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Radiation-induced modification effects in covalent-network glass formers: Phenomenological description within unified configuration-enthalpy model

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ABSTRACT

Externally-induced modification activated by high-energy excitation such as γ-irradiation from ^{60}Co source is analyzed in chalcogenide glasses in terms of radiation-structural and glass-relaxation metastability, at the example of sulphides (including stoichiometric arsenic trisulphide, As_2S_3) and selenides. Unified *configuration-enthalpy model* evolving conjugated *configuration-coordinate* (free energy in dependence on configuration coordinate) and *thermodynamic enthalpy* (temperature deviations in enthalpy, configurational entropy or free volume) diagrams is proposed to describe metastability in these glasses under external influences, such as (1) physical ageing, (2) irradiation, (3) thermal annealing, (4) rejuvenation, and their combinations. The model predicts glass stabilization in the *ground state* composed of partial sub-states related to (i) irradiation, (ii) rejuvenation, (iii) annealing, as well as (iv) ideal-glass deep states, connected by *over-barrier jumping* and *through-barrier tunneling* transitions. This model allows an adequate parameterization of optical responses related to metastability in these glasses defined through blue (bleaching) or red (darkening) shift in their optical transmission spectra.

1. Introduction

Chemical compounds of chalcogens (S, Se, Te) with some representatives from IV-V groups (mostly P, As, Sb, Bi, Si, Ge) obtained by quenching from a melt liquid state, also referred to as chalcogenide glasses (ChG), make an important class of vitreous media for promising applications in optics, optoelectronics, optotelecomunication and photonics (Adam and Zhang, 2013; Adam et al., 2015; Feltz, 1993). Because of the variety of metastable states available for ChG-forming networks possessing completely saturated covalent bonding, unique multifunctionality of ChG can be essentially governed by external factors, such as high-energy irradiation, photoexposure thermal annealing, etc. (see, Shpotyuk, 2004; Shpotyuk et al., 2013). Different levels of structural metastability can be activated in ChG under these external influences, which results in complexity of their ordering, morphology and defect arrangement (Popov et al., 1983; Popov, 2004).

To recognize externally-induced metastability in ChG, several kinds of configuration-coordinate diagrams (CCD) were developed considering specificity of modification influence (see, e.g., Amin, 2001; Balitska and Shpotyuk, 2011; Kavetskyy et al., 2008; Kolobov et al., 1981; Kolobov and Tanaka, 2001; Shpotyuk O., 2004; Wu and Chen, 1986). Typically, these CCD assume ground state built of double-well potentials with distinct inter-barrier walls separating metastable state(s), so that ChG can be transferred in metastable state under excitation and returned back under annealing (Kolobov, 2003; Tanaka et al., 2009). For high-energy excitations such as considered by (Balitska and Shpotyuk, 2011; Kavetskyy et al., 2008; Shpotyuk, 2004), these diagrams are configurational snapshot of free energy E landscape, which include metabasins built of many tiny basins corresponding to stability of smaller configurations defined by some generalized coordinate q. Appearance/disappearance of structural defects, their stability/instability in glassy network, restoration/generation in ground state are

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described within CCD by vertical transitions through intermediate *exc*-state (radiative and non-radiative), thermally-activated direct *over-barrier jumping* and horisontal *through-barrier tunneling* transitions (see, e.g., Balitska and Shpotyuk, 2011). Alternatively, the phase transformations in ChG under external excitations can be well described within thermodynamic enthalpy diagrams (TED), showing temperature variations of enthalpy, configurational entropy or free volume in melt liquid (ML), super-cooled liquid (SCL), hyper-quenched glass (HQG), crystal ground (CG) and glass ground (GG) states (see, e.g., Cangialosi, 2014; Struik, 1978). The formalism of energy landscape describing photostructural changes in ChG due to individual bond breaking and photoexcitation of bonding electrons during irradiation was developed by (Lucas, 2006; Lucas and King, 2006). The photostructural changes in As–S films under absorbed light illumination were treated by (Kimura et al., 1981) as tending the system towards or backwards equilibrium of extrapolated SCL. This idea was further employed to merge energy variations in ChG walking through configurations and thermodynamic equilibrium states within combined model, comprising simultaneous visualization of both the CCD and TED. This approach was reconsidered by (Tanaka and Shimakawa, 2011) to explain changes between ML, SCL, CG and GG states ascribing multi-well equilibria for a glass, and sharp single or double-well polymorphous minima for a crystal. Recently, (Shpotyuk et al., 2019) reconstructed the model evolving conjugated CCD and TED for As–S glasses to clarify optical responses in their functionality modified under high-energy γ-irradiation.

The objective of current work is to reconstruct unified *configuration-enthalpy model* (CEM) using conjugated CCD-TED related to metastability in diverse group of ChG exemplified by sulphides and selenides undergoing structural transformations by relaxation (enthalpy recovery or physical ageing), thermal annealing, rejuvenation, and γ-irradiation.

2. Experimental

Optical responses were examined in glassy arsenosulphides g-As_xS_{1-x} from the region of their good glass-forming ability covering the compositional range of $0.30<x<0.42$ (Shpotyuk et al., 2014, 2017, 2018). The samples prepared by vibrational melt-quenching from purified elemental ingredients were affected to below-T_g annealing before irradiation. The γ-irradiation was carried out at the ambient conditions of ^{60}Co source (1.25 MeV) with doses of $\Phi\sim(0.5–3.0)$ MGy. The optical transmission spectra were recorded for polished disc-like samples (~1–1.5 mm) in fundamental absorption edge region in few days after γ-irradiation and one month later (to exclude post-irradiation decay). The *in-situ* measurements in backward chronology (Golovchak et al., 2006; Shpotyuk et al., 2013) was utilized for γ-irradiated samples in *irr*-state under transition to post-irradiation below-T_g annealed *ann*--state, and affected to rejuvenation by the same over-T_g heating/cooling. The accuracy of *in-situ* optical transmission for all the examined ChG samples was within a typical error-bar of optical spectrophotometry (±0.5%).

Thermodynamic heat-transfer responses were derived from DSC (differential scanning calorimetry) traces collected for glassy arsenoselenides g-As_xSe_{1-x} from glass-forming region (Golovchak et al., 2005, 2006, 2010; Shpotyuk and Golovchak, 2006). The samples were prepared by vibrational melt-quenching using the high purified elemental constituents. The NETZSCH 404/3/F microcalorimeter pre-calibrated with standard elements (such as In, Sn, Zn and Al) was used for the DSC traces recording. All measurements were performed in triplicate at the ambient atmosphere and 1.67 K/min heating rate as described in more details in (Golovchak et al., 2005).

3. Results and discussion

3.1. Short overview of principal peculiarities defining externally-induced metastability

Optical measurements in *backward chronology* allows to avoid inaccuracies due to sample positioning in spectrometer chamber, providing breakthrough solution in phenomenology of *in-situ* radiation-optical measurements. As an example, the optical transmission spectra of stoichiometric g-$As_{40}S_{60}$ and over-stoichiometric g-$As_{42}S_{58}$ recorded *in-situ* for the same glass sample taken in γ-irradiated state (black curve), then annealed at 20 K below T_g (red curve), and transferred to rejuvenated state (blue curve) are reproduced on Fig. 1. Strong *bleaching* is evident for γ-irradiated samples as a result of thermal annealing followed by post-rejuvenation *darkening*, in respect to (Shpotyuk et al., 2014, 2017, 2018). The optical transmission spectra of these ChG differ essentially in the above states, providing information on magnitudes of intrinsic effects of radiation modification and thermally-assisted physical ageing.

It is known that γ-irradiation possesses acceleration effect of physical ageing in a great variety of ChG (see, Golovchak et al., 2005, 2006, 2010; Shpotyuk and Golovchak, 2006; Shpotyuk et al., 2013). Comprehensive research on γ-induced ageing in As–S and As–Se ChG (Shpotyuk, 2004) shows that despite similarity, compositional dependence of radiation-induced changes depends on chalcogen atoms. Thus, considerable radiation-induced effect was recorded in g-As_xS_{100-x} within $30\leq x\leq 42$ range (see Fig. 2), but not in g-As_xSe_{100-x}. This result correlates with γ-induced changes in mechanical properties of ChG, showing decaying in the following compositional row $As_2S_3 \rightarrow As_2Se_3 \rightarrow As_2Te_3$ (Shpotyuk, 2004).

An increased rate of recovery toward the equilibrium state was found in chalcogen-rich ChG (Shpotyuk, 2004; Shpotyuk et al., 2014). Physical ageing under γ-irradiation causes greater changes in glass-transition temperature T_g and endothermic peak area below DSC curve of glassy selenides, as shown on Fig. 3 for g-$As_{10}Se_{90}$ (Golovchak et al., 2010).

Decrease in chalcogen content reduces radiation-assisted physical ageing, so we can speak on accelerated ageing due to irradiation only in chalcogen-rich ChG (Shpotyuk et al., 2013). Bleaching is recorded in ChG after prolonged storage in normal conditions (excluding any uncontrolled influences such as sun light or thermal heating), as it follows from difference in optical transmission for 20 years aged and annealed g-$As_{10}Se_{90}$ samples determined in °C at the right panel (see Fig. 4).

3.2. Unified configuration-enthalpy model of externally-induced metastability

The unified configuration-enthalpy model of externally-induced metastability in ChG (sulphides and selenides) can be reconstructed on the basis of the above principal peculiarities in their radiation-optical and thermodynamic heat-transfer responses as shown on Fig. 5.

The left panel on Fig. 5 is CCD of structural states available in ChG for work point walking along potential energy states (sub-states) excited through transient *exc*-state. The CG state shown by dashed curve is single-well potential, corresponding to most favorable state of the system. The GG state shown by bold curve is multi-well potential composed of four wells due to rejuvenated (*rej*-state), annealed (*ann*-state), irradiated *(irr*-state) and Ideal Glass (IG) *deep* sub-states. Through-barrier tunneling transitions between these GG sub-states are denoted by bold horizontal arrows from energy minima of respective well, and over-barrier jumping transitions are shown by curved arrows above walls of neighboring free energy minima. The right panel on Fig. 5 represents TED (temperature deviations in enthalpy, configurational entropy or free volume) showing red and blue shifting in optical gap, corresponding to long- and short-wave shifts in optical transmission edge of ChG.

Radiation-optical responses dominate in melt-quenched glassy arsenosulphides (such as g-As_xS_{100-x}) due to redistribution of atomic sites in *rej*-, *ann*-, *irr*-states (Fig. 5, the left panel). The short-wave shift

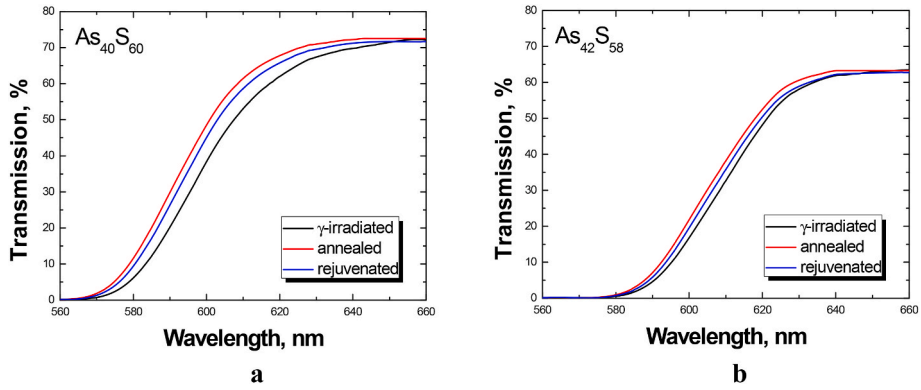

Fig. 1. Optical transmission spectra recorded in backward *in-situ* measuring chronology for samples of stoichiometric g-$As_{40}S_{60}$ (a) and over-stoichiometric g-$As_{42}S_{58}$ (b) in γ-irradiated (black curve), then below-T_g annealed (red curve) and rejuvenated (blue curve) states.

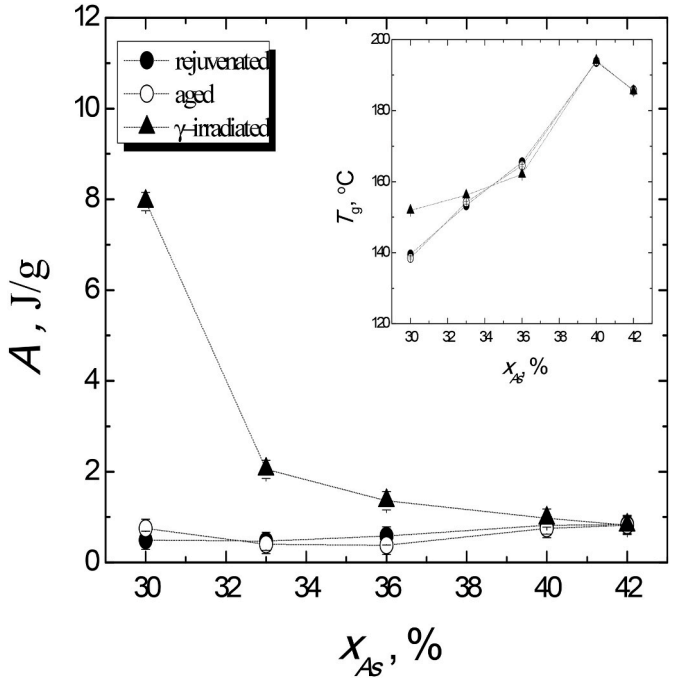

Fig. 2. Compositional dependences of DSC curve area *A* and onset glass-transition temperature T_g (insert) for g-As_xS_{100-x} in rejuvenated (full circles), aged (open circles) and γ-irradiated (full triangles) states, determined from DSC measurements with 5 K/min rate.

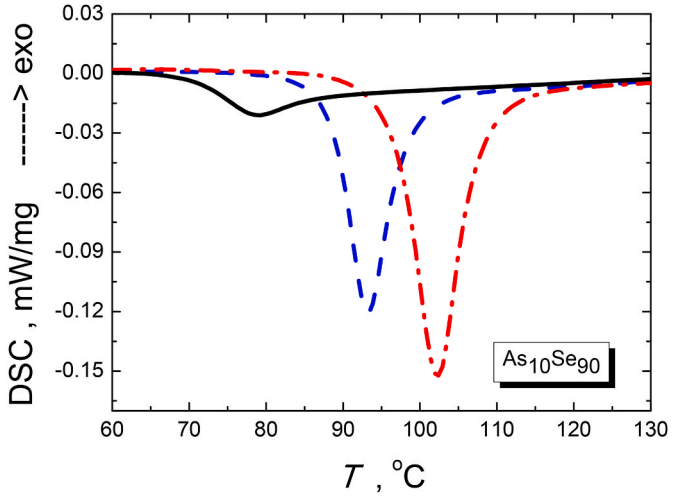

Fig. 3. DSC curves for g-$As_{10}Se_{90}$ after equal periods of natural storage (blue dash curve) and within γ-radiation (red dash-dotted curve). The black solid curve corresponds to DSC signal from glass sample in initial (as-prepared or rejuvenated) state.

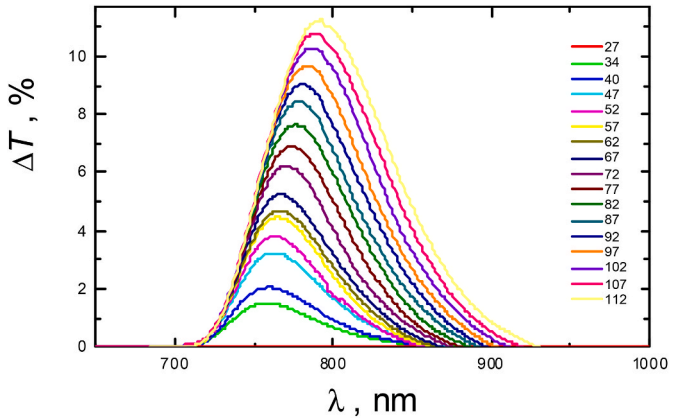

Fig. 4. Difference in optical transmission spectra (Δ*T*) for two-decades stored g-$As_{10}Se_{90}$ of ~1 mm thickness subjected to annealing with 1.67 K/min steps at the increased temperatures as indicated (in °C) at the right-side panel.

(*viz*. blue shift or bleaching) in optical transmission of γ-irradiated samples (such as g-$As_{40}S_{60}$ and g-$As_{42}S_{58}$ on Fig. 1) after thermal annealing is caused by destruction-polymerization transformations (DPT) in these ChG resulting in disappearing of coordination topological defects (CTD) in their networks. The total γ-induced effect is compared with static, which left after decaying of dynamic component (Shpotyuk, 2004). The long-wave shift in optical transmission in γ-irradiated ChG (red shift or darkening) is produced by CTD (atomic sites in unfavorable *irr*-state with highest minimum of free energy, see Fig. 5). Deviations from stoichiometry to S- or As-rich compositions reduce γ-induced darkening. For S-rich ChG rejuvenated after irradiation, the bleaching is anticipated as result of γ-assisted physical ageing (not CTD). Difference in optical transmission for glasses in *ann*- and *rej*-state confirms this conclusion, showing bleaching because of thermally-induced aging of rejuvenated ChG samples. Thus, γ-induced changes can be considered as result from balance of competitive processes, such as DPT (including CTD formation) and ageing enhanced under γ-irradiation (see, Shpotyuk et al., 2013).

Thermodynamic heat-transfer responses prevail in melt-quenched glassy arsenoselenides (such as g-As_xSe_{100-x}) due to atomic sites in *rej*-, *ann*- and/or *irr*-states redistributed in respect to *IG deep* state (Fig. 5, the

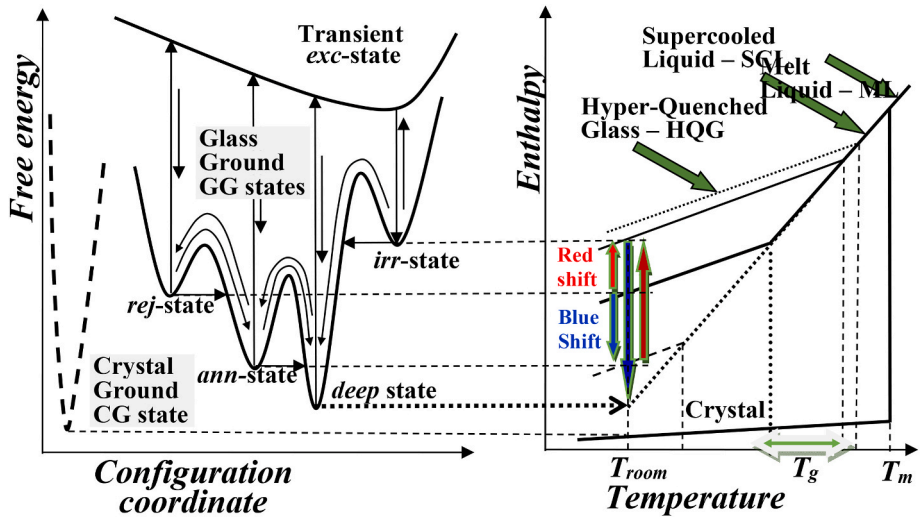

Fig. 5. Unified configuration-enthalpy model (CED) of externally-induced metastability in ChG composed of conjugated *configuration-coordinate diagram* (CCD, the left panel) and *thermodynamic enthalpy diagram* (TED, the right panel).

left panel). The *rej*- and *ann*-states fit just in intermediate position between *IG deep* and *irr*-state, so that relation between enthalpy levels on right-panel TED of Fig. 5 reflects the upwards changes as indicative of red shift (darkening) in optical transmission edge and, *vice versa*, the downwards changes as indicative of blue shift (bleaching) in optical transmission edge.

The *over-barrier jumping* transitions between GG states (sub-states) can be activated by thermal annealing corresponding to the known bleaching and darkening effects in ChG, such as (i) bleaching of rejuvenated ChG under thermally-assisted physical ageing, (ii) darkening of preliminary aged ChG subjected to rejuvenation, and (iii) bleaching of irradiated ChG under above-threshold annealing. In contrast, *through-barrier tunneling* transitions between GG states (sub-states) can be ascribed exceptionally to the known bleaching effects, such as (i) bleaching of rejuvenated ChG due to physical ageing (*rej*-to-*ann* transition), (ii) bleaching of annealed ChG due to additional physical ageing (*ann*-to-*deep* transition), (iii) bleaching of irradiated ChG under prolonged storage in ambient conditions (*irr*-to-*deep* transition).

The population of *irr*-state can be enhanced only through vertical transitions employing relaxation from transient *exc*-state as shown in left-panel CCD on Fig. 5. Direct excitation of the lowest *ann*- or *rej*-state by high-energy irradiation followed by non-radiative relaxation into *irr*-state results in red shift in optical transmission edge (Shpotyuk, 2004). Noteworthy, for glassy selenides, the both *over-barrier jumping* and *through-barrier tunneling* transitions into *IG deep* state and *ann*-state are responsible for accelerated physical ageing under irradiation.

3.3. Phenomenological description of externally-induced metastability in ChG

Balance between relaxation processes in ChG can be described analitycally within unified CED using the known formalism (see, Tanaka, 1986; Balitska and Shpotyuk, 2011).

Let's denote the respective well (basin) for *rej*-, *ann*-, *irr*- and Ideal Glass *deep* states as *R*, *A*, *I*, *D*, and basin for excited state as *E*. For simplicity, equilibrium state of crystal is excluded from consideration due to impossibility of transitions to this state without melting.

Thus, the total number of atomic sites *N* available for externally-induced modification is composed of populations of metastable GG states, Ideal Glass deep state and excited state:

$$\mathrm{N} = \mathrm{NR} + \mathrm{NA} + \mathrm{NI} + \mathrm{ND} + \mathrm{NE}, \tag{1}$$

the latter term being nonzero only under continuous irradiation.

As it was assumed by (Tanaka, 1986), the lifetimes $\tau_{(R,A,I)}$ of atomic sites in metastable GG states *R*, *A* and *I* are determined by thermally-activated transitions followed by through-barrier tunneling into more stable state over corresponding energetic barrier $\Delta E_{(R,A,I)}$

$$\tau_S^{-1} = \nu_S \exp\left(-\Delta E_{(R,A,I)} / kT\right), \tag{2}$$

where ν_s is used to denote "attempt" frequency (that is frequency of site vibrations in a well).

The rate of transitions from metastable GG states can be defined as:

$$\frac{dN_{(R,A,I)}}{dt} = -\frac{N_{(R,A,I)}}{\tau_{(R,A,I)}}. \tag{3}$$

Specifically, there are no transitions of the above type from the Ideal Glass *deep* state. The vertical transitions from metastable GG states *R*, *A* or *I* to *exc*-state *E* depend on γ-quanta flux *Q* and materials-related absorption cross-section from corresponding state $\sigma_{(R,A,I)}$:

$$\frac{dN_{(R,A,I)}}{dt} = -Q\sigma_{(R,A,I)}N_{(R,A,I)}. \tag{4}$$

In a similar manner, the radiative vertical transition of atomic sites from *exc*-state to *irr*-state is dependent on materials-related recombination rate k_r as

$$\frac{dN_E}{dt} = k_r N_E. \tag{5}$$

Thus, a set of differential rate equations describing populations of metastable GG states in ChG affected to physical ageing and γ-irradiation can be written as follows:

$$\begin{cases} \dfrac{dN_R}{dt} = -\dfrac{N_R}{\tau_R} - Q\sigma_R N_R, \\ \dfrac{dN_A}{dt} = \dfrac{N_R}{\tau_R} - \dfrac{N_A}{\tau_A} - Q\sigma_A N_A, \\ \dfrac{dN_I}{dt} = -\dfrac{N_I}{\tau_I} - Q\sigma_I N_I + k_r N_E \\ \dfrac{dN_D}{dt} = \dfrac{N_A}{\tau_A} + \dfrac{N_I}{\tau_I} - Q\sigma_D N_D \end{cases} \tag{6}$$

The system of these equation (6) allows adequate description of relaxation processes in ChG under interest within metastable GG states ascribed to natural and γ-induced physical ageing, as well as thermal annealing and rejuvenation. The real balance of the responsible structural processes depends on ChG specificity (glass composition, thermal

pre-history, and parameters of irradiation influence). Thereby, the developed unified CEM gives an adequate explanation for effects caused by separate influence on ChG, as well as more complicated effects induced by simultaneous or subsequent acting of several factors like irradiation-accelerated or light-assisted physical ageing (see, Shpotyuk et al., 2013).

4. Conclusions

Unified configuration-enthalpy model consisted of conjugated configuration-coordinate (free energy in dependence on configuration coordinate) and thermodynamic enthalpy (temperature deviations in enthalpy, configurational entropy or free volume) diagrams is developed to describe phenomenology of optical responses in structural metastability of chalcogenide glasses exemplified by sulphides (including stoichiometric arsenic trisulphide As_2S_3) characterized by radiation-induced structural metastability and selenides characterized by glass-relaxation metastability. The developed model predicts glass stabilization in the Ideal Glass deep state or metastable ground states activated by irradiation, annealing or rejuvenation, interlinked by thermally-activated over-barrier jumping and through-barrier tunneling transitions. Effects of irradiation is reflected in vertical transitions of atomic sites into excited state followed by non-radiative relaxation in irradiation-induced state. The model allows adequate parameterization of optical responses related to different structural states in glasses, defined in blue (bleaching) or red (darkening) shifting in their optical transmission spectra. The phenomenology of externally-induced metastability in chalcogenide glasses related to short-term and long-term physical ageing, high-energy irradiation, thermal annealing and thermally-stimulated rejuvenation, as well as their combinations, is shown to be adequately described within developed unified configuration-enthalpy model.

CRediT authorship contribution statement

Oleh Shpotyuk: Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Conceptualization. **Mykola Vakiv:** Resources, Funding acquisition, Conceptualization. **Andriy Kovalskiy:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **Roman Golovchak:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation. **Valentina Balitska:** Investigation, Formal analysis, Data curation. **Mykhaylo Shpotyuk:** Writing – review & editing, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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