PHYSICAL REVIEW B **78**, 014202 (2008)

Experimental verification of the reversibility window concept in binary As-Se glasses subjected to a long-term physical aging

R. Golovchak*
Lviv Scientific Research Institute of Materials of SRC "Carat," 202 Stryjska Str., Lviv UA-79031, Ukraine
and Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, Pennsylvania 18015-3195, USA

H. Jain
Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, Pennsylvania 18015-3195, USA

O. Shpotyuk
Institute of Physics, Jan Dlugosz University, 13/15, al. Armii Krajowej, Czestochowa PL-42200, Poland

A. Kozdras
Physics Faculty, Opole University of Technology, 75, Ozimska Str., Opole PL-45370, Poland

A. Saiter and J.-M. Saiter
Laboratoire PBM, UMR 6522, LECAP, Faculté des Sciences, Institut des Matériaux de Rouen, Université de Rouen, Avenue de l'Université, BP 12, 76801 Saint Etienne du Rouvray, France

(Received 28 April 2008; published 3 July 2008)

Physical aging effects caused by prolonged natural storage (~22 years) in binary As_xSe_{100-x} glasses are probed by temperature-modulated differential scanning calorimetry. It is shown that all aged samples with $x < 40$ reveal nonzero out-of-phase component of complex heat flow testifying physical aging effect. The first composition, which can be attributed to a so-called self-organized phase characterized by the absence of natural physical aging effect, is the stoichiometric As_2Se_3 glass; lack of aging within the so-called reversibility window, $28 < x < 38$, is not found. High-resolution x-ray photoelectron spectroscopy fails to show any evidence of fourfold-coordinated As atoms, which is consistent with the aging ability of glasses with $x < 40$.

DOI: 10.1103/PhysRevB.78.014202 PACS number(s): 61.43.Fs, 64.70.ph, 81.70.Pg, 82.80.Pv

I. INTRODUCTION

Recently, several groups have attempted to explain the compositional trends of physical aging of chalcogenide glasses by mean-field theory using constraint counting algorithm.[1–5] According to this approach, glasses having the number of Lagrangian constraints per atom (n_c) less than the space dimensionality [in the case of three-dimensional (3D) space, $n_c < 3$] form underconstrained networks, and those with greater n_c form overconstrained glass networks. Rigidity percolation is expected when the number of Lagrangian constraints per atom is equal to space dimensionality ($n_c = 3$, for instance). Such a glass network is called optimally constrained with fully saturated covalent bonds.[1–5] In the case of 3D space, the number of Lagrangian constraints per atom can be calculated according to[6]

$$n_c = \frac{Z}{2} + (2Z - 3) + \frac{n_1}{N} - \frac{n^{\text{ring}}}{N}, \qquad (1)$$

where $Z = (\Sigma_r r n_r / \Sigma_r n_r)$ average coordination number of the glass network constructed by n_r atoms having r bonds $\Sigma_r n_r = N$; n_1 and n^{ring} are the corrections on dangling bonds and rings, respectively.[6]

The underconstrained glasses ($n_c < 3$) are characterized by a pronounced natural physical aging effect revealed through the drift in their physical properties.[4,7–9] The overconstrained glasses ($n_c > 3$) can be affected by aging too, but the kinetics of relaxation are relatively slower so that high temperatures of storage, i.e., close to the glass transition, are required to produce a measurable relaxation process. At the same time, the glasses with $n_c = 3$ do not exhibit physical aging phenomena and form a so-called self-organized phase.[4] The compositional range of this phase is called the reversibility window.[2–4] Recently, it was suggested that the absence or marginality of "nonreversible" heat flow in temperature-modulated differential scanning calorimetry (DSC) experiments with as-prepared (or few days aged) samples determines the compositional boundaries of reversibility window for different chalcogenide glasses.[2–4] These observations amount to a discrepancy with Phillips-Thorpe percolation theory.[1,6] In As-based binary chalcogenide glasses, particularly the As-Se binary system, Se and As atoms are known to obey the well-known "8-N" rule[10] and the theory based on "pebble game" constraint counting algorithm predicts a reversibility window for such glasses within the range of average coordination numbers Z from ~2.37 to ~2.40 (even if the possibility to form small rings is taken into account).[1] This range can be theoretically extended up to $Z \approx 2.46$ using size increasing cluster approximation algorithm, which assumes that network can self-organize in order to avoid the stress arising from the cross-linking of elements.[11,12]

Thus, two compositional thresholds determine the limits of reversibility window in network glasses: (i) a rigidity transition when the network becomes rigid but remains stressfree (normally occurs at $Z \approx 2.4$ for simple 3D covalent networks such as As-Se) (Refs. 1 and 6) and (ii) a stress transition at which the network cannot avoid the percolation of stressed rigid clusters anymore (depends on constituent structural units of a glass and normally occurs at $Z > 2.4$).[11,12] In other words, the system after rigidity transition point tries to keep $n_c = 3$ as much as possible. However, temperature-modulated DSC experiments give the reversibility window for As_xSe_{100-x} system at much lower Z values, given by $2.28 < Z < 2.38$,[2–4] which corresponds 28 to 38 at. % As. To explain this discrepancy, some authors proposed that a number of As and Se atoms in As_xSe_{100-x} glasses within the $28 < x < 38$ compositional range do not obey the 8-N rule.[2–5] According to one suggestion, these atoms form quasitetrahedral $Se{=}As(Se_{1/2})_3$ structural units having double-bonded Se atoms and optimal number of Lagrangian constraints per atom $n_c = 3$.[2,3] Another suggestion assumes "repulsive interactions of lone pair electrons of As atoms" to introduce additional constraints.[5] Whichever the case, to explain the extension of the reversibility window into the $Z < 2.37$ region, fourfold-coordinated As atoms must exist. Indeed such appears to be the case with the P-(S)Se system, specifically the composition $P_2S(Se)_5$ for which a natural mineral exists.[10] However, the As-Se system is different.

The first discussions about the existence of quasitetrahedral $Se{=}As(Se_{1/2})_3$ structural units within the As-Se system are very old,[10,13,14] but to date there is no strong experimental evidence in its support. Moreover, most of the experimental data can be explained with mostly threefold-coordinated As within the Se-rich part of As-Se glass-forming region.[15,16] Even if one assumes the possibility of $Se{=}As(Se_{1/2})_3$ structural units at some distinct compositions (As_2Se_5, for example) to explain the lack of aging in all the As_xSe_{100-x} compositions within the reversibility window range, such units should exists as main glass-forming blocks along with energetically favorable corner-shared $AsSe_{3/2}$ pyramids (with $n_c = 3$). Both of these units should be observable experimentally.

In short, a basic question remains, concerning the physical aging in As-Se glass system: Is the absence or marginality of nonreversible heat flow in temperature-modulated DSC experiments an appropriate criterion of reversibility window or lack of aging in these glasses? To verify the applicability of temperature-modulated DSC for express determining the boundaries of reversibility window, we have studied in this work the thermal behavior and structure of binary As_xSe_{100-x} glasses aged for more than 20 years under natural conditions.

II. EXPERIMENTAL

The samples of binary As_xSe_{100-x} (x=0, 10, 20, 30, 40, 45, 50, 53, and 55) were prepared in 1985 by conventional melt-quenching route in evacuated quartz ampoules from a mixture of high purity (99.999%) As and Se precursors. The furnace was rocked to obtain the most homogeneous melt. All ingots were quenched by switching off the furnace. Amorphous state of the as-prepared chalcogenide glass was established visually by a characteristic conchlike fracture as well as by x-ray diffraction. Then all samples were sealed in hermetic plastic bags and stored in the dark under ambient conditions for nearly 22 years before conducting calorimetric experiments.

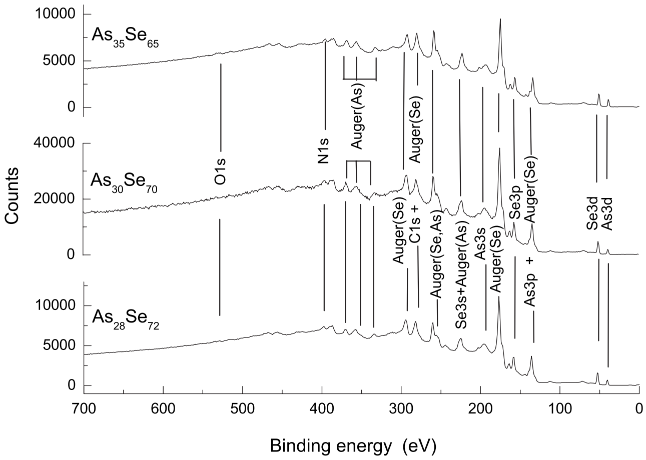

FIG. 1. Survey x-ray photoelectron spectra for selected compositions of As_xSe_{100-x} chalcogenide glasses.

To verify the possibility of the formation of $Se{=}As(Se_{1/2})_3$ units (corresponding to $As_{28.57}Se_{71.43}$ composition) in As-Se system, the $As_{28}Se_{72}$ and $As_{35}Se_{65}$ compositions were especially synthesized. Their structure was determined by x-ray photoelectron spectroscopy (XPS) together with that of the 22-year-aged $As_{30}Se_{70}$ and $As_{40}Se_{60}$ glasses.

Purity and composition of the samples were confirmed by XPS survey and As/Se $3d$ core-level spectra, which were obtained using high-resolution Scienta ESCA-300 spectrometer with monochromatic Al $K\alpha$ x ray (1486.6 eV). The well-defined peaks associated with the As and Se core levels as well as related Auger lines Fig. 1 were identified in the survey spectra using PHI handbook for XPS spectra.[17] No elements other than the glass components were observed in the spectra since the samples were broken just before the XPS measurements directly in the ultrahigh vacuum of the spectrometer. In particular, there was no evidence for oxygen on any of the surfaces. The method for calibration, analysis, and fit procedure for the Se and As $3d$ core-level XPS spectra is described in detail elsewhere.[16] The uncertainty in the peak position and the area (A) of each component of the XPS $3d$ core-level spectra of As and Se are ±0.05 eV and ±2%, respectively.

Temperature-modulated DSC measurements were performed on TA 2920 apparatus calibrated with typical standards. The sample masses were chosen to be similar and ~20 mg. Oscillation amplitude of 0.318 K over 60 s oscillation period and heating rate of 2 K/min were used for recording the temperature-modulated DSC data. Three independent measurements were performed in every case to confirm the reproducibility of the results. Temperature-modulated DSC complex heat-flow signal was decomposed into the in-phase ("reversible") and out-of-phase (nonreversible) components using standard procedure.[18] All of the obtained data were corrected according to the trend of base line, which was subtracted from the experimental DSC curves by the software. To compare the temperature-

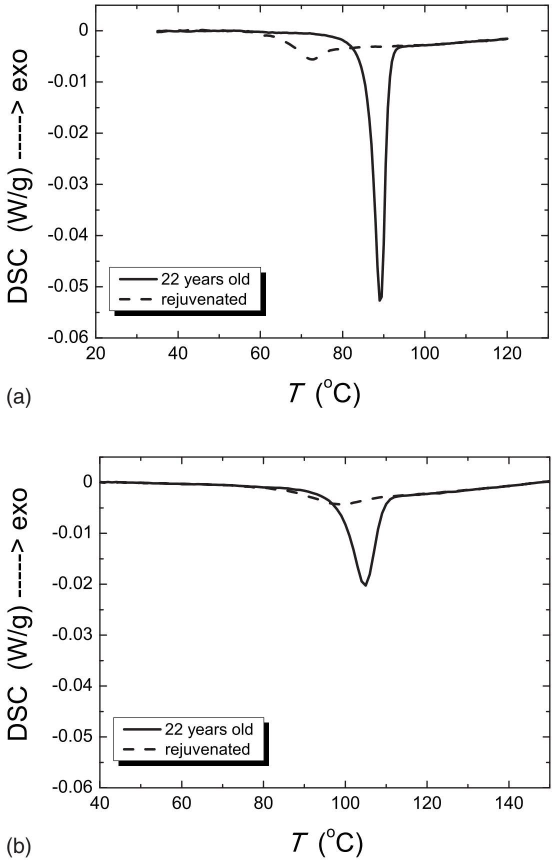

FIG. 2. Conventional DSC traces (heating rate 1 K/min) of aged and rejuvenated glasses: (a) $As_{10}Se_{90}$ and (b) $As_{20}Se_{80}$ compositions.

modulated DSC data of aged and as-prepared chalcogenide glasses, the former samples were rejuvenated by heating above the glass transition temperature T_g, waiting equilibrium at T_g+50 K, and subsequently cooling in the chosen regime at the same cooling rate.

III. RESULTS AND DISCUSSIONS

By definition, physical aging is a spontaneous transition of the glassy state into a more thermodynamically favorable state closer to the equilibrium undercooled liquid.[10,19] It is revealed as a strong endothermic peak in conventional DSC traces measured during the heating of glass sample in the region of glass-to-undercooled liquid transition, i.e., the usual glass transformation range.[7,9] Besides the structural relaxation of glass network through the transition region,[20] this peak also includes a component connected with the regaining of entropy lost during natural storage.[7,9] The greater is the aging duration, the greater is the energy loss and the greater should be the endothermic peak at T_g.[7,9] The area of the measured endothermic peak after subtracting the nonaged curve obtained for the same material is directly proportional to the energy lost during aging (ΔH). Figure 2 shows typical DSC curves obtained for two 22-year-aged Se-rich As_xSe_{100-x} glasses. As expected, a very large peak due to relaxation with a shift toward higher temperatures of the apparent glass transition is observed. If T_a is the annealing (aging) temperature, the maximum of energy that a glass can lose after an infinite aging duration can be approximated by the quantity[7]

$$\Delta H_\infty \approx \Delta C_{p(T_g)}(T_g^c - T_a), \qquad (2)$$

where $\Delta C_{p(\mathrm{Tg})}=C_{\mathrm{pl}}-C_{\mathrm{pg}}$ measured at T_g (C_{pl} is the thermal capacity in the undercooled liquid state and C_{pg} is the thermal capacity in the glassy state). T_g^c is the glass transition temperature obtained when the glass is cooled through the transition region at a given rate. In the first approximation, it is equal to the fictive temperature T_F of rejuvenated glass determined by Moynihan's method.[21]

The value of $\Delta C_{p(\mathrm{Tg})}=0.12-0.21$ J g^{-1} K^{-1} varies from one glass to another, which is not surprising. It is linked also to the number of Lagrangian constraints per atom, as demonstrated for the Ge_xSe_{100-x} and Ge_xTe_{100-x} systems.[22–24] However, for a given composition, the value of $\Delta C_{p(\mathrm{Tg})}$ does not depend on the sample's age, which confirms that the glass has undergone only physical aging. Then, from the area of measured endothermic peak, after subtracting the nonaged (rejuvenated) curve, and using Eq. (2), we have estimated for Se and $As_{10}Se_{90}$ that $\Delta H_{22\ \mathrm{years}}/\Delta H_\infty \approx 1$. It means that physical aging of these glasses is almost complete after ~22 years of storage at room temperature. For $As_{20}Se_{80}$ and $As_{30}Se_{70}$ glasses, the estimation gives $\Delta H_{22\ \mathrm{years}}/\Delta H_\infty=0.6$ and 0.2, respectively. All the remaining glasses stay far from the equilibrium, i.e., their $\Delta H_{22\ \mathrm{years}}/\Delta H_\infty$ values are <0.1. Thus, for the investigated As_xSe_{100-x} glasses significant physical aging effects are recorded by conventional DSC and verified for all compositions from pure Se($x=0$) up to stoichiometric As_2Se_3 ($x=40$ at. % of As) as a result of prolonged natural storage.[9,25] On the other hand, the glasses within the 28 to 38 at. % As compositional range (accepted as reversibility window) has been declared stable or nonaging on the basis of temperature-modulated DSC results on samples aged for relatively short duration (up to a few months).[2–4]

In the case of temperature-modulated DSC signal, physical aging results in a significant nonzero out-of-phase component of heat flow.[8,26] These components of complex heat flow are shown in Fig. 3 for the investigated 22-year-aged and rejuvenated As_xSe_{100-x} glasses. The area under the peak denoted as ΔH_{nr} (Fig. 3) may be used for describing the aging process and determining the "reversibility window." This term provides a measure of how different a glass going through the *softening process* is from the liquid in a configurational sense *at the moment of measurements*. Some researchers have introduced reversibility window for As-Se system using chalcogenide samples aged for ~100 h (Ref. 3) or a few weeks.[2] However, it is well known that ΔH_{nr} follows a sigmoidal time dependence as hypothetically shown in Fig. 4, which depends on the choice of T_a.[7,9,27] So a negligible value of ΔH_{nr} term just after preparation or relaxation over a short period of aging test can yield misleading conclusion. Long periods of storage depending on the specific kinetics of the glass composition are needed to conclude the existence of an aging process.[27] Thus, for instance, a significant difference between the ΔH_{nr} values of rejuvenated and

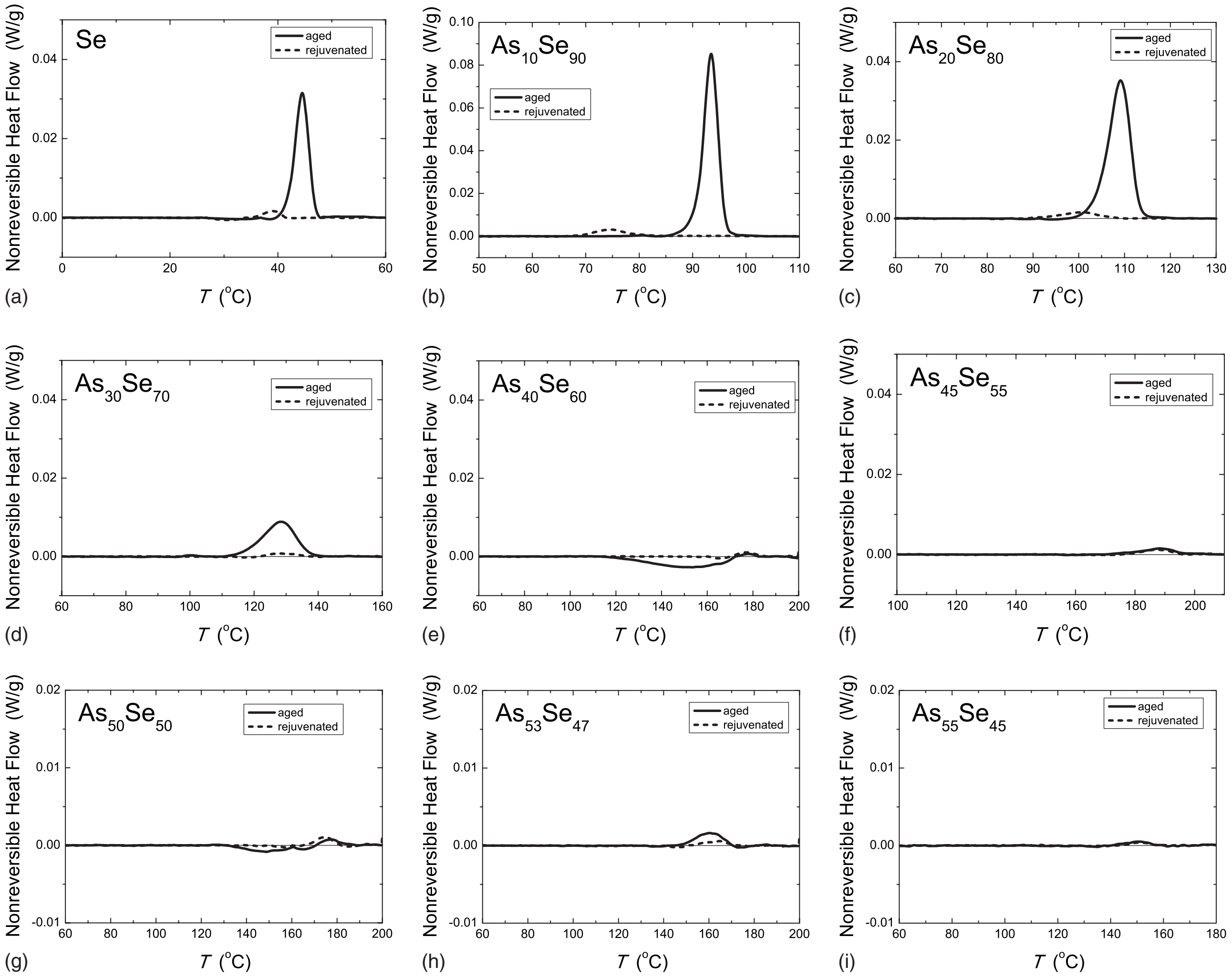

FIG. 3. Out-of-phase component (or nonreversible heat flow) of temperature-modulated DSC signal for ~22-year-aged (solid) and rejuvenated (dash) glasses.

aged samples is recorded for all the investigated As-Se glasses with $Z<2.4$, whereas rather small difference is observed for chalcogenide glasses with $Z>2.4$ (Fig. 5). After rejuvenation, a plateau of negligible ΔH_{nr} values is indeed observed [see magnified dependence in Fig. 5(b)], similar to that reported by other authors [see solid curve in Fig. 5(b)], who claimed a reversibility window in the As-Se system.[2,3] However, after prolonged natural storage the on-set point of this window shifts from $Z=2.28$ to $Z=2.4$ composition, as can be seen clearly from Fig. 5(a).

Since we have only one composition ($As_{30}Se_{70}$) of 22-year-old glass belonging to the reversibility window, one can argue this is not enough to make a strong conclusion. To verify the lowest limit of reversibility window at $x=28$, which is based on the assumption of fourfold-coordinated As atoms or $Se{=}As(Se_{1/2})_3$ units in the covalent network of glasses, we have determined the structure of $As_{30}Se_{70}$, $As_{40}Se_{60}$, $As_{28}Se_{72}$, and $As_{35}Se_{75}$ compositions by XPS (the last two glasses being aged only for two years). It is known that XPS technique is a useful tool for identifying the changes in the atomic coordination (higher and/or lower number of nearest neighbors), the ionic state (bond type, charge density, etc.) of the target atom, as well as the substitution of one or more of its neighbors by an atom of different electronegativities or charge states (charged defects, etc.).[16,28] So, if fourfold-coordinated atoms exist in sufficient concentration (more than ~2%), they would be identified by this technique as an additional component in the As/Se $3d$ core-level spectrum or significant chemical shift in binding energies (BEs).[16,17,28]

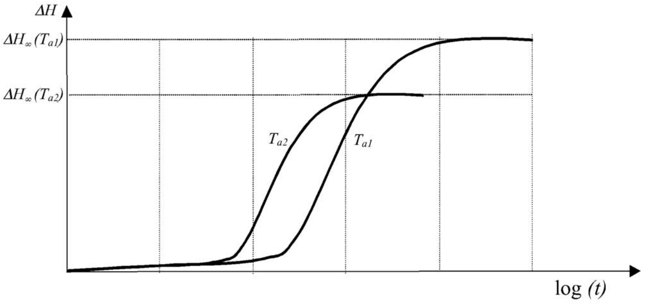

FIG. 4. Schematic of expected variation of the energy recovery associated with energy lost during aging for two annealing temperatures $T_{a1}<T_{a2}<T_g$.

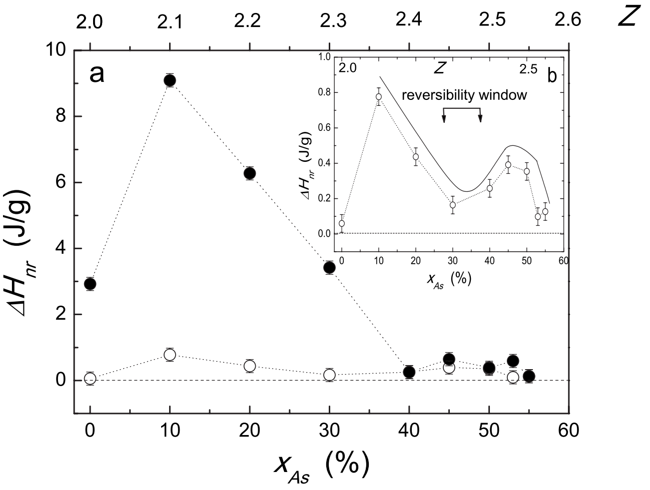

FIG. 5. Compositional dependence (a) of ΔH_{nr} term for aged (full) and rejuvenated (open) As_xSe_{100-x}. Inset (b) shows the compositional trend (solid line) of ΔH_{nr} published by Georgiev *et al.* (Ref. 2).

Figure 6 shows, for example, the As and Se $3d$ core-level XPS spectra for $As_{28}Se_{72}$ and $As_{35}Se_{65}$ glasses, calibrated using Au $4f_{7/2}$ (84 eV) line position. The corresponding fit parameters of As and Se $3d$ core-level XPS spectra are given in Table I and compared to those for the 22-year-aged $As_{30}Se_{70}$ and $As_{40}Se_{60}$. Based on the compositional dependence of XPS spectra of As-Se glasses obtained earlier,[16] the observed components in the fits of As and Se $3d$ core-level XPS spectra for As_xSe_{100-x} glasses with $x=28$, 30, 35, and 40 at. % of As could be unambiguously attributed to the structural units with threefold-coordinated As atoms and twofold-coordinated Se atoms. However, the concentration of $Se{=}As(Se_{1/2})_3$ units (assuming their presence) is obviously less than the detection limit of the technique (a couple of percents)—it is not enough to form optimally constrained backbone with $n_c=3$.

The present temperature-modulated DSC and high-resolution XPS studies confirm previous conclusions made on the basis of conventional DSC investigations[9,25] that the on-set of reversibility window in As_xSe_{100-x} system is located around $x=40$ at. % of As composition, in good agreement with Phillips-Thorpe percolation theory.[1,6] That is, the first composition, which belongs to a self-organized phase, is stoichiometric As_2Se_3 with $n_c=3$. There does not appear to be any need to introduce additional constraints on As atoms for the constraints theory to agree with the experiment. The present results correlate well also with the recent theoretical calculations performed by Mauro and Varshneya[29] using Monte Carlo simulations. They have showed for bulk As-Se chalcogenide system that pure rigidity percolation should occur at As_2Se_3 composition.[29] On the basis of present studies, we can also conclude that the criterion of marginality of nonreversible heat flow (out-of-phase component), which is used to determine the boundaries of reversibility window or the so-called intermediate phase in the sense of nonaging ability, is not universal. It does not take into account the possibility of slow kinetics of physical aging.

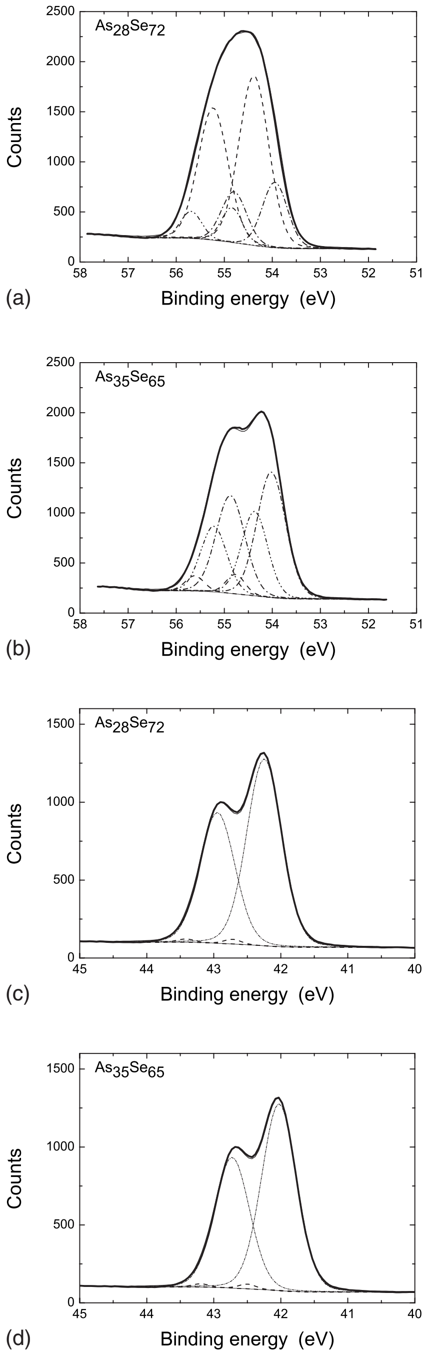

FIG. 6. Fitting of (a, b) Se and (c,d) As $3d$ core-level spectra of $As_{28}Se_{72}$ and $As_{35}Se_{65}$ glasses (bold line, experimental spectrum; thin line, fitted spectrum; dotted line, base line; and dashed line, fitted components).

IV. CONCLUSIONS

Despite significant progress in express testing of chalcogenide glasses with temperature-modulated DSC, only DSC experiments (both temperature modulated or conventional) performed in *a real time scale* from earliest stages of as prepared up to long-term aged state can be useful for the quantitative measure of physical aging and determining the boundaries of reversibility windows. Such experiments can be simply performed in *a backward chronology* using the

TABLE I. Numerical parameters ($3d_{5/2}$ components) of Se $3d$ and As $3d$ core-level spectra (the analyzed core level is written in bold font). A is the ratio obtained experimentally by XPS as partial area under the corresponding fitted peaks.

	As-**Se**-As			Se-**Se**-As			Se-**Se**-Se			Se-**As**$<$(Se)$_2$		
Fragment sample	BE (eV)	FWHM (eV)	A (%)	BE (eV)	FWHM (eV)	A (%)	BE (eV)	FWHM (eV)	A (%)	BE (eV)	FWHM (eV)	A (%)
$As_{28}Se_{72}$	53.95	0.62	22	54.38	0.73	68	54.84	0.52	10	42.25	0.61	99
$As_{30}Se_{70}$	53.97	0.66	32	54.38	0.71	62	54.82	0.48	6	42.27	0.62	100
$As_{35}Se_{65}$	54.04	0.72	63	54.40	0.66	31	54.74	0.46	5	42.29	0.66	99
$As_{40}Se_{60}$	54.07	0.74	94	54.45	0.67	6				42.27	0.63	92

well-known rejuvenation procedure. We confirm by means of temperature-modulated DSC measurements performed by this procedure that the on-set of the reversibility window in As_xSe_{100-x}, sometimes claimed to be from 28 up to 38 at. % As, in fact occurs at the stoichiometric As_2Se_3 composition. Also, we have found no evidence by XPS technique for the existence of fourfold-coordinated As atoms in the structure of Se-rich As-Se glasses.

ACKNOWLEDGMENTS

This work is supported by bilateral Ukrainian-French Project "Dnipro." The authors thank A. C. Miller for help with x-ray photoelectron spectroscopy measurements. R.G. acknowledges support from U.S. National Science Foundation (NSF Grant No. DMR-0409588) through International Materials Institute for New Functionality in Glass (IMI-NFG).

---

*golovchak@novas.lviv.ua

[1] M. F. Thorpe, D. J. Jacobs, M. V. Chubynsky, and J. C. Phillips, J. Non-Cryst. Solids **266-269**, 859 (2000).

[2] D. G. Georgiev, P. Boolchand, and M. Micoulaut, Phys. Rev. B **62**, R9228 (2000).

[3] P. Boolchand, D. G. Georgiev, M. Micoulaut, and J. Optoel, Adv. Mater. (Weinheim, Ger.) **4**, 823 (2002).

[4] S. Chakravarty, D. G. Georgiev, P. Boolchand, and M. Micoulaut, J. Phys.: Condens. Matter **17**, L1 (2005).

[5] G. Lucovsky, D. A. Baker, M. A. Paesler, J. C. Phillips, and M. F. Thorpe, J. Optoelectron. Adv. Mater. **9**, 2979 (2007).

[6] M. F. Thorpe, J. Non-Cryst. Solids **57**, 355 (1983).

[7] J. M. Saiter, M. Arnoult, and J. Grenet, Physica B (Amsterdam) **355**, 370 (2005).

[8] D. Tonchev and S. O. Kasap, Mater. Sci. Eng., A **328**, 62 (2002).

[9] R. Golovchak, Cz. Gorecki, A. Kozdras, and O. Shpotyuk, Solid State Commun. **137**, 67 (2006).

[10] A. Feltz, *Amorphous Inorganic Materials and Glasses* (VCH, New York, 1993), p. 446.

[11] M. Micoulaut and J. C. Phillips, Phys. Rev. B **67**, 104204 (2003).

[12] M. Micoulaut and J. C. Phillips, J. Non-Cryst. Solids **353**, 1732 (2007).

[13] Z. U. Borisova, *Glassy Semiconductors* (Plenum, New York, 1981).

[14] S. Tsuchihashi and Y. Kawamoto, J. Ceram. Soc. Jpn. **75**, 353 (1966).

[15] A. L. Renninger and B. L. Averbach, Phys. Rev. B **8**, 1507 (1973).

[16] R. Golovchak, A. Kovalskiy, A. C. Miller, H. Jain, and O. Shpotyuk, Phys. Rev. B **76**, 125208 (2007).

[17] J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, in *Handbook of X-ray Photoelectron Spectroscopy*, edited by J. Chastein (Perkin-Elmer, Eden Prairie, MN, 1992).

[18] S. Weyer, A. Hensel, and C. Schick, Thermochim. Acta **304–305**, 267 (1997).

[19] L. C. E. Struik, *Physical Ageing in Amorphous Polymers and Other Materials* (Elsevier, New York, 1978).

[20] M. A. DeBolt, A. J. Easteal, P. B. Macedo, and C. T. Moynihan, J. Am. Ceram. Soc. **59**, 16 (1976).

[21] C. T. Moynihan, A. J. Easteal, and J. Wilder, J. Phys. Chem. **78**, 2673 (1974).

[22] K. Chebli, J. M. Saiter, J. Grenet, A. Hamou, and G. Saffarini, Physica B (Amsterdam) **304**, 228 (2001).

[23] M. Tatsumisago, B. L. Halfpap, J. L. Green, S. M. Lindsay, and C. A. Angell, Phys. Rev. Lett. **64**, 1549 (1990).

[24] J. M. Saiter, K. Chebli, and A. Hamou, Physica B (Amsterdam) **293**, 98 (2000).

[25] R. Golovchak, O. Shpotyuk, and A. Kozdras, Phys. Lett. A **370**, 504 (2007).

[26] P. Lucas, E. A. King, A. Doraiswamy, and P. Jivaganont, Phys. Rev. B **71**, 104207 (2005).

[27] S. V. Nemilov, Glass Phys. Chem. **26**, 511 (2000).

[28] A. Kovalskiy, H. Jain, A. C. Miller, R. Golovchak, and O. Shpotyuk, J. Phys. Chem. B **110**, 22930 (2006).

[29] J. C. Mauro and A. K. Varshneya, J. Non-Cryst. Solids **353**, 1226 (2007).