Thermodynamics of heat-transfer phenomena in *multinanophase* substances exemplified by g-As-Se

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ABSTRACT. Effect of high-energy ball mechanical milling in a dry mode on glassy arsenic selenides g-As_xSe_{100-x} both under-stoichiometric ($x \le 40$) and over-stoichiometric ($x \ge 40$) was first examined with temperature-modulated DSC TOPEM® method complemented with X-ray powder diffraction analysis.
It is shown that **glass transition temperature T_g depressing** is dominant in Se-rich glasses, while an opposite **glass transition temperature T_g enhancement** is character for As-rich glasses. Milling occurs no effect near g-Se ($x < 20$), but causes increase in **the first sharp diffraction peak (FSDP)** width for glasses with $20 \le x \le 40$ due to destroyed remnants of inter-planar ordering. In over-stoichiometric g-As_xSe_{100-x} ($40 \le x \le 75$), remnants of As_4Se_4 and As_4Se_3 molecules are more essentially changed under milling, facilitating formation of chain-like networks.
This milling-driven amorphization results in drastic **increase in the FSDP position and width**, occurring **fragmentation impact on the correlation length** of the FSDP-responsible entities. **Milling-driven breakdown in intermediate-range ordering** is concomitant with destruction of distant inter-atomic correlations belonging to quasi-crystalline planes contributing to the FSDP, while longer inter-atomic correlations become more dominant in their extended-range ordering.

FSDP-related XRPD: formalism

The identity of appeared amorphous phase is clarified due to the X-ray powder diffraction (XRPD) analysis applied to the first sharp diffraction peak (FSDP), which is believed to be a signature of specific structural entities in vitreous substances forming a so-called medium range ordering over a scale of a few tens of Å. Processing of the experimental XRPD-FSDP patterns was performed using STOE WinXPOW 3.03 and PowderCell 2.4 PC programs, following normalization procedure in respect to the intensity of maximum peak. The obtained data were used for next profile fitting of these peaks by WinPLOTR program. The both angular position 2Θ and full width at half maximum (FWHM) were determined with ±0.05° accuracy (dependent on the peak sharpness), they being chosen as main parameters describing the FSDP. Then, the FSDP parameters in a reciprocal space (**scattering vector Q** and **width ΔQ**) were recalculated as:

$$Q = (4\pi/\lambda)\sin\Theta, \quad (1) \qquad \Delta Q = (4\pi/\lambda)\sin(\mathrm{FWHM}/2) \quad (2)$$

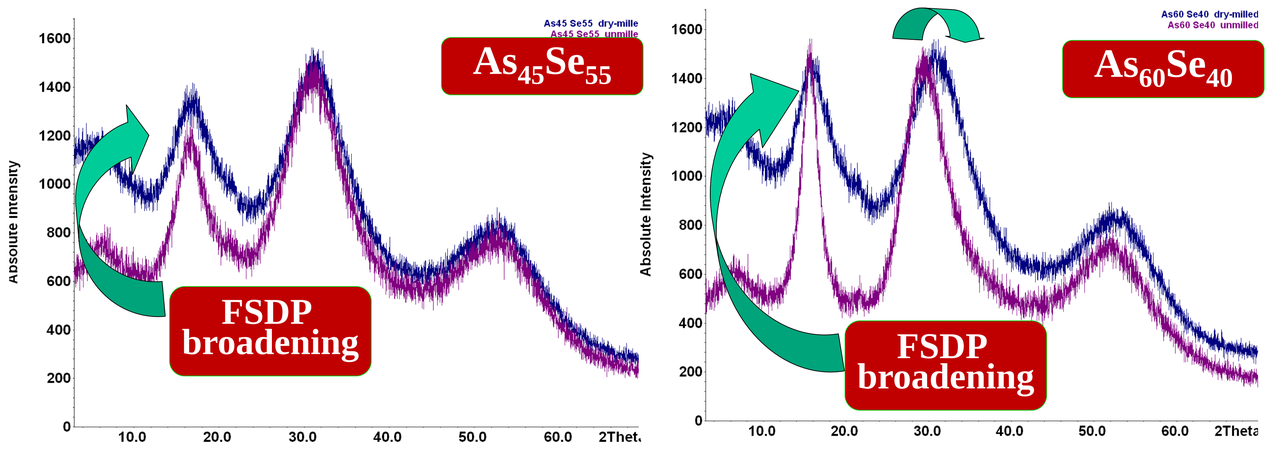
Additionally, **radius of coordination sphere R** and **correlation length L** were obtained from the FSDP parameters, using the Ehrenfest equation ($2R\sin\Theta = 1.23\lambda$) simplified as:

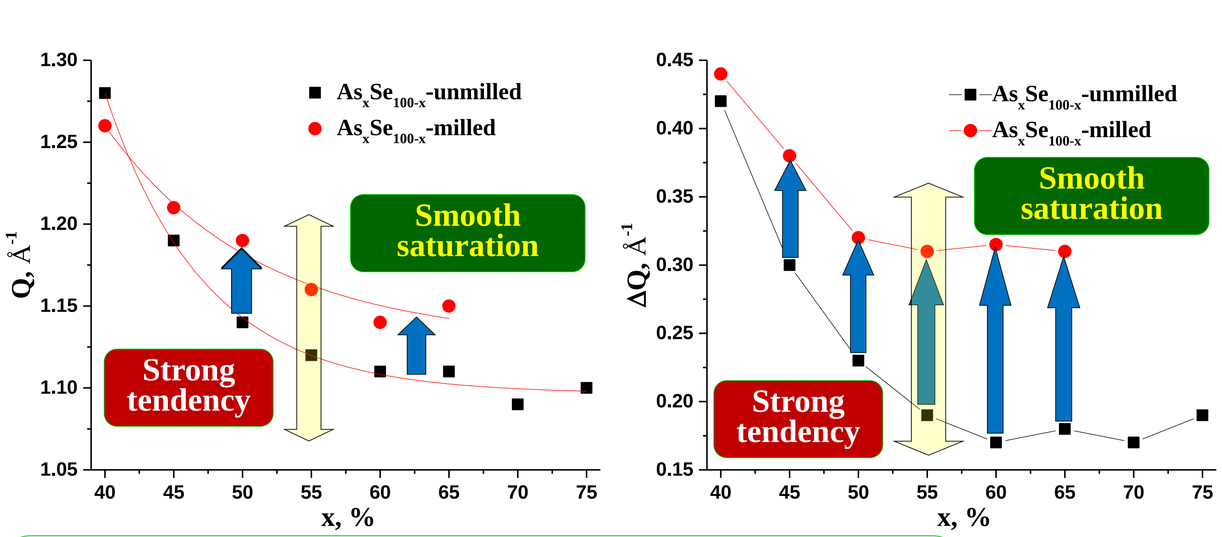
$$R = 2\pi/Q, \quad (3) \qquad L = 2\pi/\Delta Q. \quad (4)$$

FSDP-related correlations in g-As_xSe_{100-x}: effect of high-energy dry mechanical milling

x-milling	2Θ, ^{o}	FWHM, ^{o}	Q, $Å^{-1}$	ΔQ, $Å^{-1}$	R, Å	L, Å
x=75 – no	15.457(8)	2.71(3)	1.10	0.19	5.72	32.60
x=70 – no	15.318(5)	2.33(1)	1.09	0.17	5.78	37.90
x=65 – no	15.641(5)	2.49(1)	1.11	0.18	5.66	35.52
x=65, mill	16.170(13)	4.42(4)	**1.15**	**0.31**	5.48	19.98
x=60 – no	15.600(5)	2.43(1)	1.11	0.17	5.68	36.34
x=60, mill	16.108(13)	4.43(4)	**1.14**	**0.315**	5.50	19.92
x=55 – no	15.826(6)	2.63(2)	1.12	0.19	5.60	33.54
x=55, mill	16.286(12)	4.36(4)	**1.16**	**0.31**	5.44	20.26
x=50 – no	16.130(8)	3.21(2)	1.14	0.23	5.49	27.52
x=50, mill	16.608(13)	4.55(4)	**1.19**	**0.32**	5.33	19.42
x=45 – no	16.771(10)	4.20(3)	1.19	0.30	5.28	21.02
x=45, mill	17.104(16)	5.41(5)	**1.21**	**0.38**	5.18	16.33
x=40 – no	18.053(15)	5.96(5)	1.28	0.42	4.91	14.82
x=40, mill	17.842(16)	6.24(5)	**1.26**	**0.44**	4.97	14.14

FSDP in over-As-Se: correlations with dry-milled phases





Conclusion:

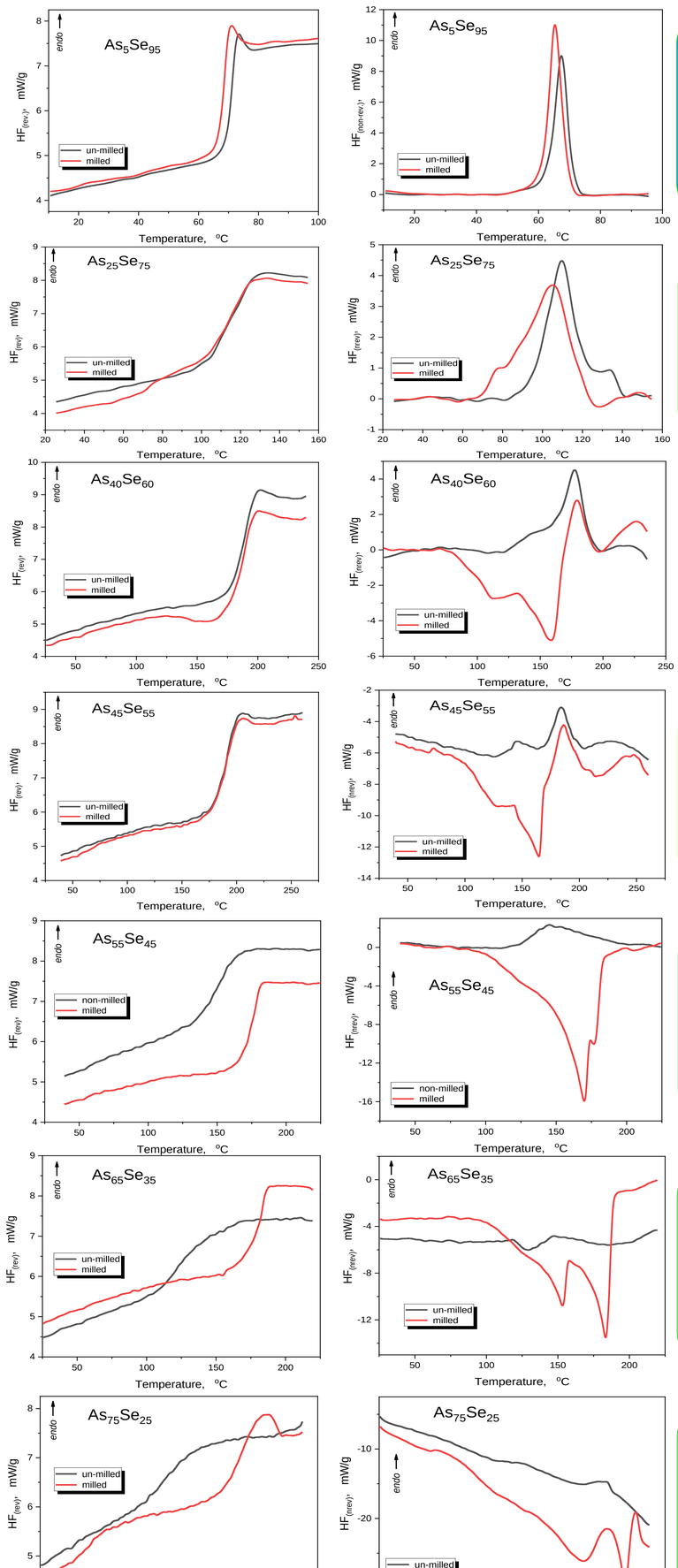
Milling-driven *molecular-to-network transition* in As-rich g-As-Se

DSC TOPEM®: formalism

Calorimetric heat capacity measurements were performed employing **multi-frequency DSC TOPEM®** with DSC-1 calorimeter (Mettler-Toledo, Switzerland). In this method, the stochastic temperature modulations are superimposed on underlying rate of conventional DSC scans, resulting in distinguished frequency-dependent and frequency-independent phenomena. This provides more information concerning thermodynamic stability of the revealed phases, which is expected to be important in the case of phase-changed nanoarsenicals affected by high-energy MM. The DSC TOPEM® instrument was equipped with FRS5+ sensor and HT100 (Huber, Germany) intracooler, the STAR^e ver. 16 software being used to control experimental conditions and process the data. The calorimeter was calibrated using In and Zn standard samples.

The tested samples (ca. 10-15 mg) were encapsulated in sealed 25μL aluminium pan kept in protective N_2 atmosphere, and scanned at the rate of 1.0 K·min^{-1} stochastically modulated in pulses between 15 and 40 s, pulse height being 1 K. All evaluations (reversive and non-reversive TOPEM® heat flow components), were adjusted using sapphire reference curve, the width and shift of calculation window being 90 s and 1 s, respectively.

Glass composition		HF_{rev} T_g^{onset} °C	HF_{rev} T_g^{mid} °C	HF_{rev} ΔC_p Jg^{-1}K^{-1}	HF_{nrev} ΔH Jg^{-1}
As_5Se_{95}	un-milled	69,3	70,7	0,14	3,32
	milled	66,7	68,0	0,15	3,86
$As_{25}Se_{75}$	un-milled	102,4	115,8	0,17	5,43
	milled	96,0	112,3	0,19	6,39
$As_{40}Se_{60}$	un-milled	179,0	187,4	0,20	6,68
	milled	178,3	185,9	0,20	-10,86
$As_{45}Se_{55}$	un-milled	183,9	190,0	0,17	3,82
	milled	182,0	188,7	0,17	-9,59
$As_{55}Se_{45}$	un-milled	134,6	151,8	0,11	5,57
	milled	170,0	174,6	0,13	-29,70
$As_{65}Se_{35}$	un-milled	106,8	132,6	0,11	0,71
	milled	176,3	180,1	0,13	-28,80
$As_{75}Se_{25}$	un-milled	116,9	148,5	0,08	-0,42
	milled	188,0	200,8	0,08	-21,39



Milling-driven decrease in glass transition temperature ΔT_g^{onset} = -2.6 K; ΔT_g^{mid} = -2.7 K

Milling-driven decrease in glass transition temperature ΔT_g^{onset} = -6.4 K; ΔT_g^{mid} = -3.5 K

Milling-driven decrease in glass transition temperature ΔT_g^{onset} = -0.7 K; ΔT_g^{mid} = -1.5 K Pre-T_g exotherm effect

Milling-driven decrease in glass transition temperature ΔT_g^{onset} = -1.9 K; ΔT_g^{mid} = -1.3 K

Milling-driven increase in glass transition temperature ΔT_g^{onset} = 35.4 K; ΔT_g^{mid} = 22.8 K Pre-T_g exotherm effect

Milling-driven increase in glass transition temperature ΔT_g^{onset} = 69.5 K; ΔT_g^{mid} = 47.5 K Pre-T_g exotherm effect

Milling-driven increase in glass transition temperature ΔT_g^{onset} = 71.1 K; ΔT_g^{mid} = 52.3 K Pre-T_g exotherm effect