

EXTERNALLY-ATTAINED FUNCTIONALITY IN NETWORK CHALCOGENIDE GLASSES exemplified by RADIATION-INDUCED EFFECTS

APPLICATIONS – Part A

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C O N T E N T

Part II: Remarkable Features and Applications

1. Externally-attained functionality in ChVS

exemplified by γ -induced changes of physical properties:

- **On the variety of radiation-induced effects in ChVSs:**

Remarkable features of radiation-induced effects in ChVSs:

- **I – sharp changes in physical properties, fundamental optical absorption**
- **II – dose and thickness dependences**
- **III – thermal threshold of restoration and reversibility**
- **IV – compositional dependence and post-irradiation instability
for quasibinary stoichiometric sulphide systems**
- **V – compositional dependence and post-irradiation instability
for non-stoichiometric sulphide systems with wide Z deviation**
- **VI – compositional anomalies and “magic” points: features**
- **VII – compositional anomalies and “magic” points: explanations**
- **VIII – kinetics of post-irradiation instability: general description**
- **IX – kinetics of post-irradiation instability: typical resolutions**

2. Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations:

- **Destroyed covalent bonds by Electron Spin Resonance**
- **Redistributed covalent bonds by Intrinsic IR Absorption**

Possible types of covalent chemical bond switching processes in ChVS:

- **1 – non-defect double-bond switching**
- **2 – transient Coordination Topological Defects formation**
- **3 – metastable Coordination Topological Defects formation**

C O N T E N T

Part II: Remarkable Features and Applications

2. Nanostructural nature of γ -induced effects in ChVSs

Metastable CTD formation in ChVS:

- energetic criterion – I
- energetic criterion – II
- geometric criterion
- topological-mathematical modeling – I
- topological-mathematical modeling – II
- topological-mathematical modeling – III

Metastable CTD formation in ChVSs exemplified by $v\text{-As}_2\text{S}_3$:

- homopolar-to-heteropolar bond-switching
- homopolar-to-homopolar bond-switching
- heteropolar-to-homopolar bond-switching
- heteropolar-to-heteropolar bond-switching
- full cycle for reversible CTD-related destruction-polymerization transformations

3. On the origin of irreversible γ -induced structural transformations in ChVS

- radiation impurities in $v\text{-As}_2\text{S}_3$ by IR Absorption
- radiation impurities in $v\text{-As}_2\text{S}_3$ by Mass Spectrometry
- types of irreversible radiation-structural transformations

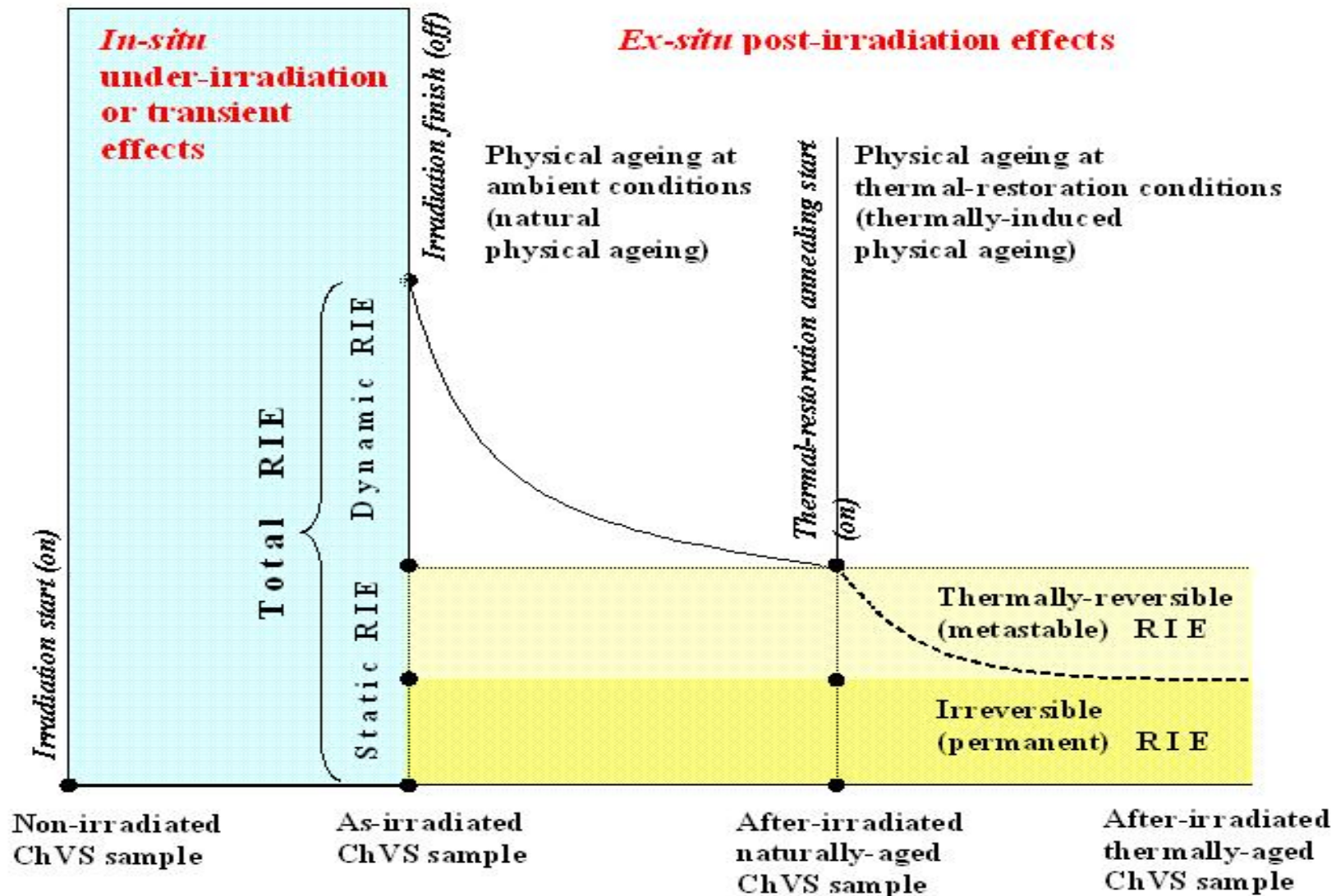
4. Some practical aspects of γ -induced effects in ChVSs

- industrial ChVS-based optical dosimetric systems – I
- industrial ChVS-based optical dosimetric systems – II
- post-technological radiation modification route

On the variety of radiation-induced effects in ChVSs

Expected results of external radiation-induced functionality in ChVSs:

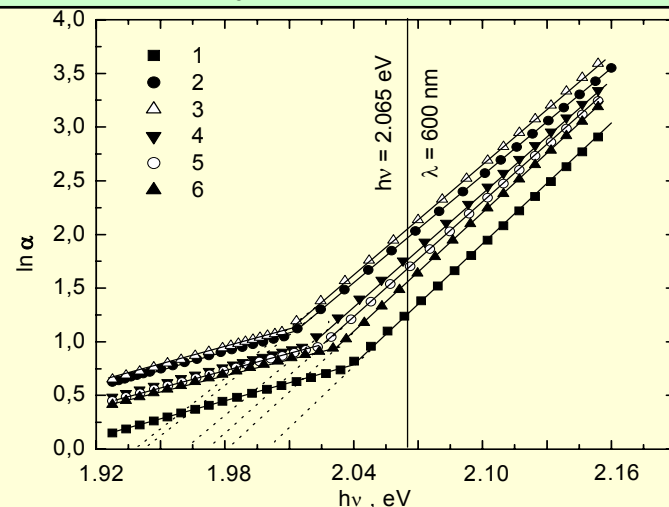
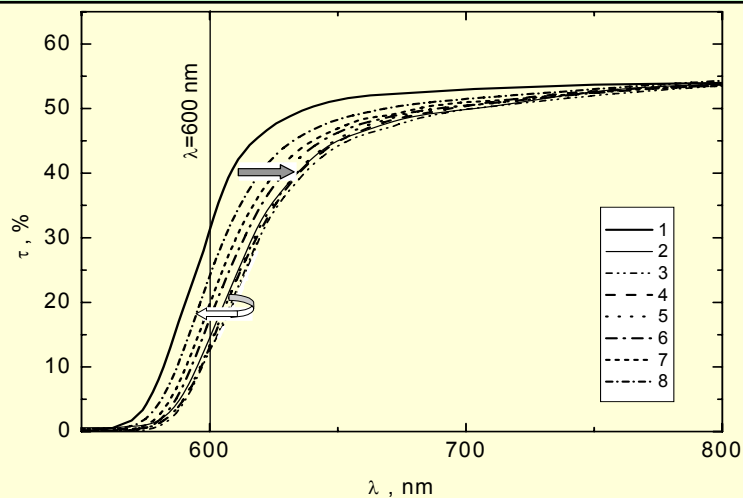
- stabilization effect (modification) due to additional input in physical ageing
- acceleration effect due to quick tending into thermodynamic equilibrium



Remarkable features of radiation-induced effects in ChVSs

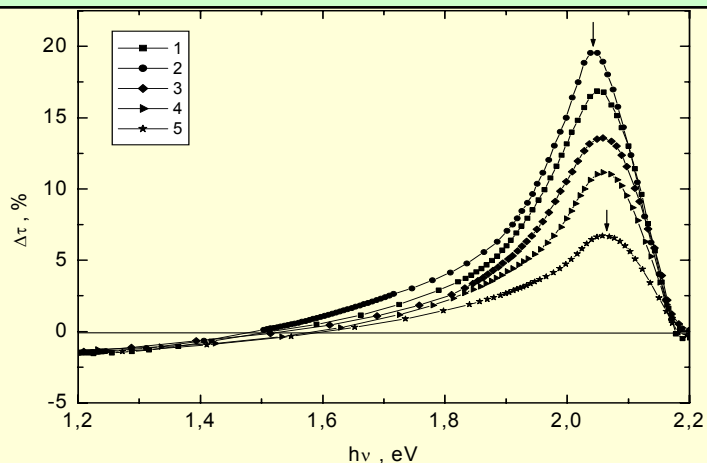
Sharp changes in physical properties (fundamental optical absorption)

Considerable changes in fundamental optical absorption of $v\text{-As}_2\text{S}_3$ after γ -irradiation at $\Phi > 0.5$ MGy



Optical transmission spectra of $v\text{-As}_2\text{S}_3$ before (1) and after (2) γ -irradiation ($\Phi=10.0$ MGy, $P=25$ Gy/s) and with further thermal annealing at 330 (3), 370 (4), 380 (5), 395 (6), 420 (7) and 440 K (8)

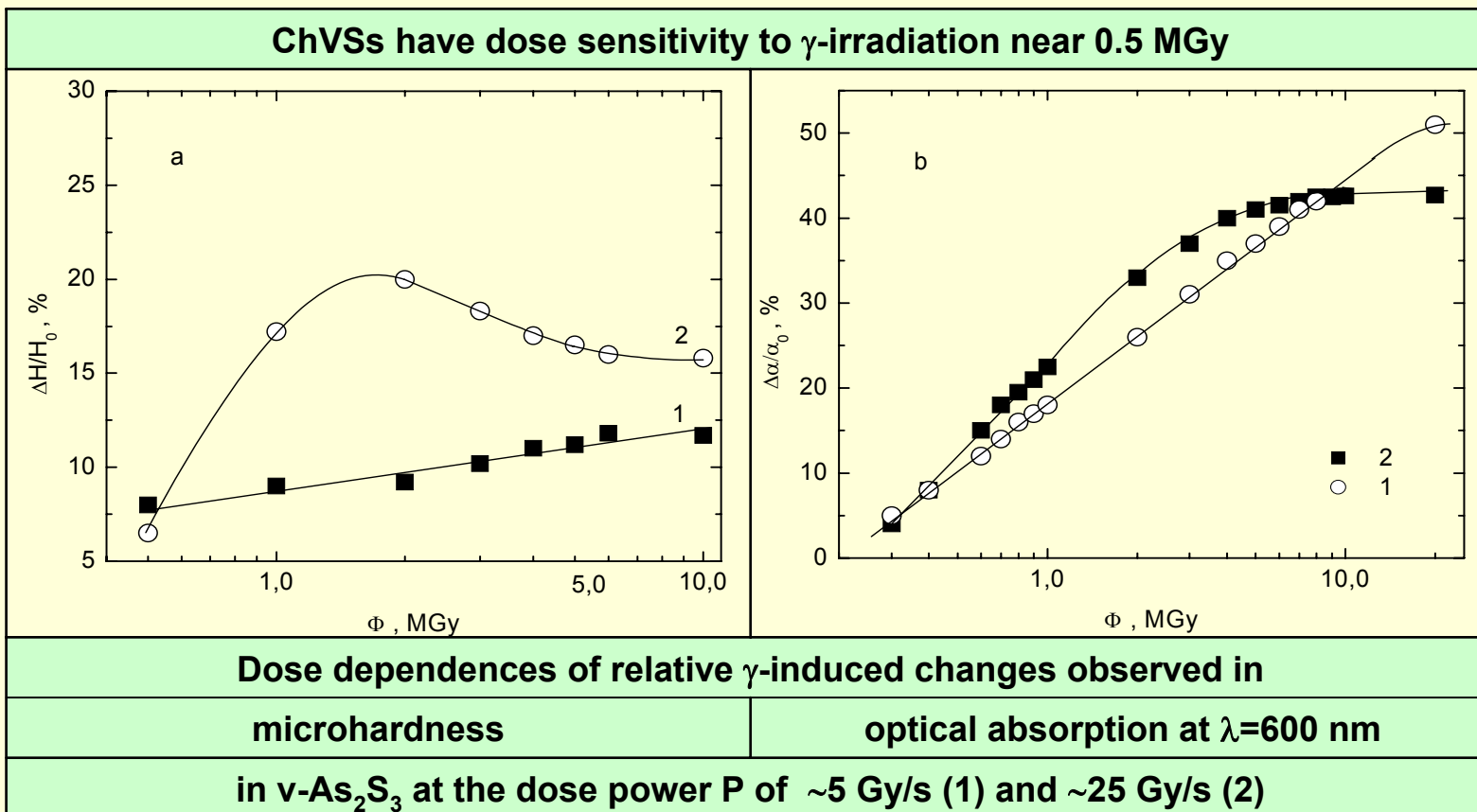
Optical absorption spectra of $v\text{-As}_2\text{S}_3$ before (1) and after (2) γ -irradiation ($\Phi=10.0$ MGy, $P=25$ Gy/s) and with further thermal annealing at 330 (3), 395 (4), 420 (5) and 440 K (6)



Spectral dependences of optical transmission differences $\Delta\tau$ in γ -irradiated ($\Phi=10.0$ MGy, $P=25$ Gy/s) $v\text{-As}_2\text{S}_3$ (1) and with further thermal annealing at 330 (2), 370 (3), 380 (4), 395 (5), 420 (6) and 440 K (7)

Remarkable features of radiation-induced effects in ChVSs

Dose dependence



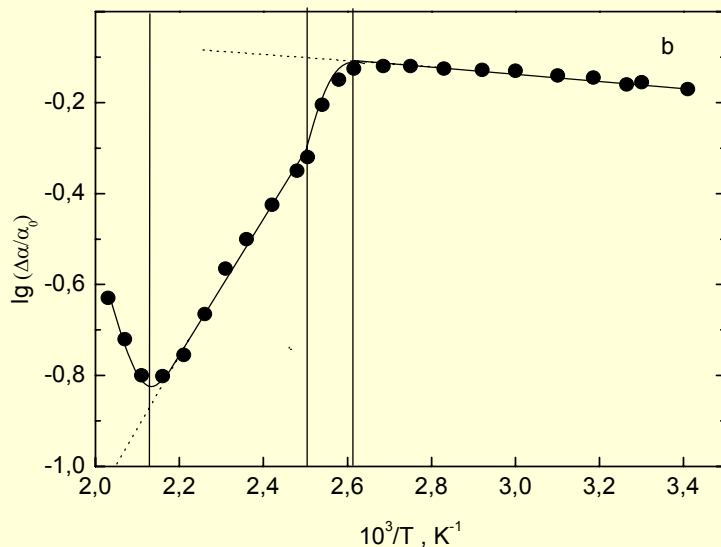
Thickness dependence

γ -induced changes in thickness-dependent properties:

$$\chi = C_0(1 - \exp(-\kappa d)),$$
 C_0 and κ – material-related constants

Remarkable features of radiation-induced effects in ChVSs

Thermal threshold of restoration



Relative optical absorption changes ($\lambda=600$ nm) in γ -irradiated ($\Phi=10.0$ MGy, $P=25$ Gy/s) $v\text{-As}_2\text{S}_3$ in dependence on the temperature of post-irradiation thermal annealing.

$$\ln(\Delta\alpha/\alpha_0) = f(10^3/T)$$

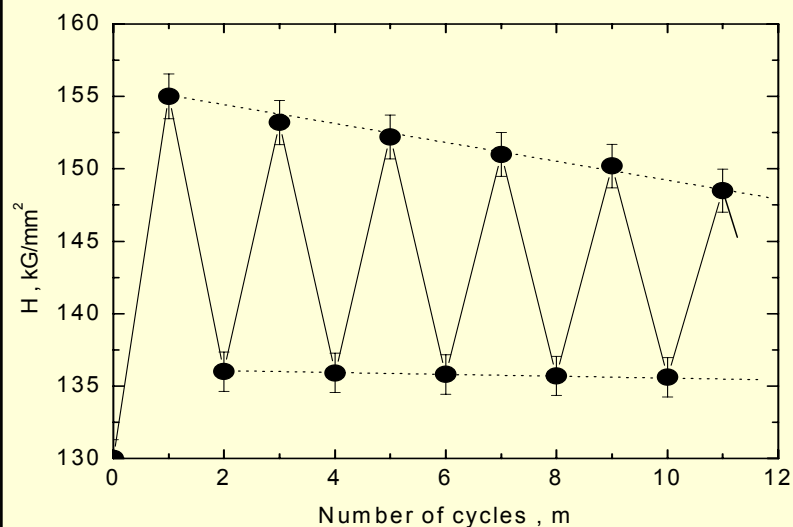
$E_a = 0.50$ eV for $390 < T < 410$ K;

$E_a = 0.27$ eV for $T > 410$ K.

$\Delta T = 390 \div 400$ K –

thermal bleaching threshold

Reversibility



Multiply observed reversible changes
In the microhardness of $v\text{-As}_2\text{S}_3$:
 γ -irradiation cycles:
 $m=1, 3, 5, \dots$; $\Phi=5.0$ MGy, $P=25$ Gy/s;
thermal annealing cycles:
 $m=2, 4, 6, \dots$; $T=423$ K, $\Delta t=12$ h

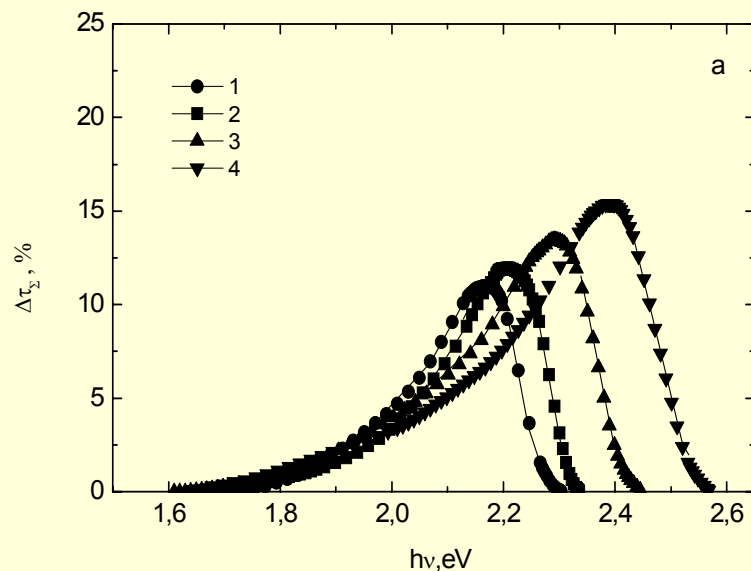
Remarkable features of radiation-induced effects in ChVSs

Compositional dependence and post-irradiation instability

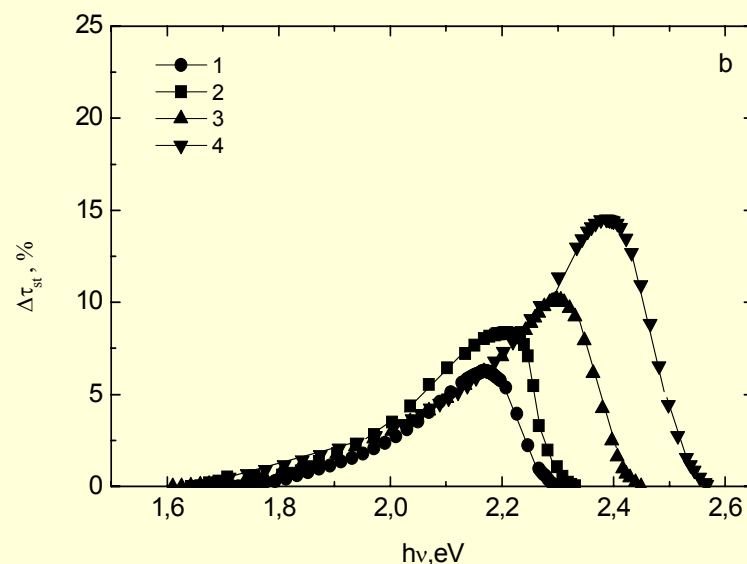
Quasibinary stoichiometric sulphide systems

Spectral dependences of optical transmission differences $\Delta\tau$
in $v\text{-(As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ ($d=1$ mm; 1 – $x=0.2$; 2 – $x=0.4$; 3 – $x=0.6$; 4 – $x=0.8$)
induced by γ -irradiation ($\Phi=2.2$ MGy, $P\sim 1$ Gy/s)

measured 1 day after γ -irradiation



measured 2 months after γ -irradiation



Conclusion:

Smooth monotonic compositional dependence of RIEs in stoichiometric ChVS systems

Remarkable features of radiation-induced effects in ChVSs

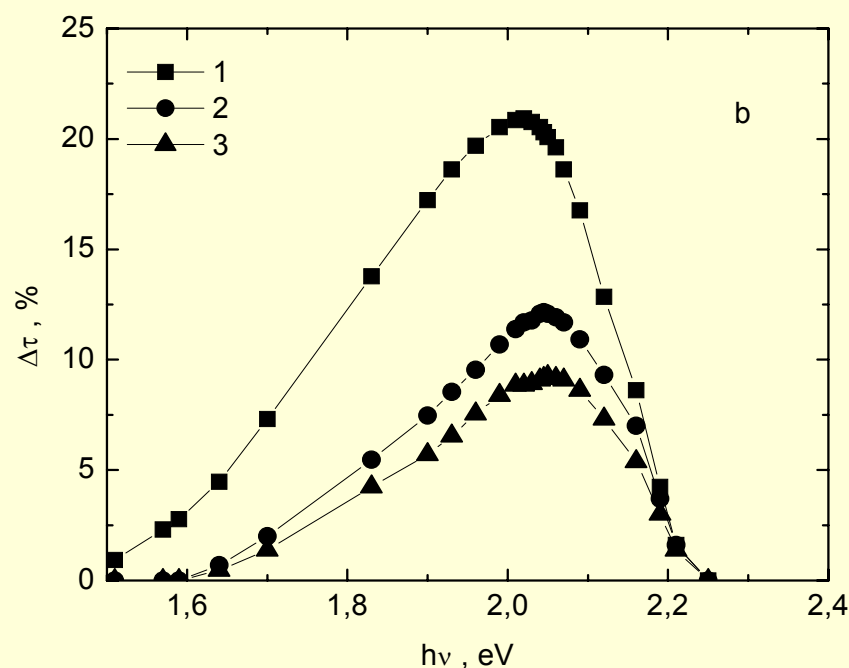
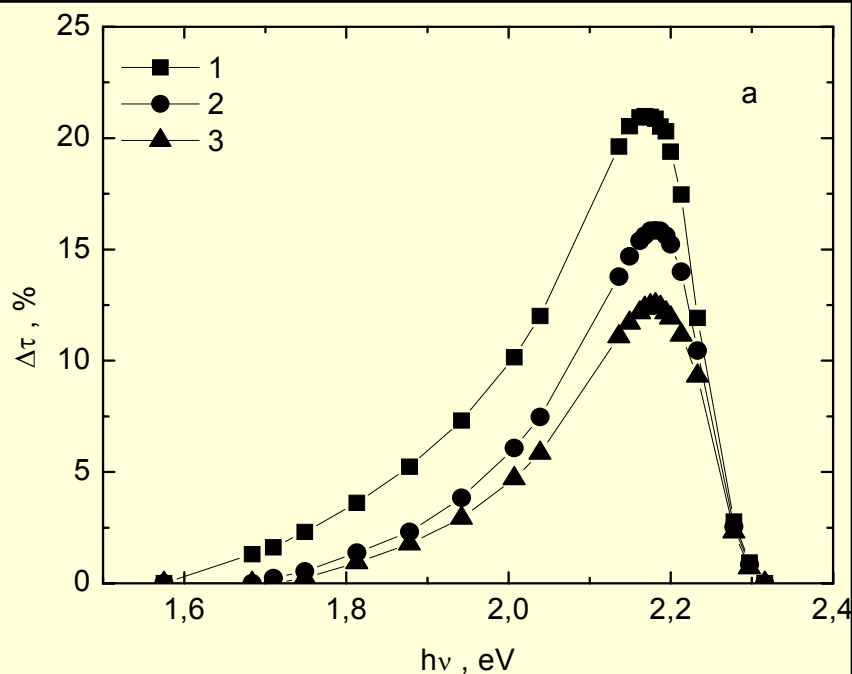
Compositional dependence and post-irradiation instability

Non-stoichiometric sulphide systems with wide Z deviation

Spectral dependences of optical transmission differences $\Delta\tau$
In $v\text{-(As}_2\text{S}_3)_x(\text{Ge}_2\text{S}_3)_{1-x}$ ($d=2$ mm) induced by γ -irradiation ($\Phi=4.4$ MGy, $P\sim 1$ Gy/s)
measured 1 day (1), 1 month (2) and 2 months (3)

Z=2.56 ($x=0.6$)

Z=2.76 ($x=0.1$)



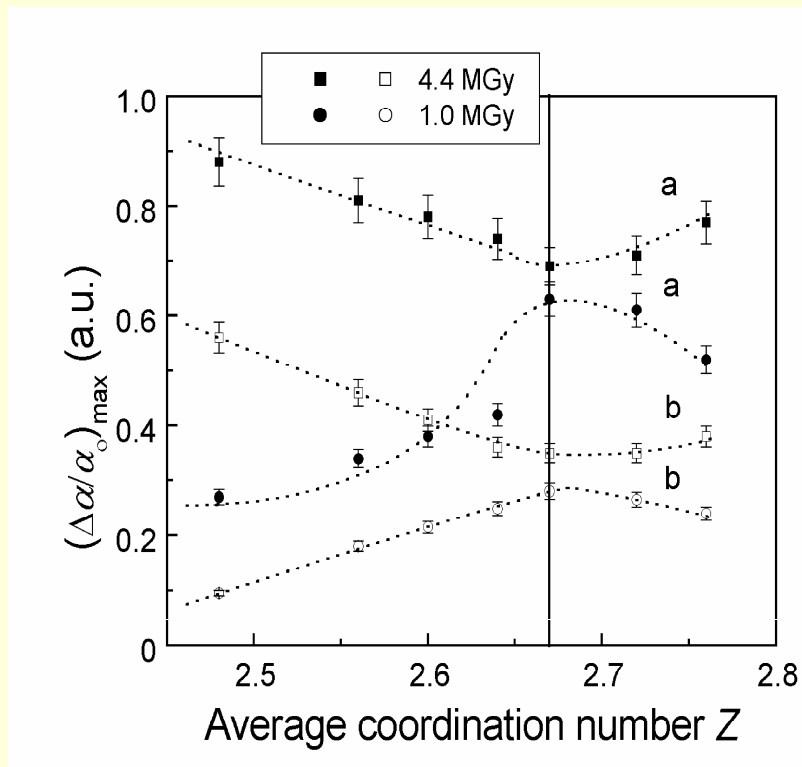
Conclusion:

Extremum-like compositional dependence of RIEs in non-stoichiometric ChVS systems

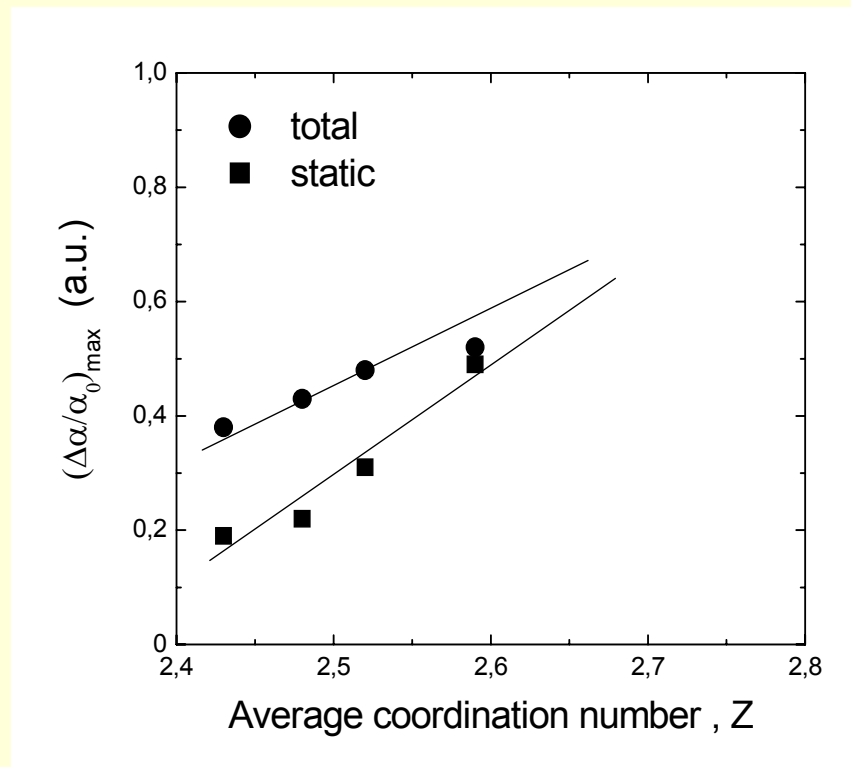
Remarkable features of radiation-induced effects in ChVSs

Compositional anomalies and “magic” points: features

Non-stoichiometric sulphide systems with wide Z deviation



Compositional dependences of total (curves – a) and static (curves – b) γ -induced changes in optical absorption for non-stoichiometric $v\text{-As}_2\text{S}_3\text{-Ge}_2\text{S}_3$ (the “magic” $Z=2.67$ point is denoted by vertical line)



Compositional dependences of total (circles) and static (squares) γ -induced changes in optical absorption for stoichiometric $v\text{-As}_2\text{S}_3\text{-GeS}_2$

Remarkable features of radiation-induced effects in ChVSs

Compositional anomalies and “magic” points: explanations

The microstructural origin of the «magic» $Z=2.67$ point has been under hot discussion up to now:

? First explanation:

topological phase transition from 2D to 3D glassy-like network [Tanaka Ke., 1989], as in the case of floppy-rigid on-set at $Z=2.4$ [Phillips J.C., 1979; Thorpe M.F., 1983], *but beyond comprehensive mean-field constraint theory*

?? Second explanation:

redistribution of covalent bonds (chemical phase transition) [Tichy L., 1999], *but mainly for tetragen-contained ChVS*

??? Third explanation:

phase segregation or separation [Boolchand P., 1999], but without strong evidences because of microscale level of the occurring processes

Alternative explanation:

Taking into account that **atomic compactness drops to the minimum near $Z \approx 2.7$** , the origin of this anomaly is expected to link with ***a high stability of the created radiation-induced CTDs*** due to ***effective blocking of backward defect annihilation*** in a more sparse atomic network.

Remarkable features of radiation-induced effects in ChVSs

Kinetics of post-irradiation instability: general description

The total RIEs determined in terms of $\chi = (\Delta\alpha/\alpha_o)_{\max}$ can be decomposed on **static and dynamic** components:

$$\chi_{\Sigma}(h\nu) = \chi_{\text{dyn}}(h\nu) + \chi_{\text{st}}(h\nu)$$

General differential equation (GDE) for dynamic radiation-induced effects in power-like form (α and β are material-specific constants):

$$\frac{d\chi}{dt} = -\lambda\chi^{\alpha}t^{\beta}$$

Boundary conditions:

$$\left\{ \begin{array}{l} t \rightarrow 0 \Rightarrow \chi \rightarrow \chi_0 = \text{const} \\ t \rightarrow \infty \Rightarrow \chi \rightarrow 0 \end{array} \right.$$

Remarkable features of radiation-induced effects in ChVSs

Kinetics of post-irradiation instability: typical resolutions

Main differential equations and their solutions (RFs – relaxation functions) for dynamic RIEs

Main types of degradation	RF and conditions for its determination
1) $\frac{d\chi}{dt} = -\lambda\chi$ (monomolecular: $\beta=0, \alpha=1$)	$\chi = \chi_0 e^{-\frac{t}{\tau}}$ $\chi_0 = e^c$ $\tau = \frac{1}{\lambda}$ (c - integration constant, $\lambda \neq 0$)
2) $\frac{d\chi}{dt} = -\lambda\chi^2$ (bimolecular: $\beta=0, \alpha=2$)	$\chi = \frac{\chi_0}{1 + \frac{t}{\tau}}$ $\chi_0 = e^c$ $\tau = \frac{1}{\lambda}$ (c - integration constant, $\lambda \neq 0$)
3) $\frac{d\chi}{dt} = -\lambda\chi t^\beta$ (stretched-exponential: $\alpha=1, 0 \leq \beta \leq 1$)	$\chi = \chi_0 \exp\left[-\left(\frac{t}{\tau}\right)^\kappa\right]$ $\tau = \left(\frac{1+\beta}{\lambda}\right)^{\frac{1}{1+\beta}}$ $\kappa = 1 + \beta$ $\chi_0 = e^c$ (c - integration constant, $\beta \neq -1, \lambda \neq 0$)

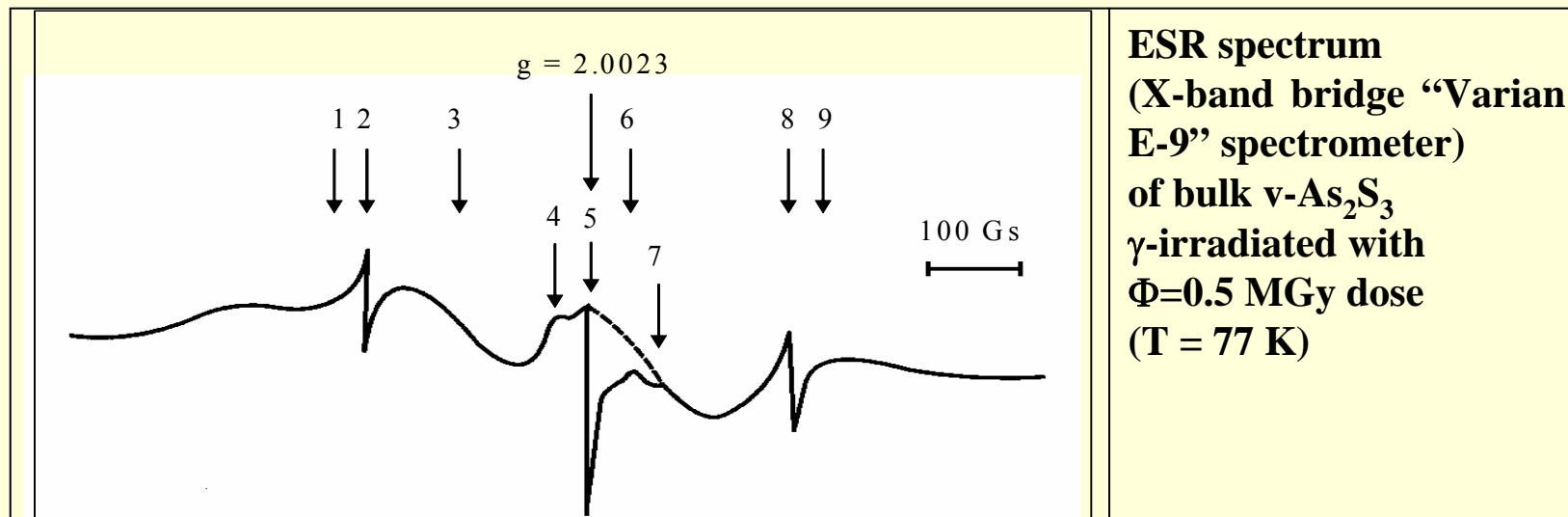
CONCLUSIONS

1. The absolutely best fitting is achieved owing to **fully-generalised resolution** of GDE.
2. If only 3 fitting parameters are used, the best result is achieved for **stretched-exponential RF**.
3. If only 2 fitting parameters are used, the best result is achieved for **bimolecular RF 2**
 (additional confirmation on CTD-related origin of dynamic radiation-induced effects in ChVSs.

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Destroyed covalent bonds by Electron Spin Resonance



Main parameters of the observed ESR signal and its identification

ESR components	Signal parameters	Identification
Four-component signal with 1, 3, 6 and 9 lines	$g_3 = 2.065$; $g_6 = 1.950$; $\Delta B_3 = 90$ Gs; $\Delta B_6 = 210$ Gs g_1 and ΔB_1 ; g_9 and ΔB_9 – difficult to identify Bleaching $T > 210$ K	Unpaired electrons localized on the destroyed =As-S- bonds (=As-S \cdot and S $_2$ -As \cdot centers)
Slight bends as 4 and 7 lines	$g = 1.970$; $\Delta B = 140$ Gs Bleaching $T > 150$ K	Unpaired electrons localized on As atoms within disturbed =As-As= bonds
Doublet signal with sharp 2 and 8 lines	Resonance splitting $A = 502$ Gs; $g_2 = 2.183$; $g_8 = 1.847$; $g_{av.} = 2.05$; $\Delta B_2 = \Delta B_8 < 1$ Gs; Bleaching $T > 160$ K	H \cdot (impurity hydrogen atoms)
Narrow single line 5	$g = 2.0023$	Hole-like centers localized on O atoms

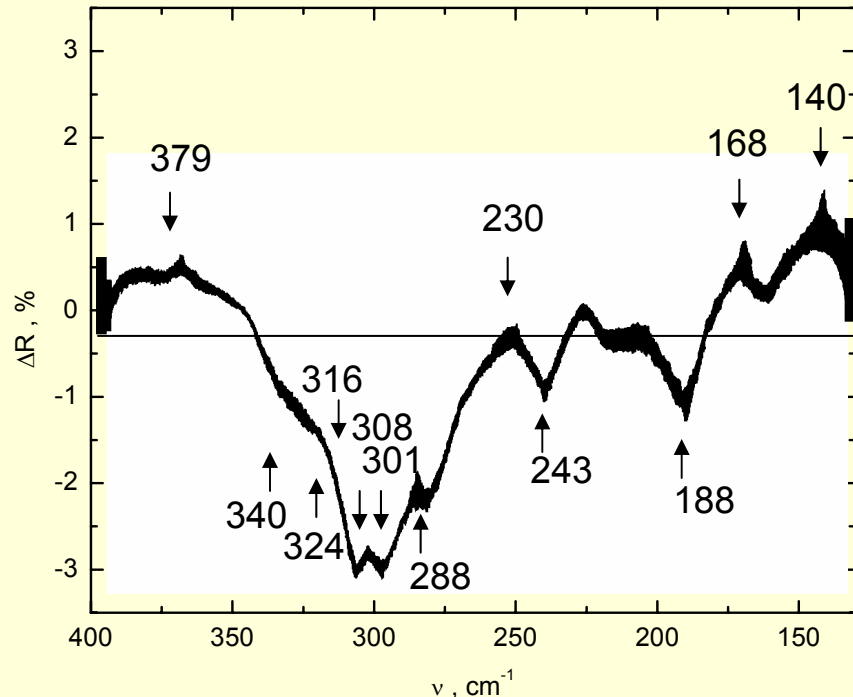
Conclusion:

Radiation-induced destruction of covalent chemical bonds within glass-forming network.

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Redistributed covalent bonds by Intrinsic IR Absorption



Signal of additional reflectivity (multiply accumulated difference in reflectivity for irradiated and non-irradiated/thermally-annealed samples) detected in $v\text{-As}_2\text{S}_3$ with IFS-113V “Bruker” IR Fourier-spectrometer at the stage of third-cycle γ -irradiation ($\Phi=10.0$ MGy, $P=25$ Gy/s).

Covalent chemical bond-switching:

- reaction No 1: **(As-S) \rightarrow (As-As)**

- reaction No 2: **(S-S) \rightarrow (As-S)**

Statistical weight of the first reaction is more than the second.

$v\text{-As}_2\text{S}_3$ – a model object for γ -induced structural transformations

because of good resolution in vibrational bands for structural complexes

with covalent chemical bonds of different types:

- **pyramidal AsS_3 units (335-285 cm^{-1}) with heteropolar As-S chemical bonds,**

as well as

- **molecular products with “wrong” homopolar As-As (379, 340, 231, 210, 168, 140 cm^{-1})**

- and **homopolar S-S chemical bonds (243 and 188 cm^{-1}).**

Conclusion:

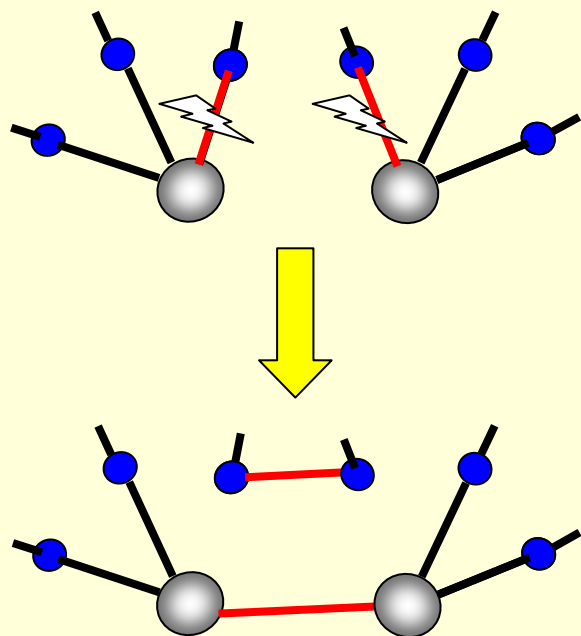
Radiation-induced switching of covalent chemical bonds within glass-forming network.

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Possible types of covalent chemical bond switching processes in ChVS

1 – non-defect double-bond switching



Non-defect double-bond switching –

simultaneous switching of two heteropolar bonds into two homopolar ones (or vice versa) without any changes in local coordination for all bond-forming atoms

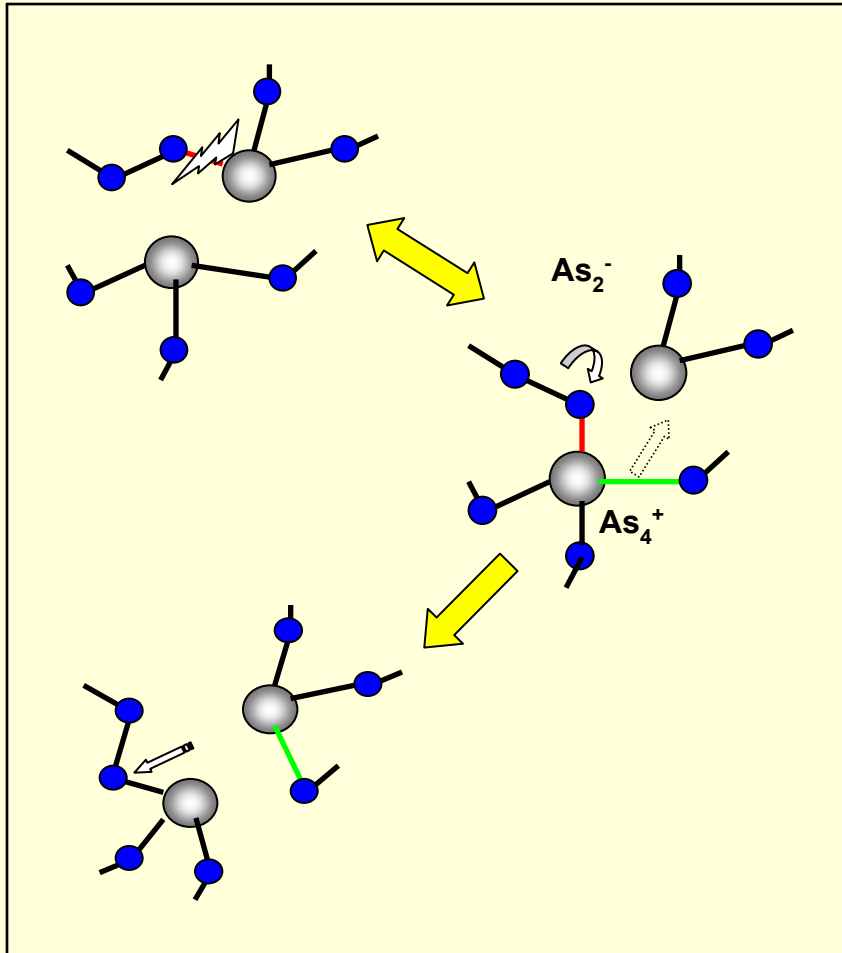
[Frumar *et al.* 1983, 1997].

The observed RIEs are explained in terms of redistribution of covalent chemical bonds within a glassy network. The above double-bond switching processes are possible only for some rare structural configurations, which allow bond switching without significant atomic displacements. All four atoms initially forming a pair of heteropolar bonds, say As–S bonds within two neighboring $\text{AsS}_{3/2}$ pyramids, should be located at the sites where pairs of homopolar bonds (As–As and S–S) can be formed. These configurations are expected to appear in the freshly evaporated thin ChVS films. However, they can exist only in negligible concentrations in bulk stoichiometric ChVSs obtained by conventional melt-quenching technique.

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Possible types of covalent chemical bond switching processes in ChVS 2 – transient Coordination Topological Defects formation



Transient CTD formation –

the first step (the initial stage):

destruction of covalent chemical bond,

the second step (the intermediate stage):

formation of transient CTD pair.,

the third step (the final stage):

annihilation of the formed CTD pair

(Fritzsche 1993, 2000).

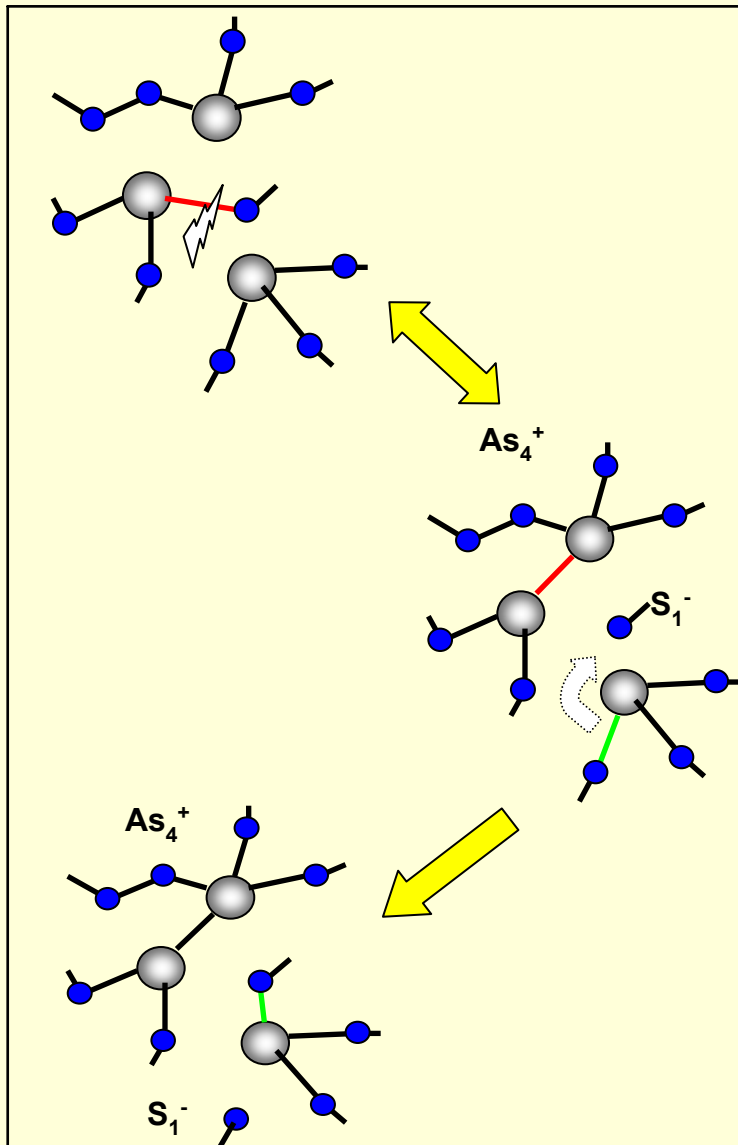
These processes are accompanied by significant configuration-deformation disturbances of the glassy structure, which result in the observed changes of physical properties. However, the reason for these disturbances is unclear. Moreover, this model evidently contradicts to a great number of experimental results testifying in a favour of reversible photoinduced heteropolar-to-homopolar bond switching in $v\text{-As}_2\text{S}_3$ [Shpotyuk *et al.*, 1989; Frumar *et al.*, 1983]

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Possible types of covalent chemical bond switching processes in ChVS

3 – metastable Coordination Topological Defects formation



Metastable CTD formation –

stabilization of CTD pair in a glassy network at the final stage, which can be achieved through additional type-conserved bond switching (transition from stage 2 to stage 3), increasing spatial separation between created CTDs and keeping them from spontaneous annihilation [Shpotyuk *et al.*, 1989; Tichy *et al.*, 1998]

Since only one covalent bond is switched into another, the atomic arrangements available for such structural transformations are not restricted by any additional steric constraints. The observed **darkening effect** in $v\text{-As}_2\text{S}_3$ at the reversible stage can be conveniently explained by switching of stronger covalent bonds into weaker ones (heteropolar As-S covalent bonds into homopolar As-As ones as well as homopolar S-S bonds into heteropolar As-S ones), **decreasing an average energy bonding of glass network**. CTD pairs appear as a direct consequence of bond switching, enhancing intrinsic electrical fields and leading finally to the observed **decrease in the slope of the fundamental optical absorption edge**.

In contrast to low concentration of CTDs frozen in bulk ChVS near glass transition (Tanaka, 2001), their concentration can be significantly increased by the influence of external factors owing to high level of free volume in network glasses [Zallen, 1973].

**EXTERNALLY-ATTAINED FUNCTIONALITY
IN NETWORK CHALCOGENIDE GLASSES
exemplified by
RADIATION-INDUCED EFFECTS**

End of Part A

To Be Followed by

APPLICATIONS - Part B

**EXTERNALLY-ATTAINED FUNCTIONALITY
IN NETWORK CHALCOGENIDE GLASSES**
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RADIATION-INDUCED EFFECTS

**APPLICATIONS – Cont.
– Part B**

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Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Metastable CTD formation in ChVS: energetic criterion – I

ENERGETIC CRITERION:

Since high-energetic γ -irradiation introduces **an additional chemical disorder** in a glassy-like network associated with some deviations in thermally-established distribution of covalent chemical bonds, it can be stated that

the weaker covalent bonds appear instead of stronger ones

as a result of radiation-induced electronic disturbances at relatively low temperatures (S.C.).

It means that only such radiation-induced bond-switching processes should be considered, which accompanied with **a negative difference ΔE in dissociation energies for created E_c and destructed E_d covalent bonds:**

$$\Delta E = E_c - E_d < 0.$$

This criterion determines, in turn, ***the low-energetic shift of fundamental optical absorption edge in γ -irradiated ChVS***, as decrease in the character energies of main glass-forming units. The greater ΔE , the more essential energetic barrier between initial and final metastable states in the configuration diagram of the investigated glassy-like system and, consequently, the more stable the created CTD pair.

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Metastable CTD formation in ChVS: energetic criterion – II

ENERGETIC CRITERION (illustration):

Diagram of radiation-induced covalent bond redistribution in stoichiometric ChVSs with a small amount of “wrong” homopolar bonds

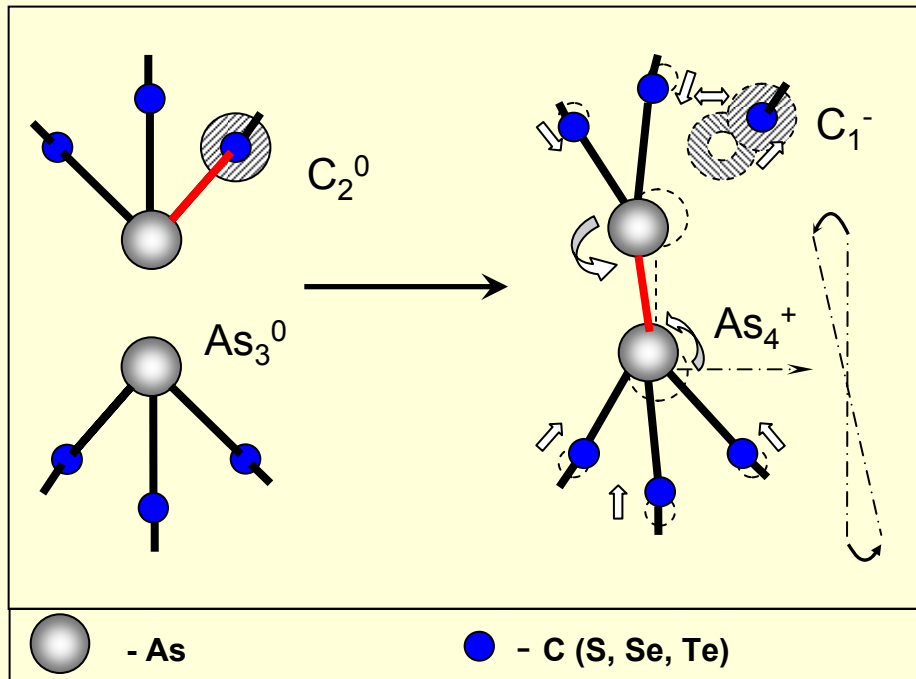
“Wrong” homopolar bonds	“Wrong” homopolar bonds	“Wrong” homopolar bonds	“Wrong” homopolar bonds
Strong heteropolar bonds	Strong heteropolar bonds	“Wrong” homopolar bonds	Strong heteropolar bonds
Thermally- maintained equilibrium:	More relaxed thermally- maintained equilibrium:	Radiation- maintained equilibrium at the ambient conditions	Radiation- maintained equilibrium at high T (close to T_g)
State 1	State 2	State 3	State 4

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Metastable CTD formation in ChVS: geometric criterion

GEOMETRIC CRITERION:



Atomic compactness of a glassy-like network in a vicinity of possible covalent bond switching accompanied by a subsequent CTD formation **should be sufficiently released** to ensure a high stability for the created CTD pair owing to blocking of backward CTD-destroyed bond-switching reaction:

$$V_{\text{CTD}}^{\Sigma} = V_0 + \Delta V_{\text{CTD}}$$

$$\Delta V_{\text{CTD}} = \Delta V_{\text{CTD}}^{\text{bond}} + \Delta V_{\text{CTD}}^{\text{relax}}$$

- V_{CTD}^{Σ} – overall free volume in a vicinity of CTD
- V_0 – initial (native) free volume near possible covalent bond switching
- ΔV_{CTD} – **additional free volume** in a vicinity of CTD
- $\Delta V_{\text{CTD}}^{\text{bond}}$ – additional free volume due to *lack of one bond* near negatively charged CTD
- $\Delta V_{\text{CTD}}^{\text{relax}}$ – additional free volume due to *MRO relaxation* near re-switched bonds

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Metastable CTD formation in ChVS: topological-mathematical modeling – I

Matrix description of CTD formation in ChVSs:

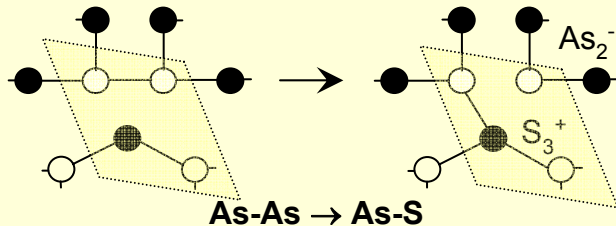
$$|X| \cdot \Gamma = |Y|$$

$|X|$ – matrix of initial non-irradiated state;

$|Y|$ – matrix of final irradiated state;

Γ – operator of covalent bond switching

The general sequence of topological-mathematical modeling procedure:



Since **metastable CTD formation** involves only nearest-neighbor atoms, destruction-polymerization transformations should be described within **four-atom configuration**, including two neighboring covalent chemical bonds of two different structural units, which can be chosen as basic elements of $|X|$ and $|Y|$ matrices.

**Initial-state matrix
in a horizontal form**

$$|X| = \begin{pmatrix} A_{11} & a_{11-12} & A_{12} \\ a_{11-21} & & a_{12-22} \\ A_{21} & a_{21-22} & A_{22} \end{pmatrix}$$

A_{ij} ($i, j=1, 2$) – atom within glass-forming element,
 a_{ij-kl} is true ($\equiv 1$), when corresponding atoms are covalently bonded,
 a_{ij-kl} is false ($\equiv 0$), when corresponding atoms are not bonded.

For convenience: **a horizontal form** of the $|X|$ matrix

$$(a_{11-12} = a_{21-22} = 1 \text{ and } a_{11-21} = a_{12-22} = 0)$$

**Final-state matrix
in a mixed horizontal-vertical form**

In a similar way, but one of horizontal (a_{11-12} or a_{21-22}) and vertical (a_{11-21} or a_{12-22}) elements are not equal to 0.

**Covalent bond-switching operator
in a cross-like form**

$$\Gamma = \begin{pmatrix} & \gamma_{11-12} & \\ \gamma_{11-21} & & \gamma_{12-22} \\ & \gamma_{21-22} & \end{pmatrix}$$

Metastable CTD formation – one covalent bond is destroyed, but another one is simultaneously formed instead of it.
Therefore, γ_{ij-kl} elements symbolize bond presence ($= 1$) or absence ($= 0$).

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Metastable CTD formation in ChVS: topological-mathematical modeling – II

The final-state matrix $|Y\rangle$ can be found by substituting a_{ij-kl} elements in $|X\rangle$ matrix with γ_{ij-kl} elements of Γ operator. Since one vertical bond appears instead of one horizontal bond during each elementary bond-switching act, a set of 4 different Γ_{1-4} operators can be used to describe a full variety of possible re-switching variants:

$$\Gamma_1 = \begin{pmatrix} & 0 & \\ 1 & & 0 \\ & 1 & \end{pmatrix} ; \quad \Gamma_2 = \begin{pmatrix} & 1 & \\ 1 & & 0 \\ & 0 & \end{pmatrix} ; \quad \Gamma_3 = \begin{pmatrix} & 1 & \\ 0 & & 1 \\ & 0 & \end{pmatrix} ; \quad \Gamma_4 = \begin{pmatrix} & 0 & \\ 0 & & 1 \\ & 1 & \end{pmatrix}$$

The total number m of initial-state matrices $|X\rangle$ for n -component ChVS:
 $m = 7$ – binary, $m = 24$ – ternary, $m = 61$ – quaternary, $m = 130$ – pentane (five-component) ChVS.

$$m = n + \frac{n!}{(n-2)!} + \frac{\left(n + \frac{n!}{2(n-2)!}\right)!}{2\left(n + \frac{n!}{2(n-2)!} - 2\right)!}$$

The final step:

The overall number of $|Y\rangle$ matrices and, consequently, the total number of bond switching schemes will be $4m$ owing to four different Γ_{1-4} operators.

This number should be decreased by the number of **topologically-equivalent variants of bond switching** depending on the symmetry of $|X\rangle$, $|Y\rangle$ and Γ .

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

Metastable CTD formation in ChVS: topological-mathematical modeling – III the sequence of topological-mathematical procedure at the example of $v\text{-As}_2\text{S}_3$

Step No 1:

A set of initial-state matrices in a horizontal form:

$$\begin{pmatrix} As & - & S \\ As & - & S \end{pmatrix} \begin{pmatrix} As & - & S \\ S & - & As \end{pmatrix} \begin{pmatrix} As & - & S \\ As & - & As \end{pmatrix} \begin{pmatrix} As & - & S \\ S & - & S \end{pmatrix} \begin{pmatrix} As & - & As \\ S & - & S \end{pmatrix} \begin{pmatrix} As & - & As \\ As & - & As \end{pmatrix} \begin{pmatrix} S & - & S \\ S & - & S \end{pmatrix}$$

Step No 2:

A set of covalent bond-switching operators in a cross-like form:

$$\Gamma_1 = \begin{pmatrix} 0 & & \\ 1 & & 0 \\ & & 1 \end{pmatrix} \quad \Gamma_2 = \begin{pmatrix} & 1 & \\ 1 & & 0 \\ & & 0 \end{pmatrix} \quad \Gamma_3 = \begin{pmatrix} & 1 & \\ 0 & & 1 \\ & & 0 \end{pmatrix} \quad \Gamma_4 = \begin{pmatrix} & 0 & \\ 0 & & 1 \\ & 1 & \end{pmatrix}$$

Step No 3:

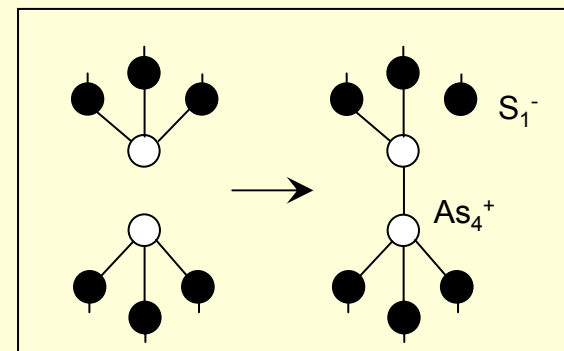
A set of final-state matrix in a mixed horizontal-vertical form:

$$\begin{pmatrix} As & - & S \\ As & - & S \end{pmatrix} \cdot \Gamma_2 = \begin{pmatrix} As & 1 & S \\ 0 & 0 & \\ As & 1 & S \end{pmatrix} \cdot \begin{pmatrix} 1 & \\ & 0 \end{pmatrix} = \begin{pmatrix} As & 1 & S \\ 1 & 0 & \\ As & 0 & S \end{pmatrix} = \begin{pmatrix} As & - & S \\ | & & \\ As & & S \end{pmatrix}$$

Final result:

by excluding topologically-equivalent variants of bond switching depending on the symmetry of $|X|$, $|Y|$ and Γ only 16 of 28 schemes can be accepted as statistically possible in $v\text{-As}_2\text{S}_3$.

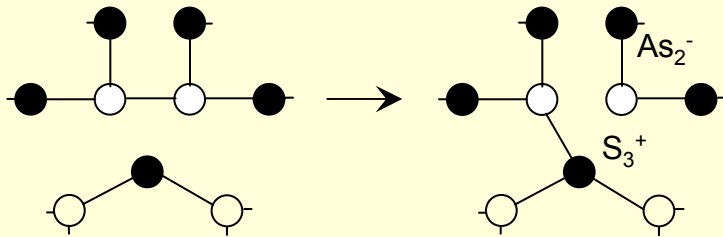
EXAMPLE:



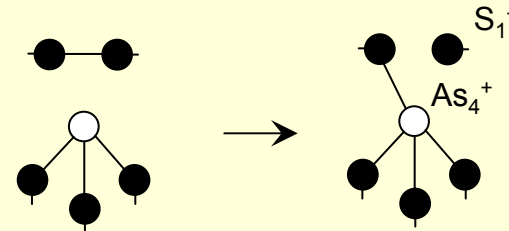
Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

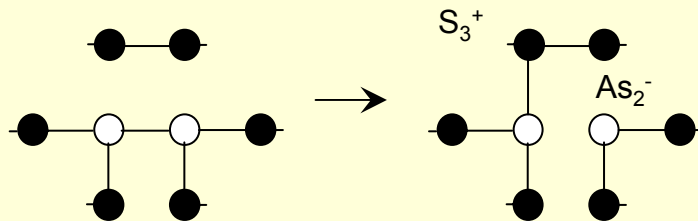
Metastable CTD formation in ChVSs exemplified by $v\text{-As}_2\text{S}_3$: homopolar-to-heteropolar bond-switching



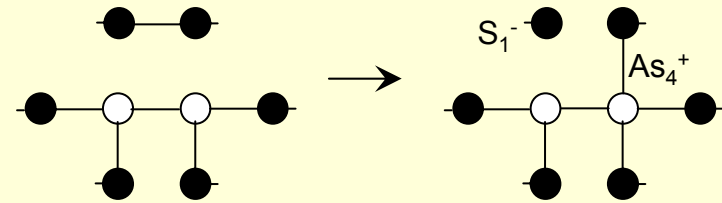
No 1: $\text{As-As} \rightarrow \text{As-S}$
No homopolar bond in the final stage



No 3: $\text{S-S} \rightarrow \text{As-S}$
No homopolar bond in the final stage

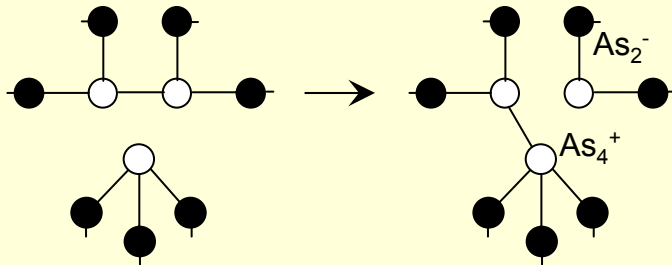


No 2: $\text{As-As} \rightarrow \text{As-S}$
(S-S) homopolar bond in the final stage

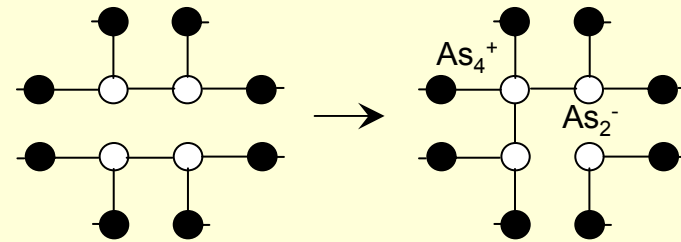


No 4: $\text{S-S} \rightarrow \text{As-S}$
(As-As) homopolar bond in the final stage

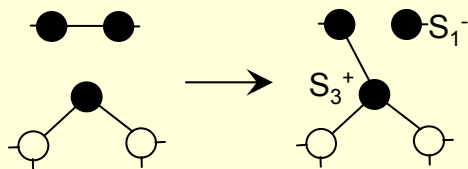
Nanostructural nature of reversible γ -induced effects in ChVSs
On the origin of reversible radiation-structural transformations
Metastable CTD formation in ChVSs exemplified by $v\text{-As}_2\text{S}_3$:
homopolar-to-homopolar bond-switching



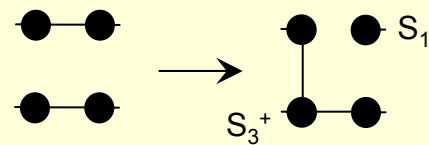
No 5: $\text{As-As} \rightarrow \text{As-As}$
(As-As) homopolar bond in the final stage



No 6: $\text{As-As} \rightarrow \text{As-As}$
2 (As-As) homopolar bonds in the final stage



No 7: $\text{S-S} \rightarrow \text{S-S}$
(S-S) homopolar bond in the final stage

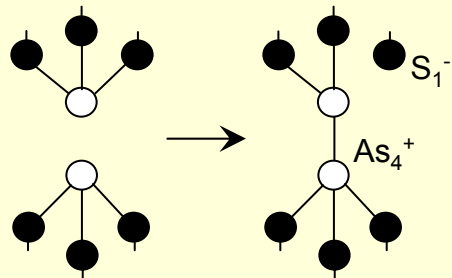


No 8: $\text{S-S} \rightarrow \text{S-S}$
2 (S-S) homopolar bonds in the final stage

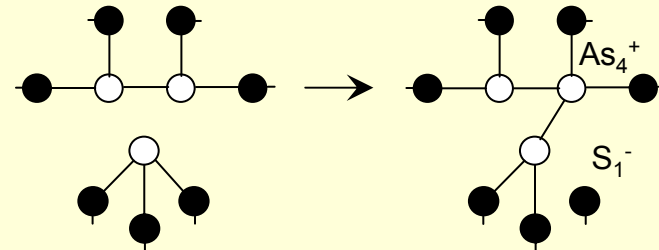
Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

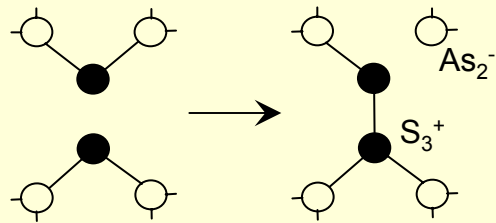
Metastable CTD formation in ChVSs exemplified by $v\text{-As}_2\text{S}_3$: heteropolar-to-homopolar bond-switching



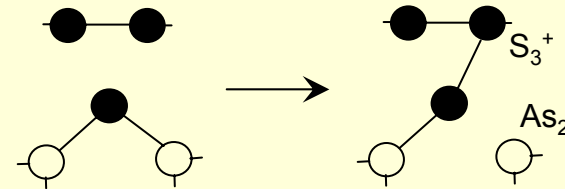
No 9: $\text{As-S} \rightarrow \text{As-As}$
No homopolar bond in the final stage



No 10: $\text{As-S} \rightarrow \text{As-As}$
(As-As) homopolar bond in the final stage



No 11: $\text{As-S} \rightarrow \text{S-S}$
No homopolar bond in the final stage

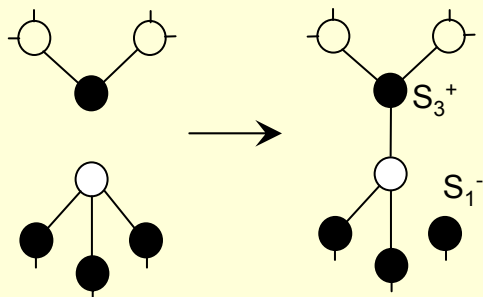


No 12: $\text{As-S} \rightarrow \text{S-S}$
(S-S) homopolar bond in the final stage

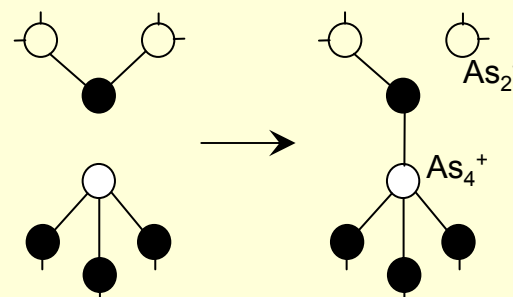
Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

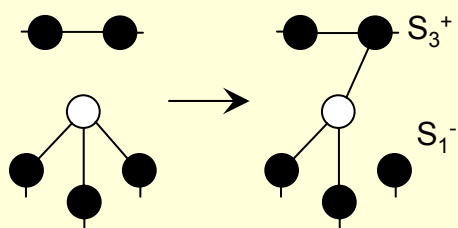
Metastable CTD formation in ChVSs exemplified by $v\text{-As}_2\text{S}_3$: heteropolar-to-heteropolar bond-switching



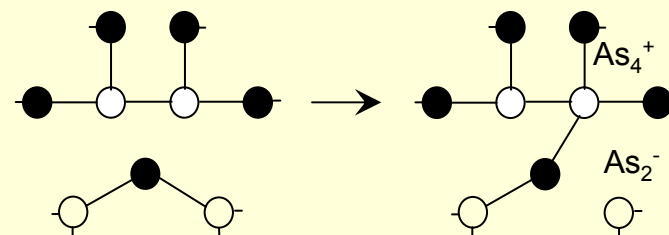
No 13: $\text{As-S} \rightarrow \text{As-S}$
No homopolar bond in the final stage



No 14: $\text{As-S} \rightarrow \text{As-S}$
No homopolar bond in the final stage



No 15: $\text{As-S} \rightarrow \text{As-S}$
1 (S-S) homopolar bond in the final stage

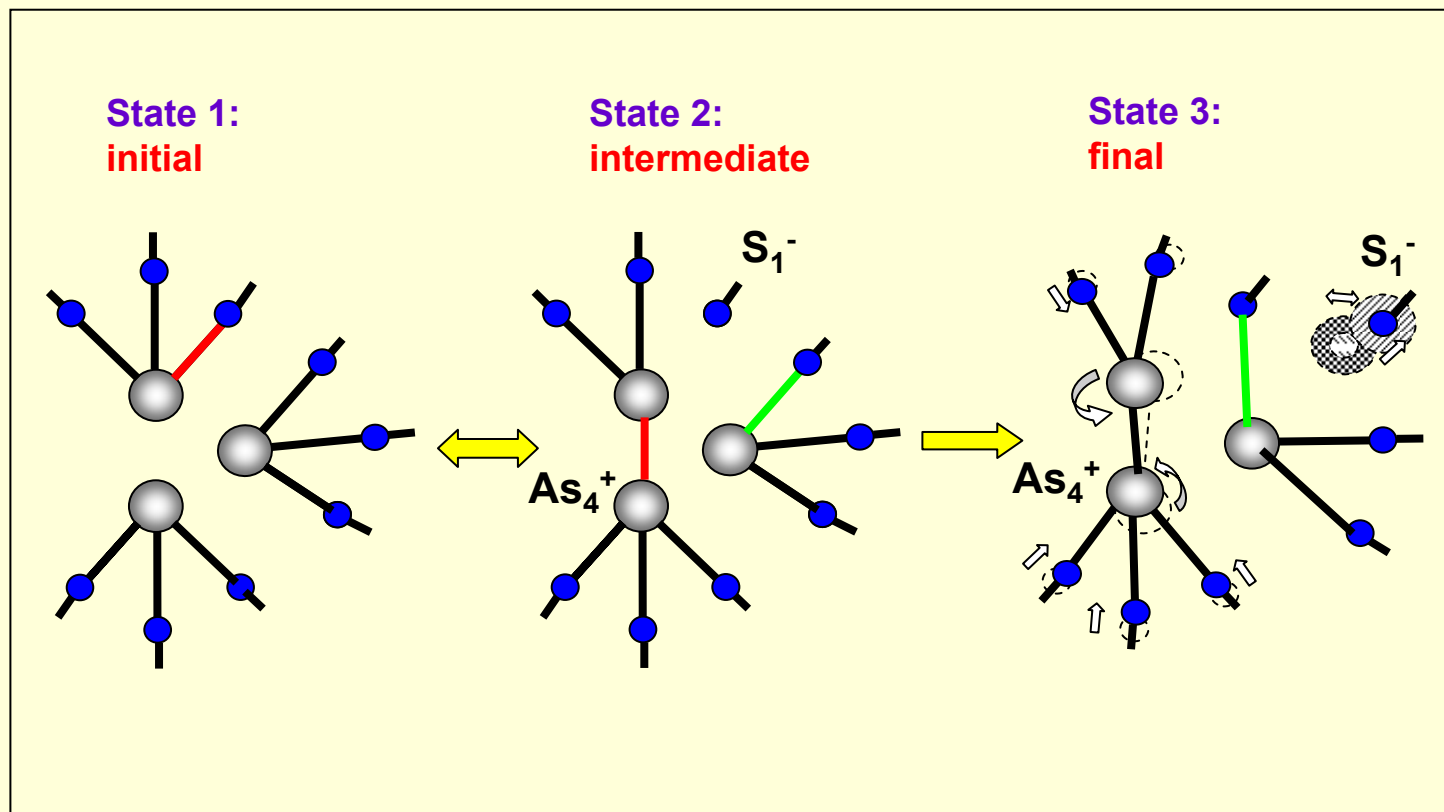


No 16: $\text{As-S} \rightarrow \text{As-S}$
1 (As-As) homopolar bond in the final stage

Nanostructural nature of reversible γ -induced effects in ChVSs

On the origin of reversible radiation-structural transformations

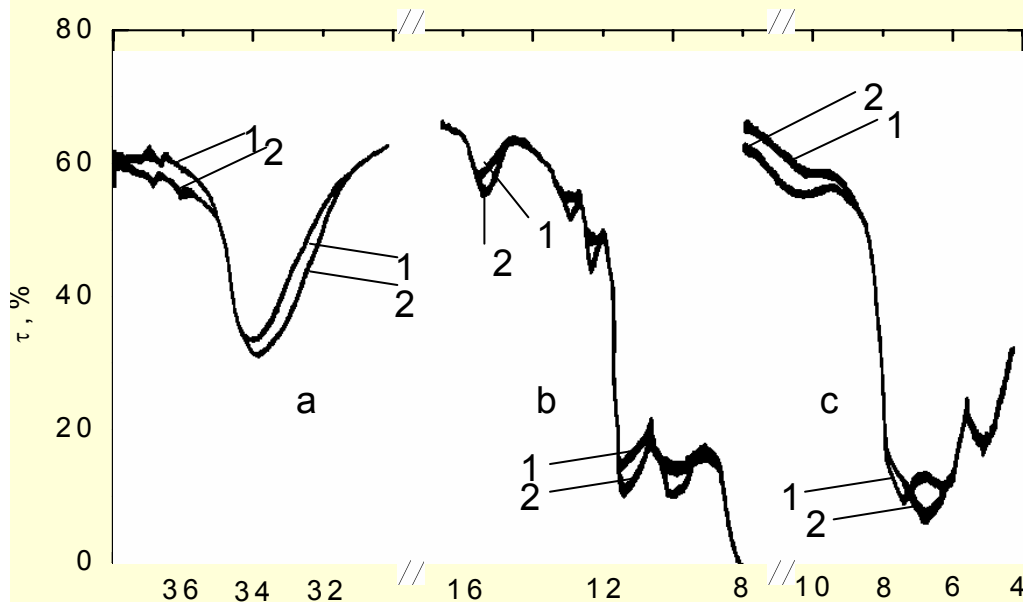
Metastable CTD formation in ChVSs exemplified by $v\text{-As}_2\text{S}_3$:
full cycle for reversible CTD-related destruction-polymerization transformations



Topological schemes of CTD-conserved bond switching in $v\text{-As}_2\text{S}_3$,
accompanied by a simultaneous separation of anomaly coordinated atoms
with an additional free volume appearance

On the origin of irreversible γ -induced structural transformations in ChVS

Radiation impurities in $v\text{-As}_2\text{S}_3$ by IR Absorption



IR transmission spectra of $v\text{-As}_2\text{S}_3$ before (1) and after (2) γ -irradiation ($\Phi=10.0$ MGy, $P=25$ Gy/s) with sample thickness of 12 (a, b) and 1.5 mm (c).

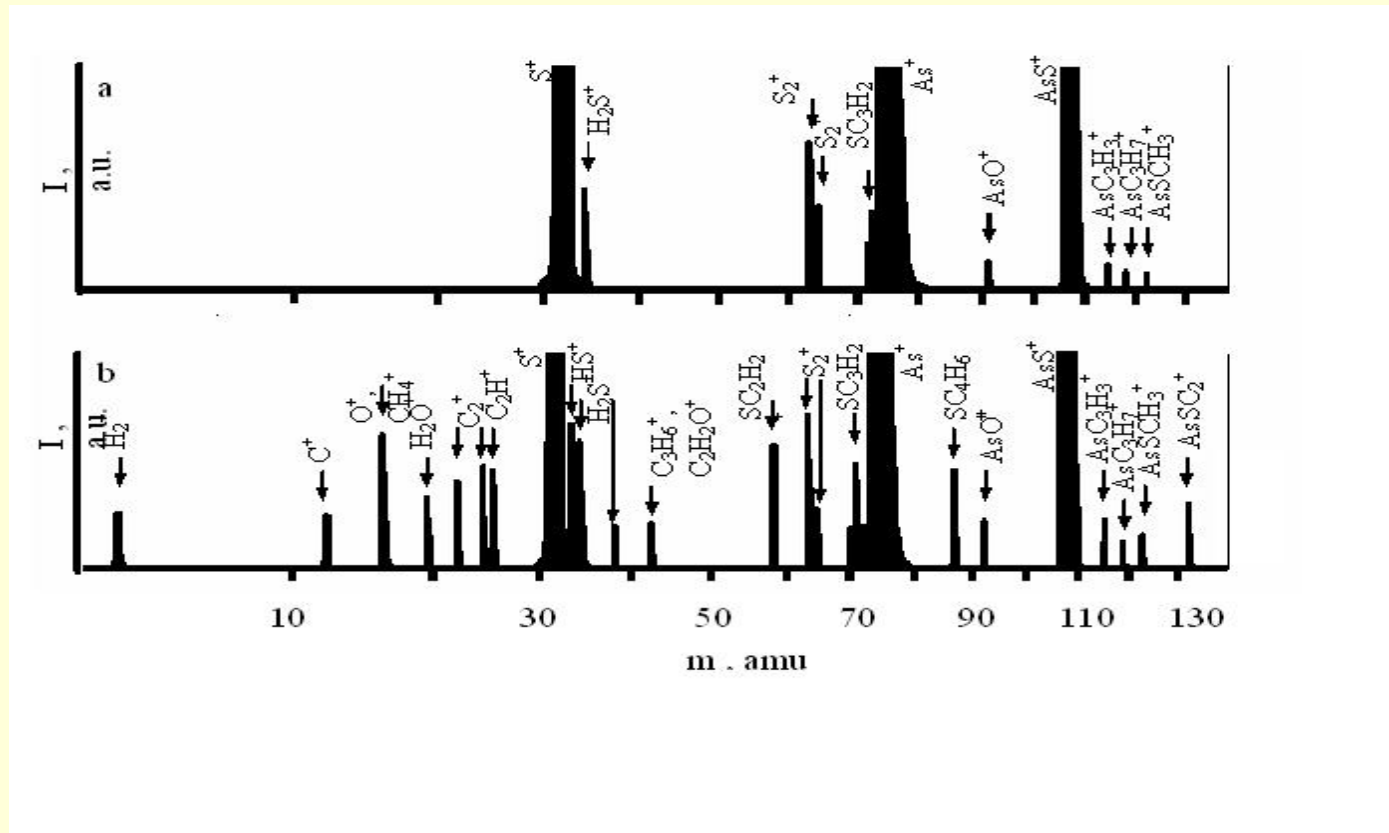
Vibration modes of some impurity complexes in $v\text{-As}_2\text{S}_3$ –

γ -induced mass-transfer chemical interactions between own and impurity structural fragments

As_4O_6	1340, 1265, 1050 and 785 cm^{-1}
SO_2	1150 and 1000 cm^{-1}
H_2S	2470 cm^{-1}
H_2O	3650-3500 cm^{-1} , 1580 cm^{-1}
=As–OH	3470-3420 cm^{-1}
Intrinsic 2- and 3-phonon vibration absorption bands:	
–S–S–	940 and 490 cm^{-1}
$\text{AsS}_{3/2}$ pyramids	750-600 cm^{-1}

On the origin of irreversible γ -induced structural transformations in ChVS

Radiation impurities in $v\text{-As}_2\text{S}_3$ by Mass Spectrometry



Fragment of mass-spectrum from the surface of non-irradiated (a) and γ -irradiated ($\Phi=10.0$ MGy, $P=25$ Gy/s) in the third cycle $v\text{-As}_2\text{S}_3$ (b)

On the origin of irreversible γ -induced structural transformations in ChVS

Types of irreversible radiation-structural transformations

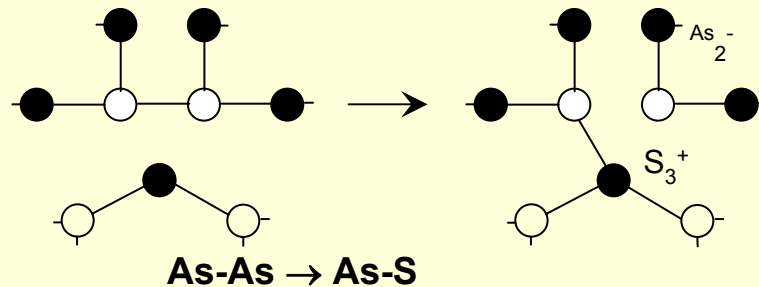
OWN INTRINSIC:

destruction-polymerization transformations having a positive difference ΔE in dissociation energies for created E_c and destroyed E_d covalent bonds with heteropolar environment in the nearest vicinity of the created CTD

IMPURITY-related:

chemical interaction between intrinsic structural complexes of a glassy-like network and absorbed impurities

Examples (for $v\text{-As}_2\text{S}_3$)



Oxidation:

molecular As_4O_6 and SO_2 ; $=\text{As}-\text{O}-\text{As}=\text{}$ bridges

Hydrogenization:

molecular H_2S ; **H-S-** fragments

Hydration:

molecular H_2O ; $=\text{As}-\text{OH}$ and $-\text{S}-\text{OH}$ complexes

Carbonization and hydrocarbonization:

C_nH_m groups linked with own structural fragments

Some practical aspects of γ -induced effects in ChVSs

Industrial ChVS-based optical dosimetric systems – I

There is a problem:

industrial dosimetric systems for high-energy ionizing irradiation

The known resolution – the coloring oxide glasses

(such as fluorite glasses) with optical band intensity dependent on the absorbed irradiation dose.

Main advantages:

- significant simplicity in the using and manufacture,
- high resistance to the external influences.

Main disadvantages:

- registered doses no more than 1 MGy,
- high-temperature annealing to restore initial optical properties (800-1000 K).

An alternative resolution – ChVS-based optical dosimetric systems:

♣ Shvets D., Shpotyuk O., Savytsky I. Solid dosimeter of ionizing irradiation //

USSR Patent certificate No 1349520, IPC G01T1/06, 1987;

♣ Kornelyuk V., Savytsky I., Shpotyuk O. Dosimeter of ionizing irradiation //

USSR Patent certificate No 1428010, IPC G01T1/06, 1988;

♣ Shpotyuk O., Kovalskiy A., Shpotyuk L. Radiation-sensitive element of semiconductor dosimeter of ionizing irradiation // USSR Patent certificate No 1482423, IPC G01T1/24, 1989;

♣ Shpotyuk O., Kornelyuk V. Material for active media for information recording by high-energy ionizing irradiation // USSR Patent certificate No 1496522, IPC G11C13/04, 1989;

♣ Shpotyuk O., Kovalskiy A., Vakiv M., Shpotyuk L. The way to determine the absorbed dose of gamma-irradiation // USSR Patent certificate No 1491188, IPC G01T1/24, 1989;

♣ Shpotyuk O., Kornelyuk V. Dosimeter of ionizing irradiation //

USSR Patent certificate No 1533519, IPC G01T1/06, 1989;

♣ Shpotyuk O., Shpotyuk L. The way to perform the sensitive element of solid dosimeter of ionizing irradiation // USSR Patent certificate No 1681656, IPC G01T1/06, 1991;

♣ Kornelyuk V., Minaev V., Shpotyuk O. Dosimeter of ionizing irradiation //

USSR Patent certificate No 1748524, IPC G01T1/06, 1992.

Some practical aspects of γ -induced effects in ChVSs

Industrial ChVS-based optical dosimetric systems – II

Typical example: $v\text{-As}_2\text{S}_3$ -based optical dosimeter for 0.1-10.0 MGy doses

Radiation-sensitive element:

- plane-parallel plate of 1-2 mm thickness alumina-polished to a high optical quality

Additional advantages:

- post-irradiation stability at the S.C.;
- independence on dose power ($P < 10$ Gy/s);
- $\lambda = 633$ nm (He-Ne laser) in optical recognition.

Control parameter:

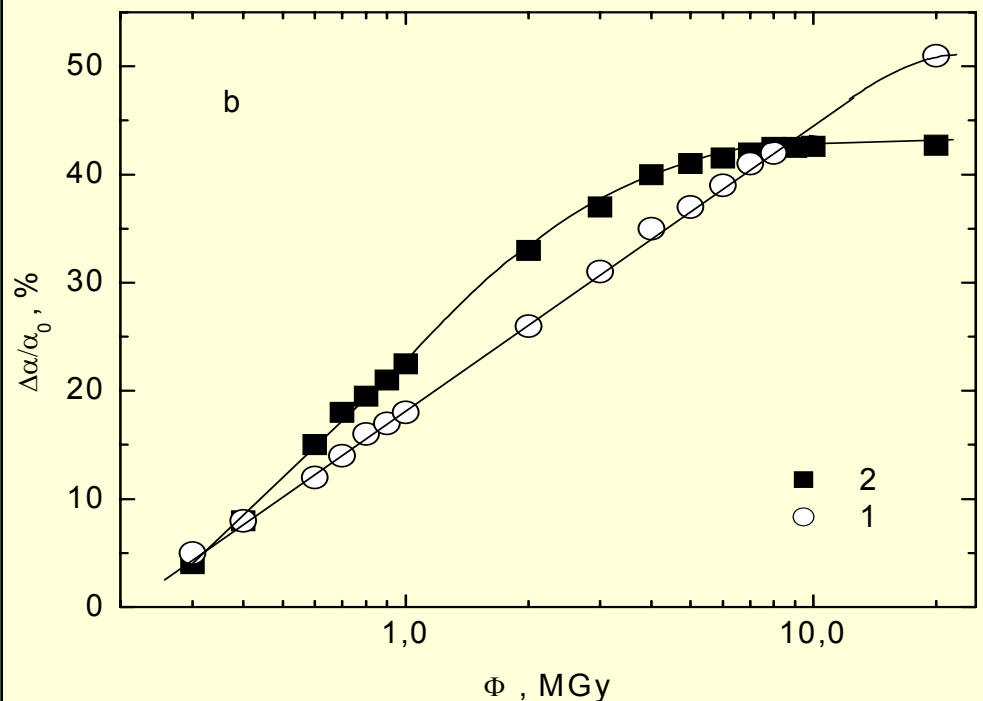
optical density D (or optical absorption α) measured at the wavelength corresponding to the middle point of the upward part of optical transmission edge (in the fundamental optical absorption edge region).

Dose equation:

$$\Delta D/D_0 = S \cdot \lg \Phi + A,$$

D_0 is optical density of non-irradiated glass, S and A – material-related constants.

Dosimetric characteristics (1 – $P \sim 5$ Gy/s; 2 – $P \sim 25$ Gy/s)



Modeling function for dose dependence – de Bast-Gilard, Williams-Watts or Kohlrausch-Williams-Watts (KWW) relaxation function:

$$\chi_0 = 42.49; \kappa = 0.84; \Phi_0 = 1.3$$

$$\chi = \chi_0 \left(1 - e^{-\left(\frac{\Phi}{\Phi_0}\right)^\kappa} \right)$$

Some practical aspects of γ -induced effects in ChVSs

Post-technological radiation modification route

Historical background of the problem:

The first experiments on post-technological utilization of high-energetic ionizing irradiation (accelerated electrons with $E > 2$ MeV energy) to modify physical properties of bulk ChVSs were performed by scientific group of **Sh.Sh. Sarsembinov** (Kazakh State University, Alma-Ata, Kazakhstan) in the early 80-s.

Possibilities for γ -aided post-technological modification route:

A number of exploitation properties of ChVSs can be well modified by high-energy ^{60}Co γ -irradiation ($E = 1.25$ MeV) performed within a stationary radiation field with accumulated doses of $\Phi = 0.5 - 10.0$ MGy:

- *microhardness and other mechanical properties;*

- *optical properties* (spectral position and slope of the fundamental optical absorption edge):

[Shpotyuk O., Kushnir Z., Vakiv M. Chalcogenide glass for optical fiber // USSR Patent certificate No 1380183, IPC C03C3/32, C03C13/00, 1987]

[Shpotyuk O., Kovalskiy A., Shpotyuk L. The way to perform fiber // USSR Patent certificate No 1452050, IPC C03B37/00, 1988]

- *acoustic velocity and acoustooptical figure of merit:*

[Shpotyuk O., Savchuk R., Savytsky I. The way to perform acoustooptical element // USSR Patent certificate No 1394966, IPC G02F1/11, G02F1/33, 1988]

- *photosensitivity (of thin ChVS-based films):*

[Shpotyuk O., Matkovsky A., Kornelyuk V., Savytsky I. The way to perform optical information vehicle based on arsenic selenide //

USSR Patent certificate No 1241931, IPC H01L21/263, G03H1/18, 1986]

- *electrical conductivity:*

[Shvets D., Shpotyuk O., Matkovsky A., Kavka I., Kovalskiy A. The way to change electroconductivity of arsenic selenide //

USSR Patent certificate No 1330944, IPC C03C23/00; C03B25/00, 1986]

Instead of Final Remarks:

How far should we go to control externally-attained functionality in ChVSs

? ? ?

Unresolved problems in the field of externally-attained functionality:

♥ **Compositional trends:**

fragile vs. strong glass-formers,
sulphide- vs selenide- vs telluride-contained glassy-like networks
monoatomic vs binary vs ternary vs quaternary glass-forming systems

♥ **Structural trends:**

atomic- vs void-species structure
atomic vs electron-defec sub-systems

♥ **Technological trends:**

glass-making through combined
conventional melt-quenching and post-technological routes