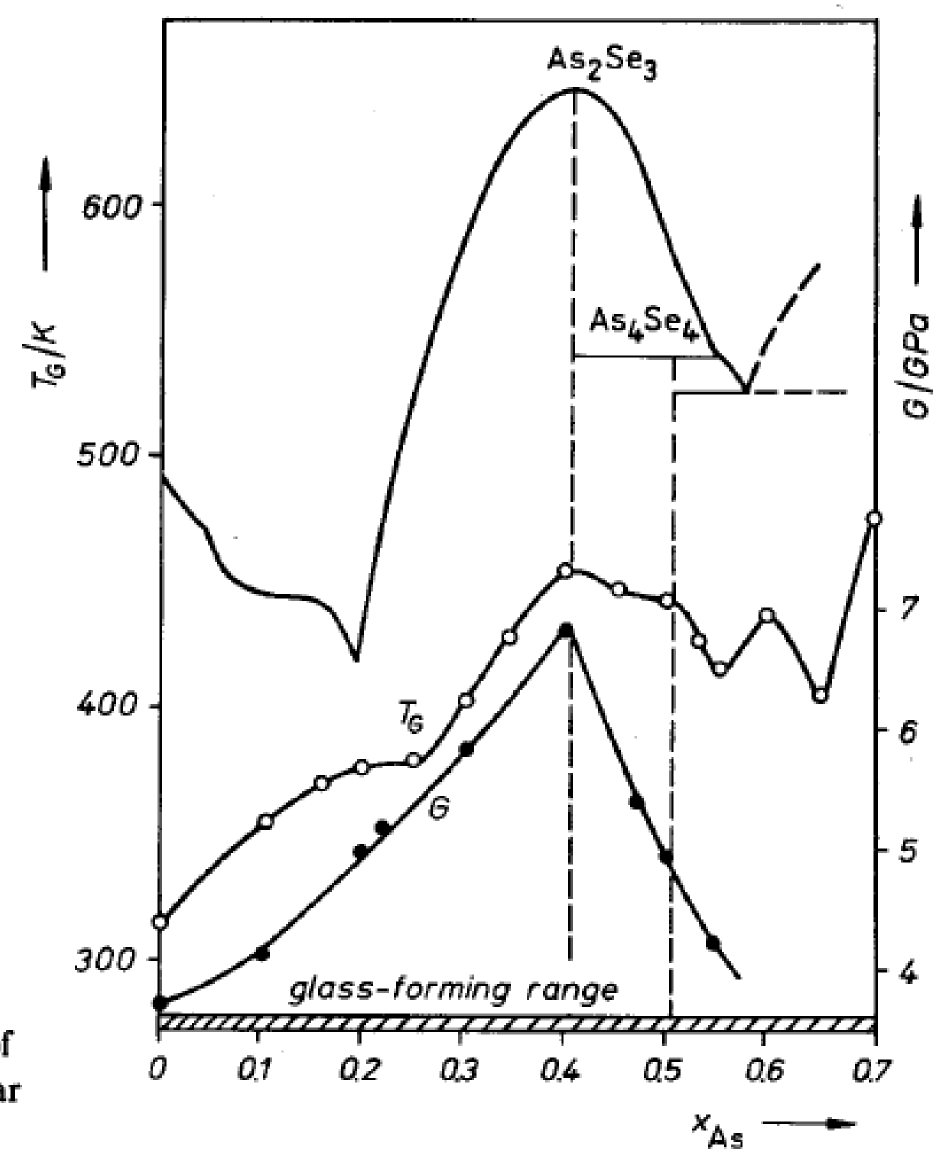
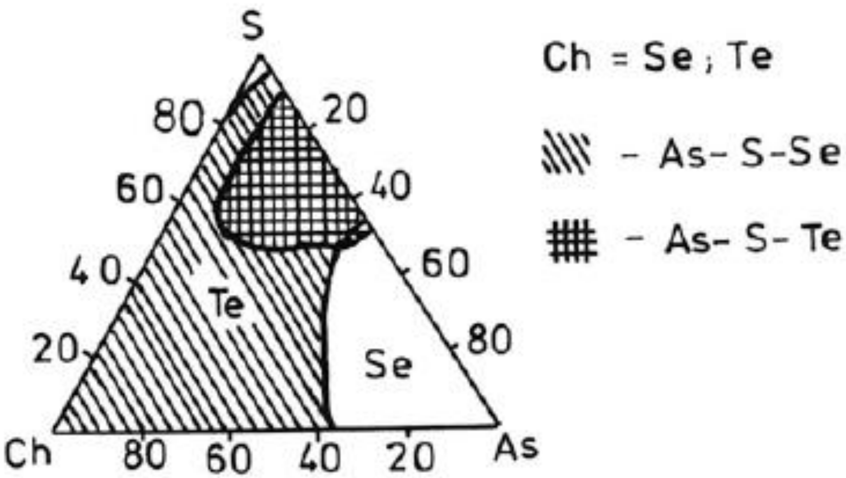


Fig. 3.33. Phase diagram and glasses formation range in the system As_xSe_{1-x}, and dependence of the glass transition temperature T_G (○) and shear modulus G (●) on molar fraction x.

Feltz book, p. 209.

As-S-Se glass



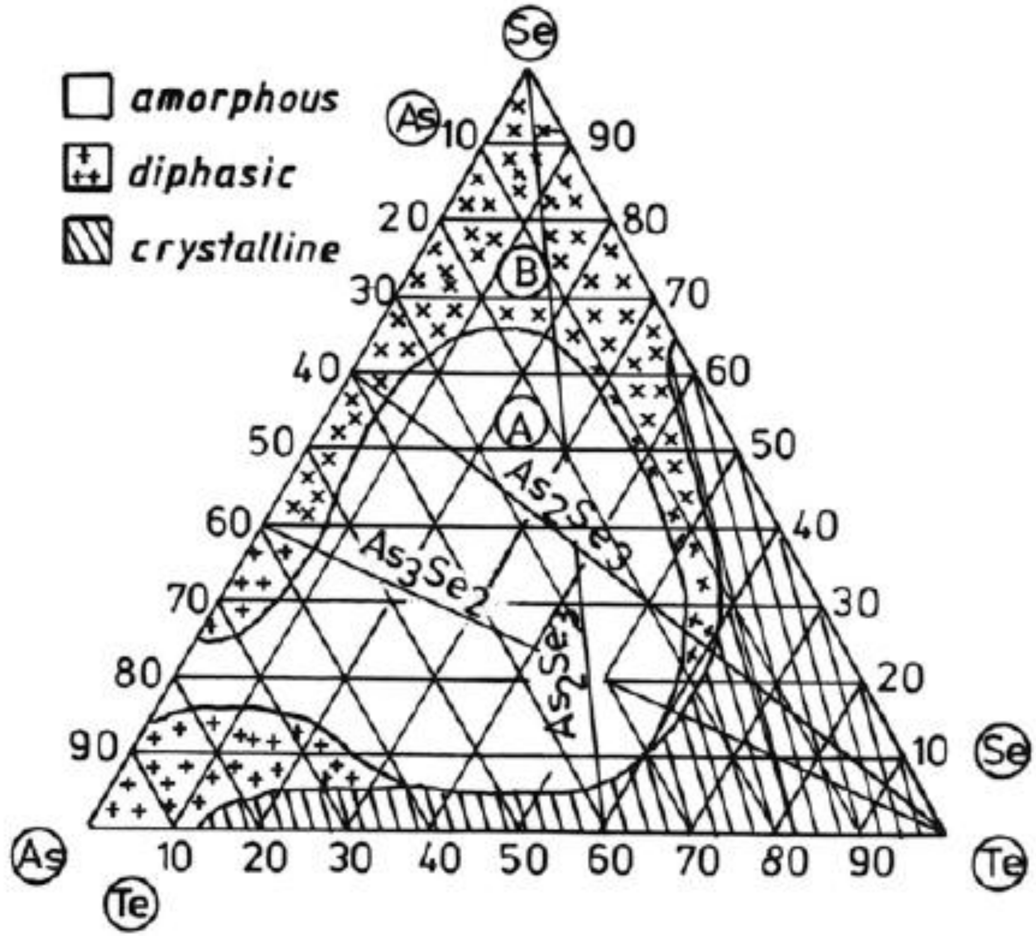


Figure 1.15. The vitrification domains in the system **As-Ch₁-Ch₂**.

Popescu book, ch. 1.

As-S-Se glass

JOURNAL OF APPLIED PHYSICS VOLUME 88, NUMBER 5 1 SEPT

Structural properties of the glass system As–Se–S studied by x-ray absorption spectroscopy

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(Received 4 January 2000; accepted for publication 4 April 2000)

The structural properties of As–Se–S glass system were investigated by x-ray absorption spectroscopy (XANES and EXAFS) using synchrotron radiation. A preliminary characterization by x-ray powder diffraction, differential scanning calorimetric and thermogravimetric measurements was also carried out. The changes in glass transition temperature (T_g) and glass decomposition temperature (T_d) associated with glass compositions indicate that sulfur contributes to the instability of the ternary As–Se–S glass system. The XANES and EXAFS results suggest that arsenic is in trivalent state with approximately threefold coordination and selenium is in approximately twofold coordination in all the glass compositions under study. The homopolar bonding (As–As and Se–Se) has a significant contribution in $AsSe_{1.42}$ glass matrix unlike in $AsS_{1.56}$ glass where homopolar bonding (As–As) is negligible. However, the homopolar bonding (As–As) is increasingly eliminated with increasing replacement of selenium by sulfur in ternary glasses. In addition, the contribution of sulfur to the coordination of arsenic is more dominant than selenium even when glass matrices contain a larger quantity of selenium. Thus the present XANES and EXAFS results demonstrate that the As–Se–S glass system is well represented by the *chemically ordered network model.* [S0021-8979(00)09513-X]

As-Te glass

- As_2Te_3 is the only crystalline form in the system As_xTe_{1-x}.

- The tendency for glass formation is much lower.

- The arrangement of Te atoms in As_2Te_3 is close to haxagonal close packing. The gaps are filled by As atoms with CN of 3 and 6, leading to the formation of ribbons where [$AsTe_6$] and [$AsTe_3$] are connected with each other.

- Vitreous As_2Te_3 forms a continuous random network in which trigonal $AsTe_{3/2}$ units predominate.

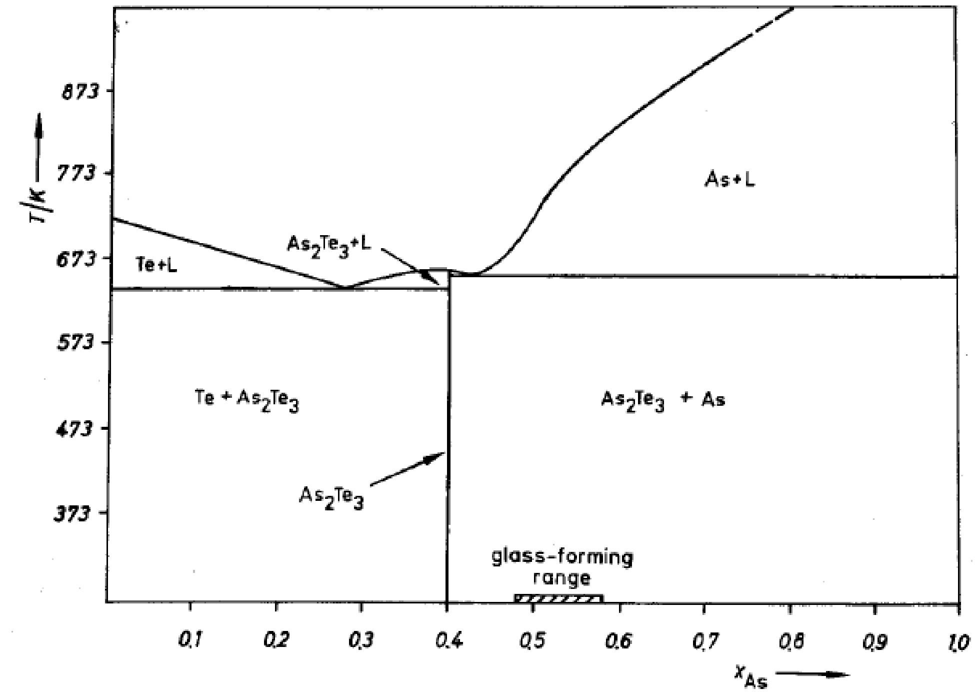


Fig. 3.35. Phase diagram and range of glass formation in the system As_xTe_{1-x}.

Feltz book, p. 213.

Ge-S glass

- $GeS_{4/2}$ units link the sulfur chains in a three-dimensional network.

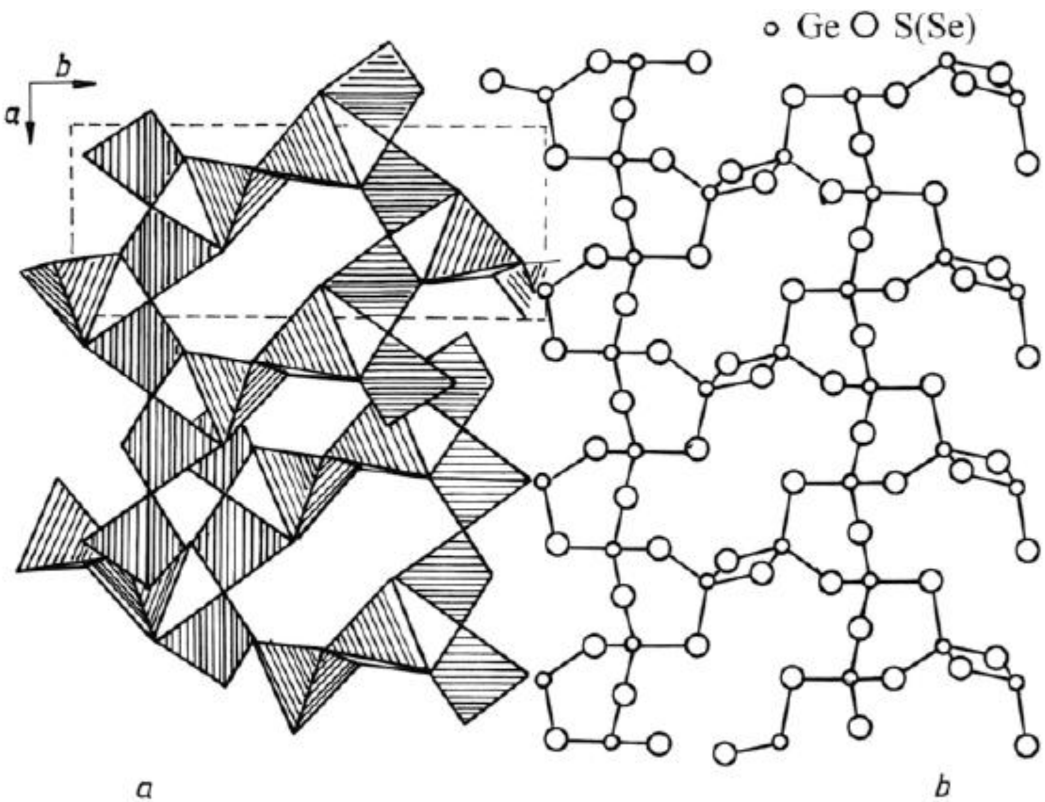
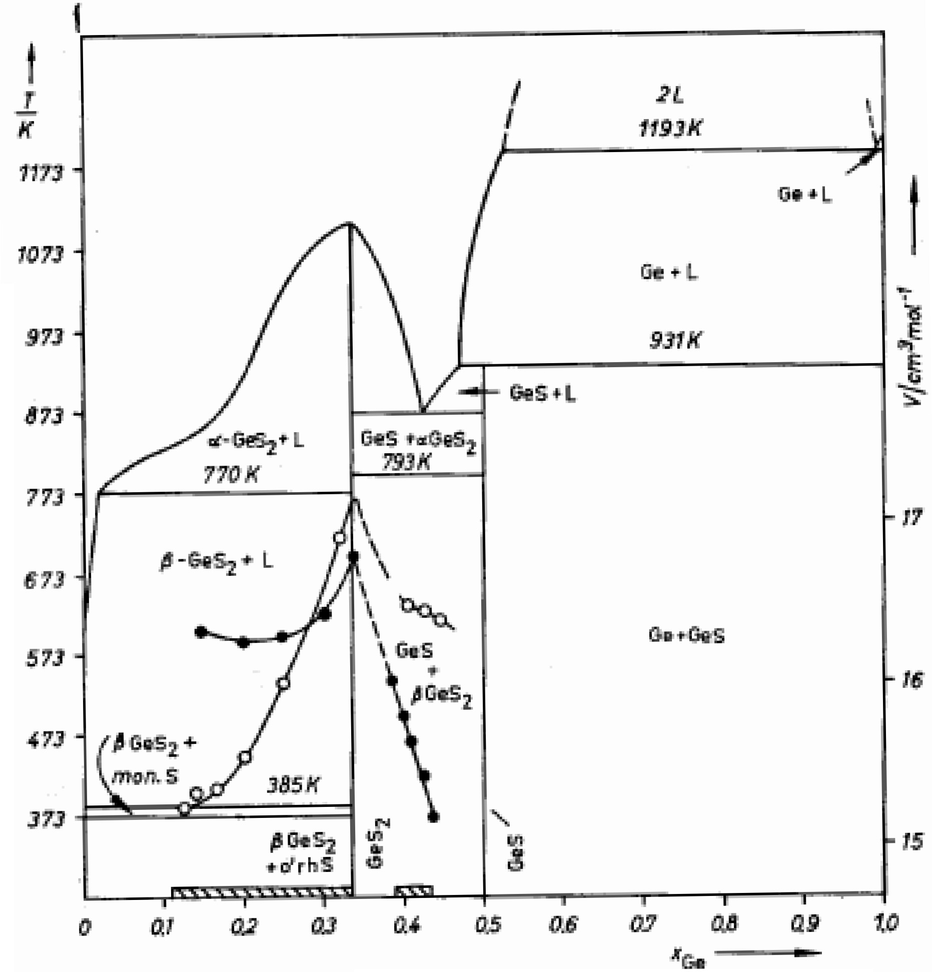


Figure 1.22. The structure of GeS_2 ($GeSe_2$) viewed along the normal to the atom layers, a. the $GeCh_4$ tetrahedron configuration above and below the layer plane, b. the bonding configuration between the atoms of the upper layer.

Popescu book, ch. 1.



Feltz book, p. 224.

Fig. 3.37. Phase diagram and glass formation range in the system Ge_xS_{1-x}. Molar volume V(●) and T_G (○) as functions of mole fraction x.

Ge-Se glass

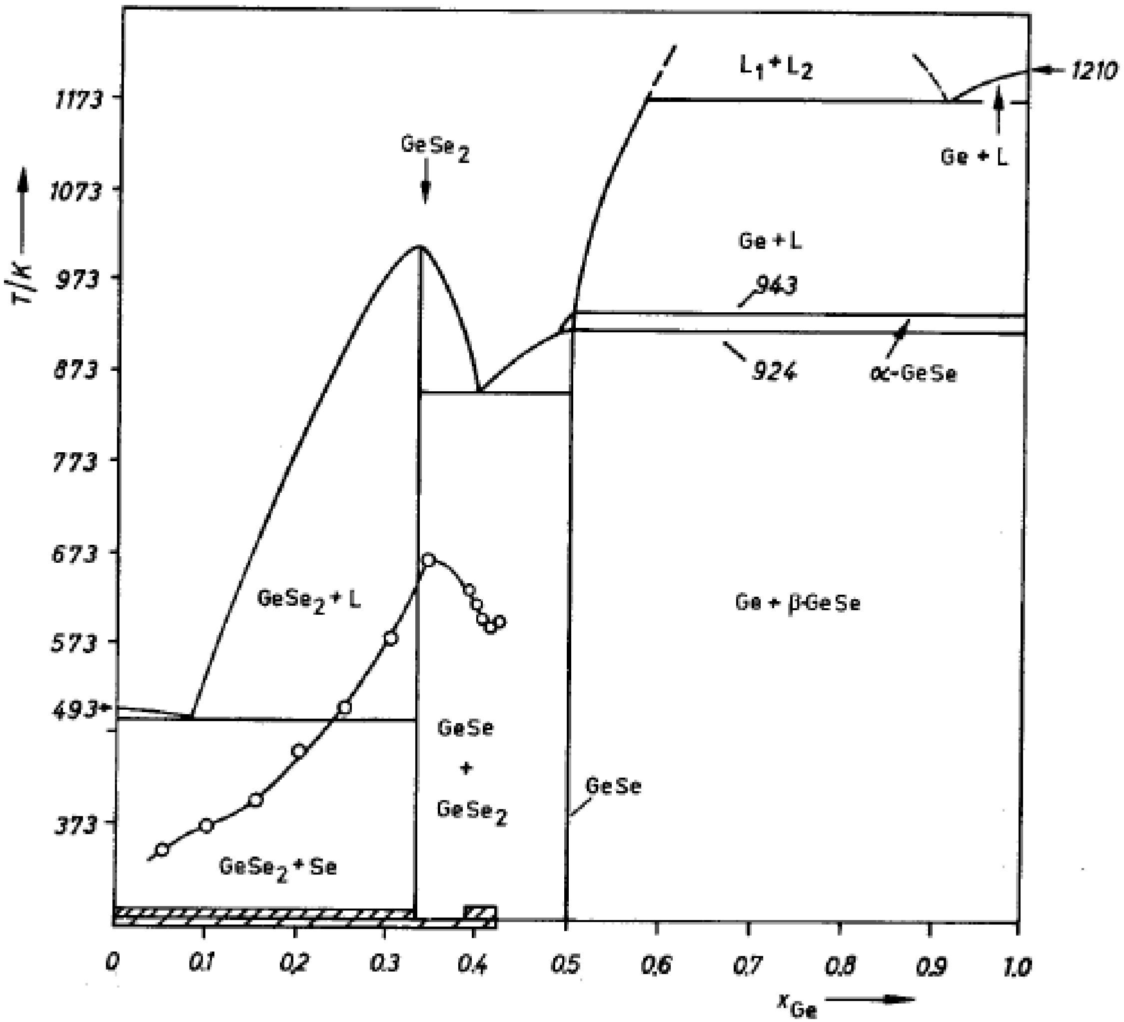


Fig. 3.39. Phase diagram and glass-forming range in the system Ge_xSe_{1-x}, showing T_G values (○) as functions of mole fraction x.

- Two glass-forming ranges are found, namely 0<x<0.33 and 0.388<x<0.417, when batches of >20 g are cooled at 2 K/s.

Feltz book, p. 230.

Ge-Se glass

PHYSICAL REVIEW B VOLUME 43, NUMBER 3 15 JANUARY 1991-II

Structure of germanium-selenium glasses: An x-ray-absorption fine-structure study

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X-ray-absorption fine-structure (XAFS) data in the binary chalcogenide glass system Ge_xSe_{100-x} system are presented and discussed. Phase-corrected Fourier transforms in a curved-wave XAFS simulation formalism are employed in analysis of the data, and near-edge structures are compared for the various compositions studied. Analysis of the XAFS data confirms the presence of chemical ordering. Least-squares-fitting results show that short-range order in the first shell is well preserved throughout the composition range studied. The coordination numbers for germanium and selenium (4 and 2, respectively) are unchanged for the composition $20 \le x \le 40$. For $x \le 33$, there exist stable tetrahedral $Ge(Se_{1/2})_4$ units that are connected by either double or single selenium atoms. For $x > 33$, Ge—Ge bonds appear, and the structure becomes more disordered compared to that of glassy $GeSe_2$.

J. Phys.: Condens. Matter 10 (1998) 1931–1950. Printed in the UK PII: S0953-8984(98)86081-5

Electronic structures and local atomic configurations in amorphous GeSe and GeTe

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For a-GeTe, on the other hand, the situation is not so controversial as it is for a-GeSe. The structural x-ray diffraction studies made by Betts, Bienenstock and Ovshinsky [14] in 1970 revealed that the interatomic distance and the coordination number of a-GeTe are in poor agreement with those of c-GeTe. From detailed analysis of the peak, they concluded that a random covalent model with a 4(Ge):2(Te) local coordination was the most appropriate as a local coordination model for a-GeTe. The later electron diffraction studies [15, 16] obtained similar radial distribution functions. Only the neutron scattering result of [17] suggested a 3(Ge):3(Te)-coordinated local structure due to the small coordination number obtained. The 4(Ge):2(Te)-coordinated structure was also suggested on the basis of an EXAFS measurement around the Ge K edge made by Maeda and Wakagi [18].

Raman scattering and far-infrared absorption spectra for a-GeTe were taken by Fisher, Tauc and Verhelle [19] and were explained in terms of the presence of $GeTe_4$ tetrahedra. Their results strongly supported a random covalent network model of the 4(Ge):2(Te)-coordinated atoms, and excluded the possibility of a c-GeTe microcrystalline structure. Besides the neutron scattering measurement of [17], a 3(Ge):3(Te) local structure of a-GeTe was only supported by the Mössbauer spectrometry of ^{125}Te nuclei performed by Boolchand *et al* [20].

[14] Betts F, Bienenstock A and Ovshinsky S R 1970 *J. Non-Cryst. Solids* **4** 554
[15] Dove D B, Heritage M B, Chopra K L and Bahl S K 1970 *Appl. Phys. Lett.* **16** 138
[16] Uemura O, Sagara Y, Tsushima M, Kamikawa T and Satow T 1979 *J. Non-Cryst. Solids* **33** 71
[17] Pickart S J, Sharma Y P and de Neufville J P 1979 *J. Non-Cryst. Solids* **34** 183
[18] Maeda Y and Wakagi M 1991 *Japan. J. Appl. Phys.* **30** 101
[19] Fisher G B, Tauc J and Verhelle Y 1974 *Amorphous and Liquid Semiconductors* ed J Stuke (London: Taylor and Francis) p 1259
[20] Boolchand P, Triplett B B, Hanna S S and de Neufville J P 1974 *M¨ossbauer Effect Methodology* (New York: Plenum)

Ge-Te glass

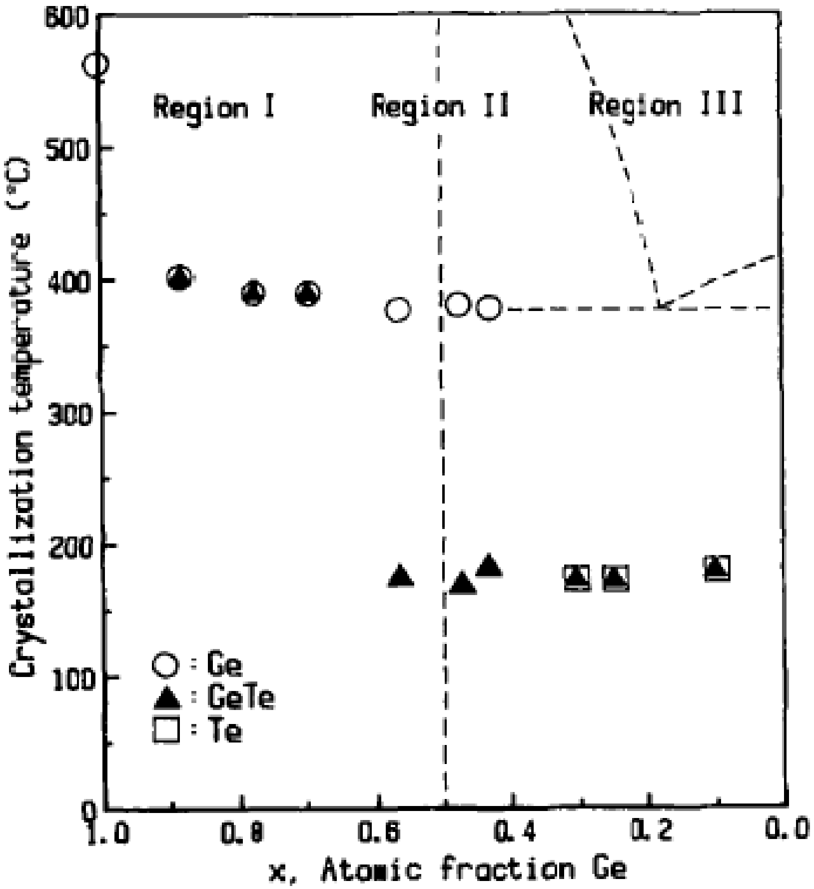

Fig. 4. Compositional dependence of the crystallization temperature T_c. Also indicated in the figure are the crystalline phases, which appeared after each step of the crystallization, and liquidus lines of the phase diagram of the Ge–Te system with dashed lines.

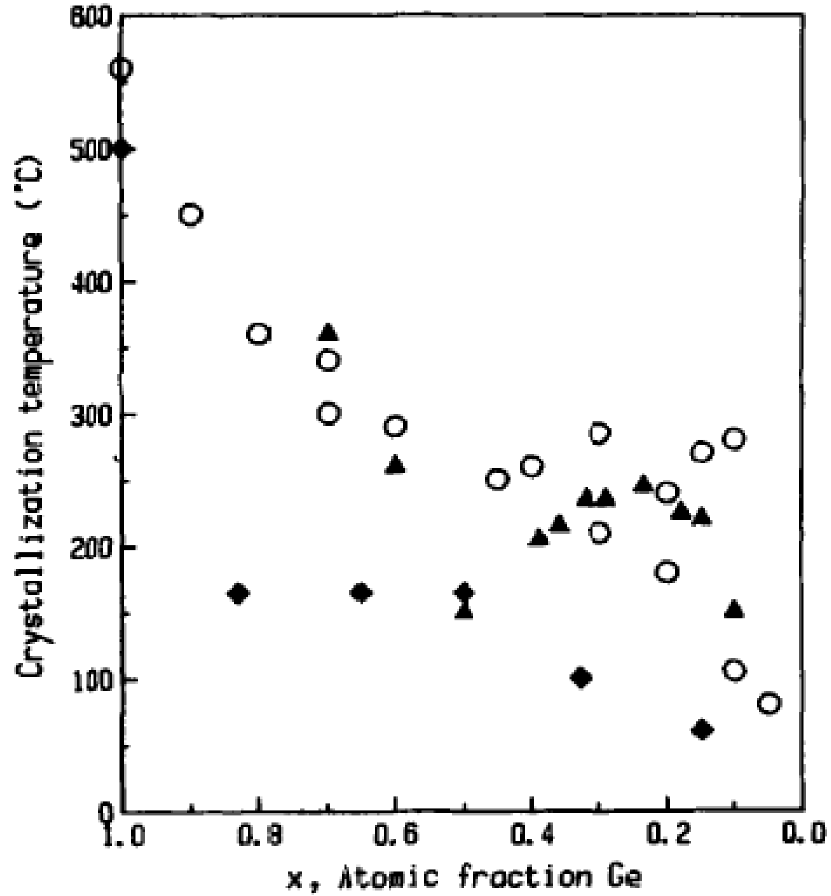

Fig. 5. Compositional dependence of the crystallization temperature, T_c, already reported in the literature by using some other techniques: (○) resistance [9], (▲) calorimetric [11], and (◆) resistivity [8] measurements.

Okabe and Nakagawa, J. Non-Cryst. Solids 88 (1986) 182.

Ge-Te glass

APPLIED PHYSICS LETTERS **95**, 043108 (2009)

Nanosecond switching in GeTe phase change memory cells

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The electrical switching behavior of GeTe-based phase change memory devices is characterized by time resolved experiments. SET pulses with a duration of less than 16 ns are shown to crystallize the material. Depending on the resistance of the RESET state, the minimum SET pulse duration can even be reduced down to 1 ns. This finding is attributed to the increasing impact of crystal growth upon decreasing switchable volume. Using GeTe or materials with similar crystal growth velocities, hence promises nonvolatile phase change memories with dynamic random access memorylike switching speeds. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3191670]

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **17** (2005) 1529–1536 doi:10.1088/0953-8984/17/10/008

Local atomic environment in amorphous $Ge_{15}Te_{85}$

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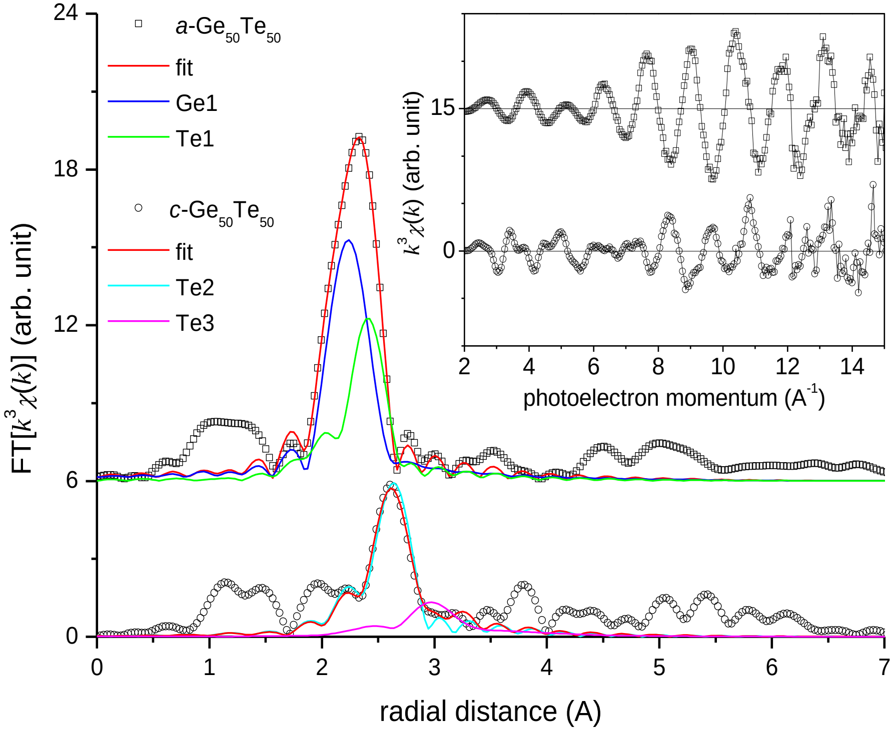
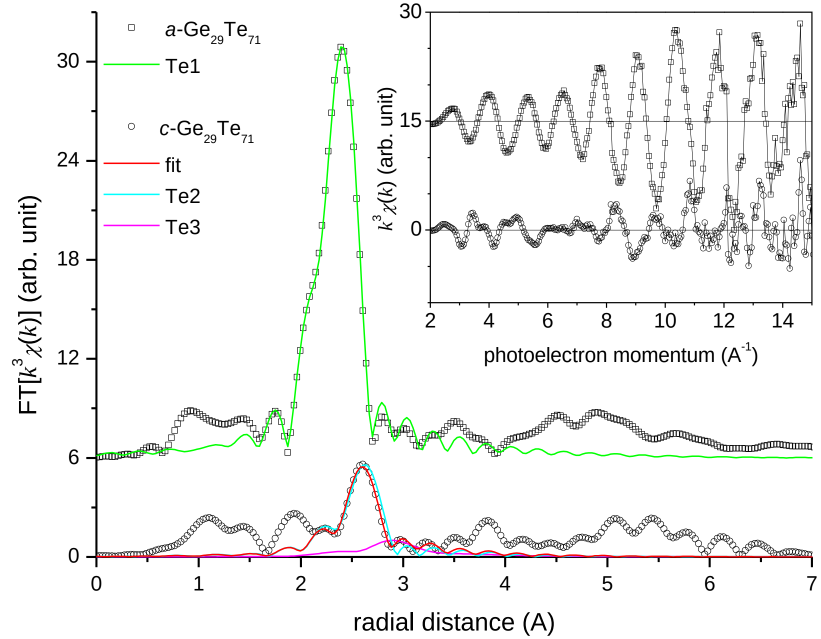
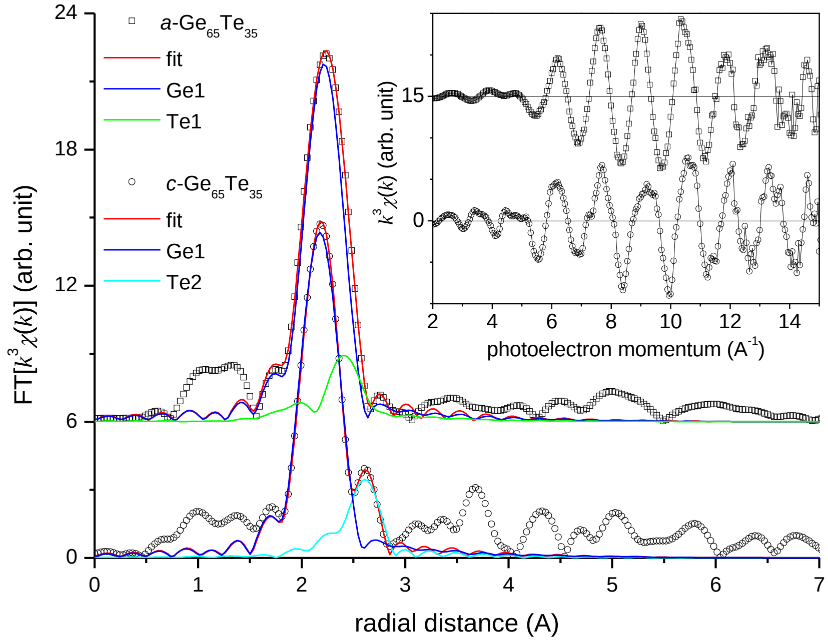
Table 2. Bond lengths r, coordination numbers N and Debye–Waller factors σ in Ge–Te glasses determined by diffraction and EXAFS. In [9, 10] sample compositions are far from $Ge_{15}Te_{85}$; therefore, coordination numbers are not shown.

Method	Reference	r_{GeTe} (Å)	r_{TeTe} (Å)	N_{GeTe}	N_{TeTe}	σ_{GeTe} (Å)	σ_{TeTe} (Å)
ND + XRD	This study	2.62–2.63	2.72–2.74	3.40–3.95	1.62–1.79	0.3	0.3
ND	[5]	2.59	2.76	—	—	—	—
XRD	[6]	2.62(1)	2.78(1)	4.14(2)	1.27(3)	0.11(1)	0.12(1)
EXAFS	[6]	2.605	—	—	—	—	—
EXAFS	[7]	2.60	2.78	3.6	1.2	0.05	0.053
ND	[8]	2.68	—	6.3(4)	—	0.30	—
EXAFS	[16]	2.59/2.61	—	—	—	0.076/0.081	0.063
EXAFS	[17]	2.60	—	—	—	—	—

[5] Kameda Y, Uemura O and Usuki T 1996 *Mater. Trans., JIM* **37** 1655
[6] Uemura O, Hayasaka N, Tokairin S and Usuki T 1996 *J. Non-Cryst. Solids* **205–207** 189
[7] Sakurai M, Kakinuma F, Matsubara E and Suzuki K 2002 *J. Non-Cryst. Solids* **312–314** 585
[8] Ichikawa K, Kameda Y, Xu Q and Misawa M 1987 *J. Non-Cryst. Solids* **95/96** 185
[9] McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359
[10] McGreevy R L 2001 *J. Phys.: Condens. Matter* **13** R877
[17] Hirota K, Nagino K and Ohbayashi G 1997 *J. Appl. Phys.* **82** 65
[18] Kolobov A V, Fons P, Tominaga J, Ankudinov A L, Yannopoulos S N and Andrikopoulos K S 2004 *J. Phys.: Condens. Matter* **16** S5103



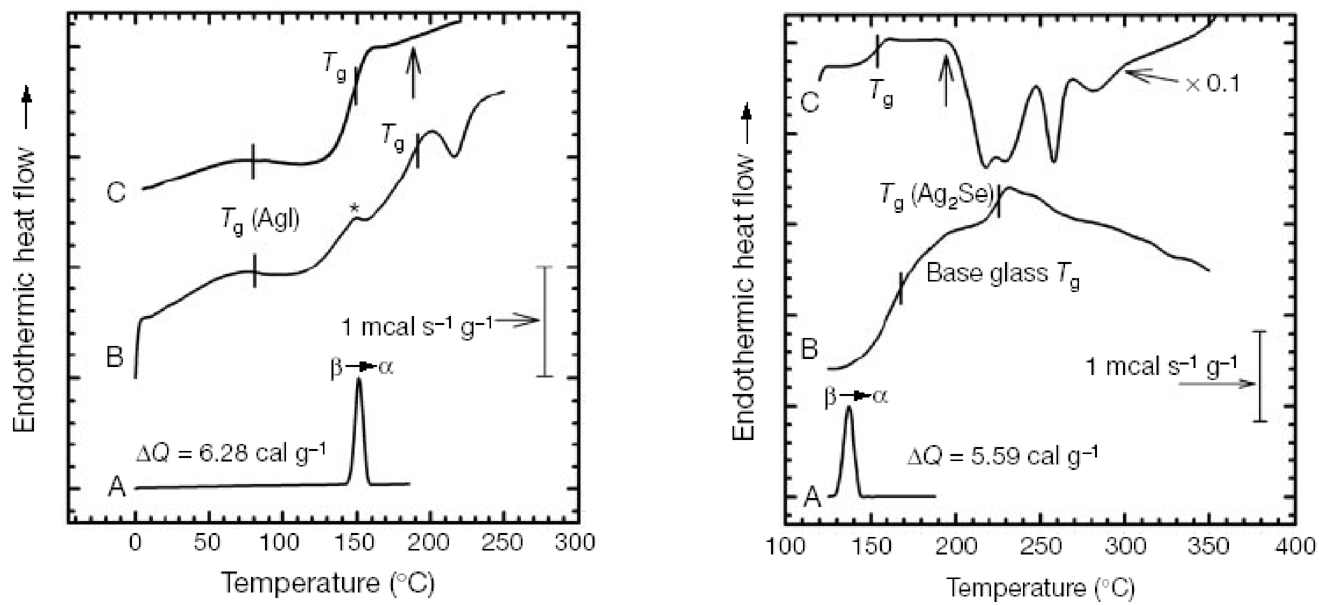




Choi et al, unpublished results.

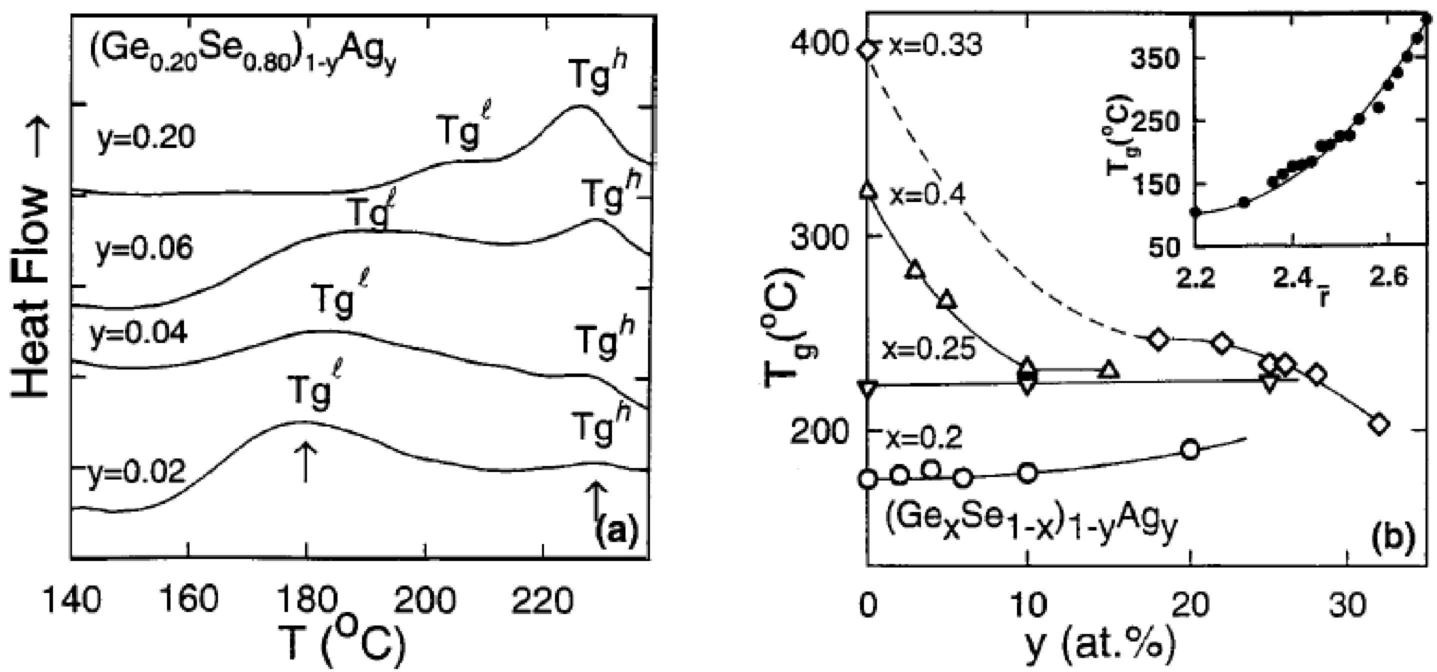
Ag-Se glass

- ✓ AgI or Ag_2Se containing chalcogenide glasses;
  - ➢ High ionic conductivity up to ~10^{-1} $ohm^{-1}cm^{-1}$ at RT
  - ➢ $(AgI \text{ or } Ag_2Se)_x(GeSe_4 \text{ or } As_2Se_3)_{1-x}$ glasses exhibit two distinct types of molecular structures- intrinsic phase separation and microscopically homogeneous network.



❖ P. Boolchand and W. J. Bressor, Nature 410 (2001) 1070.

- ✓ AgI or Ag_2Se containing chalcogenide glasses;
  - ➢ Ternary $(Ge_xSe_{1-x})_{1-y}Ag_y$ bulk glasses in the Se-rich region (x<0.33) are shown to be intrinsically *phase separated* with Ag acting as a *network modifier.* The glasses are FICs.
  - ➢ In contrast, Ge-rich glasses (x>0.4) are homogeneous, wherein Ag acts as a *network former.* These are semiconductors.



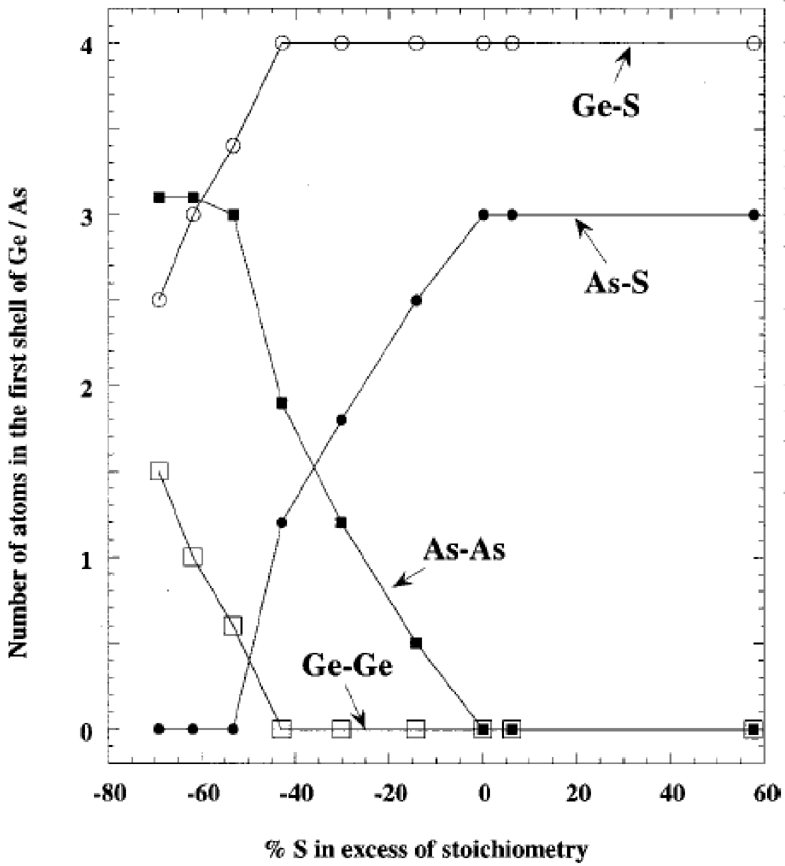
❖ M. Mitkova et al, Phys. Rev. Lett. 83[9] (1999) 3848.

Ge-As-S glass

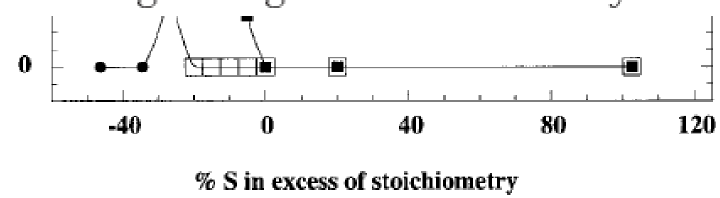
✓ One of the strong covalent ChGs

✓ Group 4 and 5 elements together with S and (or) Se

- ➢ Ge, Si, As, Sb, and so on
- ➢ Obeys the 8-*N* rule



S-deficient Ge-As-S glasses on the other hand, show formation of metal-metal homopolar bonds that are exclusively between As atoms, especially at low and intermediate S deficiencies. Ge atoms take part in metal-metal bonding only at intermediate to high levels of S deficiency. Such clustering of like atoms and violation of chemical order has been argued to result in topological changes of the intermediate-range structural units in ternary Ge-As-S glasses as a function of composition. These structural and topological changes are likely to result in extrema in the compositional variation of the relevant physical properties of these materials at non-unique composition-dependent $\langle r \rangle$ values. This scenario renders the concept of a universal, single $\langle r \rangle$ value ($\langle r \rangle = 2.4$)-based rigidity transition untenable, at least in the case of chalcogenide glasses in the ternary Ge-As-S system.



- S. Sen et al, Phys. Rev. B64 (2001) 104202.

Ge-As-S glass

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Section 1. Glass structure

GeAs sulfide glasses with unusually low network connectivity

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Available online 9 September 2004

Abstract

As-rich, S-deficient GeAsS glasses with compositions ranging from 1% to 15% Ge, 40% to 59% As and 35% to 47% S were synthesized. Within this field, glasses with Ge content ⩽5% were found to have physical properties that resemble those of organic polymers, including low glass transition temperature (⩽50 °C) and unusually high thermal expansion coefficient (~100 ppm/°C). Raman spectroscopy has revealed that their structure is dominated by molecular As_4S_3 species. Despite their high nominal average coordination number, these materials are good examples of zero-dimensional network glasses, as the constituent As_4S_3 clusters clearly do not contribute towards network connectivity. To rationalize the properties of these inorganic molecular glasses with predictions based on constraint-counting theory, the usual procedure for calculating $\langle r \rangle$ must be modified in order to account for the presence of such molecular species.

Ge-As-S(Se) glass

PHYSICAL REVIEW B **66**, 134204 (2002)

Atomic structure and chemical order in Ge-As selenide and sulfoselenide glasses: An x-ray absorption fine structure spectroscopic study

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(Received 28 May 2002; published 11 October 2002)

The nearest-neighbor coordination environments of Ge and As atoms in $Ge_xAs_ySe_{1-x-y}$ glasses with $x:y = 1:2$ and 1:1 and in $Ge_{0.154}As_{0.308}(S,Se)_{0.538}$ sulfoselenide glasses with wide-ranging Se contents have been studied with Ge and As *K*-edge extended x-ray absorption time spectra spectroscopy. The average coordination numbers of Ge and As atoms are found to be 4 and 3, respectively, in all glasses. The compositional makeup of the first coordination shells of Ge and As atoms indicate that chemical order is largely preserved in stoichiometric and Se-excess $Ge_xAs_ySe_{1-x-y}$ glasses. On the other hand, chemical order is found to be strongly violated in the case of Se-deficient $Ge_xAs_ySe_{1-x-y}$ glasses where the chalcogen deficiency is entirely taken up by the formation of As-As homopolar bonds at low and intermediate levels of Se deficiency. The Ge atoms take part in homopolar bonding only in strongly Se-deficient glasses indicating clustering of As atoms. In the case of sulfoselenide glasses the distribution of S and Se atoms in the first coordination shells of Ge and As atoms is found to be random, signifying a chemically ordered chalcogen "sublattice." It is shown that the intermediate-range structural and topological aspects of such compositional variation of chemical order may play a central role in controlling properties such as the molar volume of chalcogenide glasses.

Ge-Ga-S and Ga-In-S glasses

- ✓ Weak covalent ChGs
- ✓ Group 3 elements together with S and (or) Se
  - ➢ Ga and In do not follow the the 8-*N* rule
  - ➢ Sometimes RE containing ChG: Ga-La-S glass

Fit Results Concerning the S Shell around Ga Atoms, in Ga_2S_3–GeS_2 Glasses at Room Temperature

	$n = \frac{Ga}{Ga + Ge}$	N	R (Å)	σ (Å)[a]	ΔE_o (eV)	RF[b] ($\times 10^{-2}$)
$La_6Ga_2Mn_2S_{14}$		4	2.28(2)	0.09	6.0	1.3
Sample 1	0.10	4.1(4)	2.28(2)	0.10	6.2	1.8
Sample 2	0.30	4.1(4)	2.28(2)	0.09	6.3	1.4
Sample 3	0.40	4.1(4)	2.28(2)	0.10	5.8	1.7

In K-edge EXAFS structural parameters for GeIn sulfide and selenide glasses

Composition	$N_{S/Se}$	$R_{S/Se}$ (Å)	$2\sigma^2_{S/Se}$ (Å^2)	N_{Ge}	R_{Ge} (Å)	$2\sigma^2_{Ge}$ (Å^2)
S-excess	4.0	2.42	0.015	0.0	–	–
Stoichiometric sulfide	3.7	2.41	0.015	0.4	2.66	0.012
S-deficient	3.6	2.43	0.015	0.4	2.68	0.015
Stoichiometric selenide	4.0	2.55	0.015	0.0	–	–

- A.M. Loireau-Lozac’h et al, J. Solid State Chem. 123 (1996) 60.
- S. Sen et al, J. Non-Cryst. Solids 351 (2005) 1710.

Ga-La-S glass

Journal of Non-Crystalline Solids
Volume 110, Issue 1, July 1989, Pages 89-100

An EXAFS structural approach of the lanthanum-gallium-sulfur glasses

S Benazeth, M.H Tuilier, A.M Loireau-Lozac‘h, H Dexpert, P Lagarde and J Flahaut

Abstract

Three La: Ga:S glassy compositions spanning the range of the vitreous region, have been investigated by EXAFS (gallium K-edge, lanthanum LIII edge). As a first result, the gallium is found tetracoordinated for any composition and the GaS_4 polyhedra are the glassy former units. The lanthanum modifying cation has the same mean surrounding as in the crystalline state, but with more dispersed La---S distances (average La---S surrounding = seven first neighbors, situated from 2.91 to 2.93 Å). However disordered, this environment is well defined. A structural model is then proposed as a covalent network of GaS_4 tetrahedra, intercalated by the essentially ionic La---S channels. This model is close to the modified random network usually presented for the oxide glasses.

Ga-La-S glass

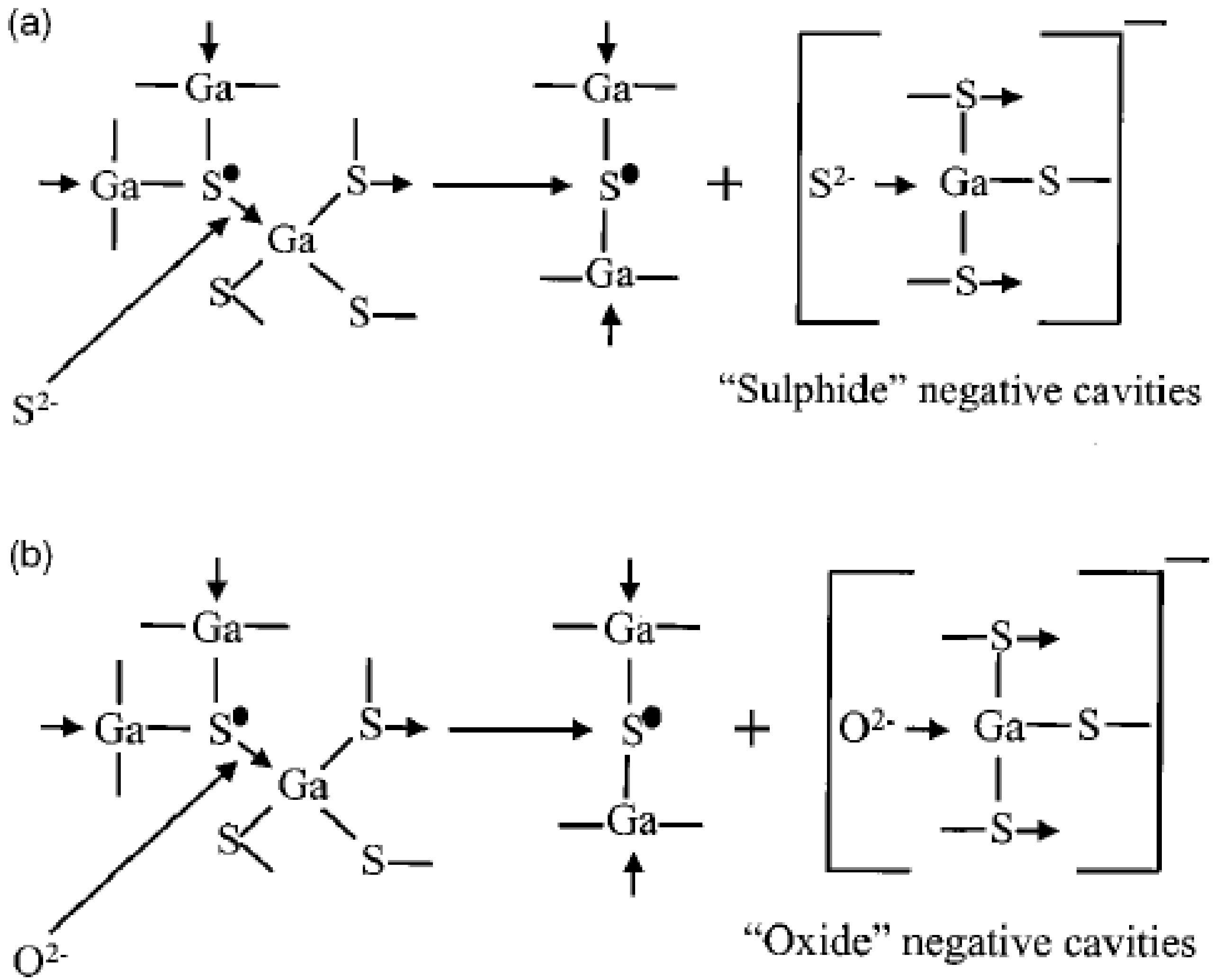

Fig. 8. Formation of (a) negative sulphide cavities (reaction 1, GLS) and (b) negative oxide cavities (reaction 2, GLSO).

Schweizer et al, J. Opt. Soc. Am. B 18 (2001) 1440.