# INTERMEDIATE PHASES, REVERSIBILITY WINDOWS, STRESS-FREE AND NON-AGING NETWORKS, AND STRONG LIQUIDS

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Network glasses usually display glass transitions that are *hysteretic*, i.e., a second scan across a glass transition endotherm usually does not replicate the first one. But in recent years, examination of glass transition endotherms of several inorganic systems [1-4] reveal a different pattern: one observes compositional windows across which glass transitions become almost completely *non-hysteretic*. Specifically, the non-reversing enthalpy ($\Delta H_{nr}$) associated with the glass transition ($T_g$) accessed from modulated Differential Scanning Calorimetry is found to nearly vanish [1-4]. These compositional windows, also called *reversibility windows*, usually occur [5] in the $2.29 < r < 2.52$ range, where *r* represents the mean coordination number, a measure of network connectivity.

Glasses in reversibility windows form *ideal stress-free networks*. The ideality derives from the optimization of glass forming tendency. The stress-free character of binary $Ge_xSe_{1-x}$ glasses in the reversibility window, $0.20 < x < 0.25$, was recently demonstrated [5] in Raman pressure measurements. In these experiments one found that select vibrational modes blue-shift as a function of external pressure (P), but only once P exceeds a threshold value ($P_c$). The threshold pressures, $P_c$, serve as a measure of network internal stress. Chemical trends in $P_c(x)$ are found [5] to closely track those of $\Delta H_{nr}(x)$. In particular, both terms nearly vanish in the reversibility window. Thus, networks in reversibility windows are in a state of a quasi-equilibrium, and represent a new topological phase of glassy solids [6]. This new phase shares some functionalities with crystalline solids including the absence of aging as evidenced [3] by the fact that the $\Delta H_{nr}(x)$ term does not evolve with time at $T < T_g$.

In reversibility windows, the vanishing of $\Delta H_{nr}$ suggests that configurational entropy change between glasses and corresponding melts is small, i.e., liquid and glass structures are quite similar. Indeed, optimization of glass forming tendency in this new phase would appear to be a natural consequence of this finding. Glassy networks belonging to this new phase generally form efficient space filling networks. Furthermore, one also finds that activation energy of viscosity ($\Delta E_a$) of the melts in this compositional window displays a global minimum as well, i.e., these liquids are *strong* in the fragile-strong classification [7,8] of glass forming melts. Here the term *strong* denotes robust local structures that apparently give rise to Arrhenius activation of viscosity. The correlation is illustrated for the case of two chalcogenide glass systems (Fig. 1) where fairly complete results [9-12] are available in the literature. The correlation of reversibility windows with windows in activation energies for viscosity, highlights the very special relation of glasses and corresponding liquids.

What is so special about molecular structures of glasses in reversibility windows?

Local structures comprising these glassy networks include tetrahedra and/or quasi-tetrahedra and/or pyramids, and each of these shares a common property. They are mechanically rigid with no redundant bonds. Such local structures are described as isostatic. Constraint counting algorithms [13] have proved to be remarkably incisive in decoding whether a local structure is floppy (underconstrained), isostatic (optimally constrained) or stressed rigid (overconstrained). Raman scattering has been extremely powerful in identifying vibrational modes of characteristic local structures of glasses including those in reversibility windows. Thus, the width of the reversibility window in binary As-Se glasses is largely controlled [12] by *two* As-centered isostatic local

structures; $As(Se_{1/2})_3$ pyramids and $Se=As(Se_{1/2})_3$ quasi tetrahedra. On the other hand, the much wider reversibility window [14] in ternary $As_xGe_xAs_{1-2x}$ glasses (Fig. 1) includes *four* isostatic local structures; two of these are the same As-centered ones mentioned above, and other two include Ge-centered corner-sharing $Ge(Se_{1/2})_4$ and edge-sharing $GeSe_2$ tetrahedra. But there are clearly challenges ahead. Aspects of medium range structure of glasses that lead to the special structural organization in reversibility windows continue to be a subject of discussions in the field. Experiments have unequivocally shown that the wide reversibility windows present in binary Ge-Se and Ge-S glasses, for example, are dramatically collapsed by alloying terminal atoms such as iodine [15]. These experiments underscore the crucial importance of medium range structures in self-organizing networks in reversibility windows, a view that is corroborated by numerical simulations [16, 17].
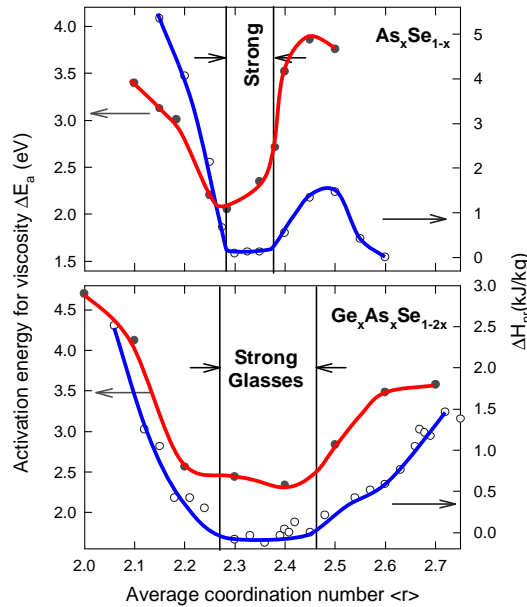


Fig. 1. Compositional variations of non-reversing enthalpy, $\Delta H_{nr}(x)$ and activation energy of viscosity, $\Delta E_a(x)$, in binary $As_xSe_{1-x}$ (top) and ternary $(As_xGe_xSe_{1-2x})$ glasses taken from ref. 9-12 displaying a clear correlation. Note that the windows in $\Delta H_{nr}(x)$ are far deeper changing by a factor 10 or more than windows in $\Delta E_a(x)$ that change by a factor of 3 or less.

In summary, reversibility windows appear to be signatures of a new topological phase of disordered condensed matter. There is growing evidence for a certain universality in structure and functionality of this phase in the properties of $Si/SiO_2$ interfaces [18], of protein-folding [19], of computational complexity [20], of high-temperature superconductivity [21], and of network glasses [22]. It is a pleasure to acknowledge discussions with Professor Jim Phillips, Professor Bernard Goodman and Ping Chen during the course of this work. This work is supported by NSF grant DMR-04-56472.

### References

[1] P. Boolchand, D. G. Georgiev, M. Micoulaut, Nature of glass transition in chalcogenides, J. Optoelectron. Adv. Mater. **4**, 823 (2002).

[2] D. Selvanathan, W. J. Bresser, P. Boolchand, Stiffness transitions in $Si_xSe_{1-x}$ glasses from Raman scattering and temperature-modulated differential scanning calorimetry. Phys. Rev. B **61**, 22, 15061 (2000).

[3] S. Chakravarty, D. G. Georgiev, P. Boolchand, M. Micoulaut, "Ageing, fragility and the reversibility window in bulk alloy glasses", J. Phys. Condens. Matter. **17,** L1-L7 (2005).

[4] D. G. Georgiev, P. Boolchand, H. Eckert, M. Micoulaut, A. Jackson, The self-organized phase of bulk $P_xSe_{1-x}$ glasses. Europhysics Letters **62**, 49 (2003).

[5] F. Wang, S. Mamedov, P. Boolchand, B. Goodman, M. Chandrasekhar, "Pressure Raman effects and internal stress in network glasses", Phys. Rev. B **71**, 174201 (2005).

[6] P. Boolchand, D. G. Georgiev, B. Goodman, Discovery of the intermediate phase in chalcogenide glasses. J. Optoelectron. Adv. Mater. **3**, 703 (2001).

[7] M. L. Williams, R. F. Landel, D. J. Ferry, The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids, J. Am. Chem. Soc. **77**, 3701-3707 (1955).

[8] C. A. Angell. Relaxation in liquids, polymers and plastic crystals – strong fragile patterns and problems, J. Non-Cryst. Solids **131**, 13 (1991).

[9] Y. Wang, P. Boolchand, M. Micoulaut, Glass structure, rigidity transitions and the intermediate phase in the Ge -As -Se ternary. Europhys. Lett. **52**, 6, 633 (2000).

[10] N. Tatsumisago, B. L. Halfpap, J. L. Green, S. M. Lindsay, C. A. Angell, Fragility of Ge-As-Se glass-forming liquids in relation to rigidity percolation, and the Kauzmann paradox. Phys. Rev. Lett **64**, 1549 (1990).

[11] S. V. Nemilov, G. T. Petrovckii, Zh. Prikl. Khim. **36**, 977 (1963).

[12] D. G. Georgiev, P. Boolchand, M. Micoulaut, Rigidity transitions and molecular structure of $As_xSe_{1-x}$ glasses. Phys.Rev. B **62**, 14, 9268 (2000).

[13] J. C. Phillips, Topology of covalent non-crystalline solids I: Short range-order in chalcogenide alloys, J. Non Cryst. Solids **34**, 153(1979).

[14] Tao Qu, D. G. Georgiev, P. Boolchand, M. Micoulaut, The intermediate phase in ternary $Ge_xAs_xSe_{1-2x}$ glasses. in "Supercooled Liquids, Glass Transition and Bulk Metallic Glasses" (eds T. Egami, A. L. Greer, A. Inoue, S. Ranganathan), Mater. Res. Soc. Symp. Proc. vol. **754**, CC8.1.1 (2003).

[15] Y. Wang, J. Wells, D. G. Georgiev, P. Boolchand, Koblar Jackson, M. Micoulaut. Sharp Rigid to Floppy Phase Transition Induced by Dangling Ends in a Network Glass. Phys. Rev. Lett. **87**, 18, 5503 (2001).

[16] M. F. Thorpe, D. J. Jacobs, M. V. Chubynsky, J. C. Phillips, Self-Organization in network glasses, J. Non-Cryst. Solids, **266-269**, 859 (2001).

[17] M. Micoulaut, J. C. Phillips, Rings and Rigidity transitions in network glasses, Phys. Rev. B **67**, 104204 (2003).

[18] G. Lucovsky, J. C. Phillips, Bond strain and defects at $Si-SiO_2$ and internal interfaces in high-k gate stacks, J. Phys.: Condens. Matter **16**, S5139-S5151 (2004).

[19] A. J. Rader, B. M. Hespenheide, L. A. Kuhn, M. F. Thorpe, Protein unfolding: Rigidity lost. Proc. Natl. Acad. Sci. USA, **99**, 3540 (2002).

[20] J. Barre, A. R. Bishop, T. Lookman, A. R. Saxena, Adaptability and Intermediate Phases in Randomly Connected Networks, Phys. Rev. Lett. **94**, 208701 (2005).

[21] J. C. Phillips, Topological Theory of Electron Phonon Interactions in High Temperature Superconductors, Phys. Rev B **71**, 184505 (2005).

[22] P. Boolchand, G. Lucovsky, J. C. Phillips, M. F. Thorpe, "Self-Organization and the Physics of Glassy networks", Phil. Mag. **85**, 3823 (2005).