Evidence of Negative Heat Capacity, Rigidity Percolation and Intermediate Phase in Fast Ion Conducting Conditional Glasses

B. Tanujit and S. Asokan

Department of Instrumentation and Applied Physics
Indian Institute of Science, Bangalore – 560 012, India

Abstract

In this work, we report the rigidity percolation phenomena in a fast ion conducting (FIC), conditional glass forming system, \((\text{AgI})_{75-x}-(\text{Ag}_2\text{O})-(\text{MoO}_3)_x\). In the pursuit of where and why the rigidity percolation thresholds appear within the glass forming range of \(20 \leq x \leq 37.5\), calorimetry and photoelectron spectroscopy experiments have been performed. It is found that the temperature dependence of normalized, in-phase heat capacity, at glass transition temperature, exhibits more fluctuations for samples with higher AgI concentration. This suggests a fragility threshold within the composition range, since the fluctuations indicate a non-Arrhenius type relaxation behavior related to fragile glass. Furthermore, we observe a sign shift in the measured, in-phase heat capacity value that reveals the fragility threshold. The negative heat capacity in the non-Arrhenius region has been corroborated with the thermodynamic behavior of nanoclusters. The negative heat capacity and presence of nanoclusters have been used and discussed to provide evidence for a Nanoscale phase separation. The photoelectron spectroscopy study shows the formation of essential covalent structural units, \([-\text{Mo}–\text{O}–\text{Ag}–\text{O}–]\) and complex molybdenum oxides in the Arrhenius type rigid region. Finally, the non-reversing enthalpy profile has been studied over the whole composition range. The global, square well minima sandwiched between floppy and stress rigid phase has been found to denote the intermediate phase, in the range \(32.25 \leq x \leq 35\).

a) Corresponding Author email: sundarrajansasokan@gmail.com, sasokan@iisc.ac.in

Fax: 91-80-23608686; Phone. +91-80-22933195, 91-80-22932271
1. Introduction

Kauzmann’s glass condition states that $\frac{\partial (H_{\text{liquid}} - H_{\text{crystal}})}{\partial T}$ drops to zero during glass transition [1] where $H$ denotes the enthalpy of the indexed state, $T$ is the temperature; i.e. across glass transition temperature ($T_g$), configurational entropy ($S_c$) remains continuous during liquid to solid transition [1], at $T_g$, $\Delta S_c = (S_{c\,\text{liquid}} - S_{c\,\text{solid}}) = 0$ [2]. To microscopically realize this phenomena, J. Phillips and M. Thorpe [2-5] introduced a site-bond type mechanical constraints model, for systems that constitute covalent bonds, dominantly. This formalism considers only the nearest-neighbor, central, two-body bond-stretching and non-central, three body bond-bending forces. The model, when associated with the entropic glass condition $\Delta S_c = 0$, incorporating average first coordination number ($n_1$) and medium range order, convolutes into a constraints equation $N_{\text{Con}} = N_d$, where $N_{\text{Con}}$ is the number of interatomic force field constraints per atom and $N_d$ is the number of vector degrees of freedom per atom [2, 5]. In a covalent network structure, the constraints condition acts like rigidity percolation threshold. The condition $N_{\text{Con}} < N_d$ refers to floppy (FP), polymeric phase, e.g. a linear network in three dimension, $N_{\text{Con}} = 2$ and $N_d = 3$. As more constraints get accommodated within the system, the interconnectivity among the sites increases and rigidity percolates through the system; this phase is known as stressed rigid amorphous phase (SRP) when $N_{\text{Con}} > N_d$ [5].

Contemporaneous study on the phenomena of photo-melting in As$_2$S$_3$ glass [6] and giant photo-contraction in obliquely deposited porous GeSe$_2$ [7] could relate to another stable phase where the network is mechanically rigid but stress free [8]. This ‘trapped in limbo’ phase in rigidity transition corresponds to $N_{\text{Con}} = N_d \implies \Delta S_c = 0$ [9]. Boolchand et al. [8-11] rigorously investigated and identified this stress-free phase as Intermediate Phase (IP) that appears in between FP and SRP. IP glasses exhibit non-aging behavior, optimal glass forming tendency [12] and possess self-organization functionality [9] which is the global reconnection of chemical bonds to form stress-free networks [12]. This functionality along with the constraints model has been used to understand protein folding and protein phase transition [13]. The self-organization and IP have been recognized in thin-film transistor used in liquid crystal display [14] and further exploited in various disciplines e.g. soft condensed matter, computer science, electrical engineering, protein science [12, 14].

Early studies on rigidity transition [8-11] have been conducted on chalcogen (S, Se, Te) based glasses which exhibit continuous covalent random network (CRN) topology that is essential for rigidity transition. Oxygen, having high electronegativity and tendency to form O$^-$ and O$_2^-$, differs significantly from other chalcogens [15] in terms of network topology and chemical properties. When network modifier is introduced into base oxide glass, non-bridging oxygen (NBO) forms and ionically bonds with
modifier cation; these phenomena alters the network topology [15]. Interestingly, three phased rigidity transition has been observed in oxide glasses, such as AgI based FIC glasses e.g. (AgI)x(AgPO3)1-x [16-17], (Na2O)x(GeO2)1-x [18] and (Na2O)x(SiO2)1-x [19]. However, the constituent glass forming agents for these glasses are P2O5, GeO2 and SiO2 respectively, all of which are strongly covalent glass formers [20-21] and follow Zachariasen's rules for glass formation as CRN [20].

Upon increasing the modifier oxide concentration within the base glass environment, the depolymerization of CRN occurs by bridging oxygen (BO) to NBO conversion and formation of Qₙ species, where \[ Q_n = [\text{AO}_n\text{O}_m]^m- \] (n + m ≤ 4 and A = P, Ge, Si) and there are gradual changes from ultra to ortho [20]. However, heavy transition metals e.g. Mo, W capable of existing in multiple valance states, are 'conditional' glass formers [20]. Pure liquids of these transition metal oxides require modifier or another network forming oxide for glass formation, BO-NBO conversion, different Qₙ species and modifier cation formation. The ionic character of these metals and ionic bonding or 'partial covalence' [22-23] between modifier cations and NBOs, significantly enhance the non-covalent, non-directional bonding of these type of glasses. These bonds disconnect the covalent graph and form fragile molecular solid where interatomic strong and intermolecular weak force coexist [15].

Besides, in the viscosity-temperature profile, liquids that deviate from Arrhenius type behavior, exhibit small changes in heat capacity at \( T_g \); this change is large for fragile glasses with lack of directional bonds [24] i.e. non-directionality of bond enhances the non-Arrhenius type behavior. The structural disparity, in terms of the origin of First Sharp Diffraction Peak (FSDP), between these two types of glasses, has been reported by Swenson et al. [25]. In case of molecular (oxide) glasses, FSDP is significantly contributed by oxygen which is in contrary with other glass formers, e.g. phosphate [26] and borate [27] glasses. Thus, these conditional glass formers are significantly different, in a chemical and topological sense, from CRN forming Chalcogenide and metalloid/non-metal oxides.

In this present work, we report the rigidity percolation phenomena in a FIC glassy system, (AgI)₇₅₋ₓ-(Ag₂O)ₓ-(MoO₃)x, for 20 ≤ x ≤ 37.5, pursuing the questions where, why and how rigidity transition should occur? In order to answer these questions, Alternating Differential Scanning Calorimetry (ADSC) and X-ray Photoelectron Spectroscopy (XPS) have been conducted.

At first, the fragility behavior from the fluctuating nature of heat capacity at \( T_g \) is studied. The fragile nature of the system transforms rapidly at a composition threshold. The compositional range below this threshold has been identified as Nanoscale phase separation (NSPS). To describe this transformation, we have studied the absolute value of the heat capacity of all the samples. This value shows a change in sign
in that threshold. The thermodynamic meaning of negative heat capacity has been corroborated with nanostructure heterogeneity of the system.

To summarize, a threshold has been identified below which the glassy system exhibits NSPS. This threshold segregates two regions based on the nature of bonding. NSPS consists of non-directional, long range ionic bonds that gradually get replaced by covalent bonds beyond the threshold with increasing MoO₃ concentration. The XPS study recognizes the bonds as [–Mo–O–Ag–O⁻––] and complex molybdenum oxide. Finally, the non-reversing enthalpy (ΔHₚ) profile identifies the IP, sandwiched between under-constrained FP and over-constrained SRP. Our observations establish the rigidity percolation in a FIC conditional glass forming system and it proposes a novel method to find the fragility threshold and NSPS.

2. Experimental

A. Glass Preparation

(AgI)₇₅₋ₓ(Ag₂O)ₓ(MoO₃)ₓ solid electrolyte glasses, for 20 ≤ x ≤ 37.5, have been synthesized, by thoroughly mixing constituent compounds as fine homogeneous powder, and melting it in a 2450 MHz-900 watts microwave oven for 10-12 minutes and subsequently quenching the melt, down to room temperature between two steel plates. The idea of keeping Ag₂O concentration constant while varying AgI and MoO₃ concentration, along with the novelty of using microwave heating technique has been discussed elsewhere. [28]

B. Material Characterizations and Analysis

ADSC studies are carried out using Mettler Toledo 822e ADSC instrument operated at 3°C/min scan rate with 1°C scan amplitude, in the temperature range 40°C-200°C for ‘as quenched’ samples (~ 15 mg). The obtained heat flow and heat capacity data have been analyzed using STAR² and OriginPro software. The XPS study has been carried out in AXIS Ultra XPS instrument with monochromatic Al X-ray source. The binding energy scale has been calibrated with C1s 284.8 eV peak. The obtained data are fitted with Gaussian-Lorentzian profile after U2 Tougaard background subtraction with Casa XPS software.

3. Results and Discussions

A. Fragility Threshold and Negative Heat Capacity

ΔSₜ is directly related to two measurable quantities, ΔHₚ and T_g by the form of ΔSₜ = ΔHₚ/T_g [12]. When the model solid is glass, ΔSₜ = 0, which indicates that the configurational freedom of glass and liquid are same, otherwise ΔSₜ > 0. Apparently, this feature of configurational entropy is directly
reflected upon $\Delta H_{nr}$. In ADSC, the non-reversing heat flow signal exhibits a Gaussian profile encompassing $T_g'$; area under that profile yields $\Delta H_{nr}$ [17]. Furthermore, as ADSC involves a sinusoidal modulated heat flow response, the resultant heat flow gets associated with non-zero phase lag ($\varphi$). Hence, total heat capacity ($C^*$) is represented by using complex notations; real, in-phase, phase-corrected reversing heat capacity ($C_{p\text{PCR}} = C^* \cos \varphi$) and out-of-phase, kinetic heat capacity ($C_{p\text{K}} = C^* \sin \varphi$). Other than melting, out-of-phase correction of heat capacity is negligible i.e. $C^* \approx C_{p\text{PCR}}$ [29]. Measuring $C_{p\text{PCR}}$ along with $\Delta H_{nr}$ has played necessary roles from two different perspectives.

A large fluctuation in heat capacity near $T_g$ is a manifestation of deviation from Arrhenius type relaxation behavior due to increasing non-directional bonds. Significant amount of directional covalent bonds form strong system [30, 31] which is a necessary requirement for rigidity transition. This non-Arrhenius type behavior suggests system’s high vulnerability towards thermal and structural degradation. Thus, determining the fragile and strong compositions for the present glass has a significant importance in the context of rigidity transition, fragility and relaxation.

Figure-1(a) shows normalized $C_{p\text{PCR}}$ versus $T/T_g$ plot for two different representative samples, (AgI)$_{50}$-(Ag$_2$O)$_{25}$-(MoO$_3$)$_{25}$ and (AgI)$_{42.25}$-(Ag$_2$O)$_{25}$-(MoO$_3$)$_{32.75}$. Clearly, near $T_g$, glass with higher AgI concentration, (AgI)$_{50}$-(Ag$_2$O)$_{25}$-(MoO$_3$)$_{25}$ exhibits more fluctuations than the other, indicating the fragile nature and deviation from Arrhenius type relaxation in viscosity. The role of AgI is to expand the free volume to enhance the ionic conductivity [32]. The present result corroborates with this understanding of the role of AgI. The expansion of glass matrix causes creation of free volume and lower coordination that directly impact the $C_{p\text{PCR}}$-$T/T_g$ profile; with higher AgI concentration, the system becomes more fragile.

It is interesting to explore how this fluctuating $C_{p\text{PCR}}$-$T/T_g$ profile gets stabilized or how the fragile-strong transition occurs over compositions. Interestingly, there is a threshold where the nature of fluctuation changes abruptly. This occurs in the sign of the absolute value of $C_{p\text{PCR}}$. As the sign of $C_{p\text{PCR}}$ for an individual sample remains same over the ADSC scanning range, $C_{p\text{PCR}}$ at $T_g$ i.e. $C_{p\text{PCR}}(T_g)$ is considered as an indicator of the sign of $C_{p\text{PCR}}$.

Figure-1(b) shows $C_{p\text{PCR}}(T_g)$ values for all the compositions along with $T_g$. The $T_g$ increases monotonically with the increase in MoO$_3$ concentration. However, $C_{p\text{PCR}}(T_g)$ shifts from negative (Region-I) to positive (Region-II), at a threshold between (AgI)$_{30}$-(Ag$_2$O)$_{25}$-(MoO$_3$)$_{45}$ and (AgI)$_{31.25}$-(Ag$_2$O)$_{25}$-(MoO$_3$)$_{43.75}$. Besides, samples with negative $C_{p\text{PCR}}(T_g)$, exhibit more fluctuations in normalized $C_{p\text{PCR}}$-$T/T_g$ profile than the samples with positive $C_{p\text{PCR}}(T_g)$.
Figure 1(a) Normalized $C_{p,PCR}$ ($Jg^{-1}K^{-1}$) versus $T/T_g$ plot for two representative samples, $(AgI)_{50-}$ $(Ag_2O)_{25-}(MoO_3)_{25}$ and $(AgI)_{42.25-}(Ag_2O)_{25-}(MoO_3)_{32.75}$. (b) Absolute values of $C_{p,PCR}(T_g)$ ($Jg^{-1}K^{-1}$) and $T_g$ °C vs. MoO₃ concentration (mole percentage).

This scenario needs to be considered from two perspectives; what does negative $C_{p,PCR}$ mean exclusively for this sample and thermodynamically? A study on the effect of pressure on conductivity in AgI-Ag₂O-MoO₃ glass by H Senapati et al. [33] suggested a tissue and cluster type structural model where the whole glass structure is composed of clusters, connected by less dense and compressible tissue material. Initially, the applied pressure influences the tissue by reorganizing it to yield a structure similar to that of cluster.

The schematic in Figure-2 shows this [33] effect of pressure on the total volume ($V_{total}$) that constitutes of tissue with volume $V_{tissue}$ and cluster with volume $V_{cluster}$. With pressure (p), $V_{total}$ decreases in expense of the increase in $V_{cluster}$ i.e. in an isothermal process, $V_{total}$ under pressure remain constant:

$$V_{total} = V_{tissue} + V_{cluster} = \text{Constant}$$  \hspace{1cm} (1)
Figure-2(a) A segment of $V_{\text{Total}}$ which is under pressure constitutes dense cluster ($V_{\text{cluster}}$) and less dense, compressible tissue ($V_{\text{tissue}}$). (b) With increasing pressure, the tissue reorganizes to yield a structure similar to the cluster. (c) Higher pressure changes tissue region in between two clusters and connects them while increasing the $V_{\text{cluster}}$. Pressure increases from (a) to (c)

Thus, the thermodynamic quantity,

$$\left(\frac{\partial p}{\partial V}\right)_T = 0$$

(2)

The thermodynamic relation,

$$C_p - C_v = -\left(\frac{\partial p}{\partial V}\right)_T T \left(\frac{\partial V}{\partial T}\right)_p^2$$

(3)

Where $C_p$ and $C_v$ are isobaric and isochoric heat capacities respectively, becomes

$$C_p - C_v = 0$$

(4)

Hence the experimentally obtained $C_{\text{pPCR}}$ and relation (4) substantiate same sign for $C_v$.

Now, in the thermodynamic context, negative $C_v$ is undoubtedly a compelling topic in the branch of thermodynamic behavior of nanoclusters where two different structural phases separated by free energy barrier [34]. Negative $C_v(\equiv (\partial E/\partial T)_V)$ is a consequence of the ‘$S$’ shaped bend in the caloric curve, which has been argued to be the indication of dynamic phase coexistence [35-37, 39]. In a critical temperature, small finite system undergoes critical oscillation between two metastable states, giving rise to negative slope in the caloric curve [34-40].

Thus, incorporating these two assertions, ‘sample based’ and thermodynamic, it is suggested that negative $C_{\text{pPCR}}$ is a result of structural phase, consisted of tissue and cluster. This type of nanoclustering, segregated from backbone forming glass matrix, is the NSPS phenomena. NSPS has been observed earlier in certain glassy systems in some studies on rigidity transition while their detection of NSPS has
been based on structural characterizations e.g. X-ray diffraction, Raman etc. [8, 12, 16, 41-44]. Within NSPS, samples exhibit non-Arrhenius behavior. The NSPS occurs within the compositional range because of loss of network connectivity. Thus this fragility threshold, defined as the sign shift of $C_{p\text{PCR}}$, can be regarded as a shift from a less connected to a highly connected network. To explain this nature of network connectivity or bonding in terms of chemical states of the constituents, we performed XPS for some of the samples from Region-I and Region-II.

**B. XPS study**

High resolution XPS peaks for Ag3d, Mo3d and O1s spectrums have been obtained. The binding energy (BE) for Ag3d5/2 peak is at 367.3 eV for Region-I and 366.8 eV for Region-II i.e. $\Delta BE = BE(\text{inal}) - BE(\text{initial}) < 0$. Early studies have assigned 367.3 eV peak to Ag3d5/2 peak for Ag2O where the oxidation state of Ag is $+$1 and 366.8 eV peak for AgO that contains equimolar mixture of Ag($+$1) and Ag($+$3) oxidation states that appear to have average valency of Ag$^{2+}$ [45,46]. Surface content of silver, mostly gets oxidized, giving rise to only Ag3d5/2 peak for Ag-O bond, whilst Ag-I remains very weak, indicating that the features of AgI comes within the bulk property of the sample. The binding energy for Mo3d5/2 in the spectrum appears at 230.63 eV and 231.18 eV. This suggests that the oxidation of Mo consisted of Mo$^{4+}$ and Mo$^{5+}$ species respectively [47, 48]. The relative intensities for peaks of both Ag3d5/2 and Mo3d5/2 remain unchanged over the whole composition range.

Figure-3 shows deconvoluted O1s spectrum for representative samples, $(\text{AgI})_{47.5}-(\text{Ag}_2\text{O})_{25}-(\text{MoO}_3)_{26.25}$ and $(\text{AgI})_{42.5}-(\text{Ag}_2\text{O})_{25}-(\text{MoO}_3)_{32.5}$ from Region-I and Region-II, respectively. The O1s spectrum consists of lattice oxygen (O$_L$) that is related to Ag-O bonding, adsorbed oxygen (O$_A$) that contains hydroxyl group, lattice defects and surface organic contaminations that result in C1s spectrum, oxygen bonded with Mo$^{4+}$ (O$_{\text{Mo(IV)}}$) and Mo$^{5+}$ (O$_{\text{Mo(V)}}$). The peak at 528.8 eV has been assigned to O$_L$, 530.7 eV to O$_A$ [49], 531.7 eV to O$_{\text{Mo(IV)}}$ [50] and 530.0 eV to O$_{\text{Mo(V)}}$. 

8
Figure-3 O1s spectrum for representative samples (a) (AgI)$_{47.5^-}$ (Ag$_2$O)$_{25^-}$ (MoO$_3$)$_{26.25^-}$ (Ag$_2$O)$_{25^-}$ (MoO$_3$)$_{32.5^-}$ (b) (AgI)$_{42.5^-}$ (Ag$_2$O)$_{25^-}$ (MoO$_3$)$_{32.5^-}$

Figure-4 shows the change in relative intensities of all the oxygen peaks. The relative intensity increases rapidly for O$_L$ from Region-I to Region-II in expense of other oxygen species.

Figure-4 Relative intensities of oxygen species

The O$_A$ intensity decrement and its contribution to O$_L$ intensity is interpreted by the equation,

$$O_2^{(absorbed)} + 4e^- \rightarrow 2O^2^-(lattice)$$

(5)

Part of these excess O$_L$ populates around Ag while eventually increasing its oxidation state; this situation gets associated with the shift of Ag3d$_{5/2}$ peak, a transition from Ag(I)-O in Region-I to Ag(I, III)-O in Region-II. O$^{2^-}$ is nucleophilic with a tendency to form metal-oxygen-metal bonds [50] and hence, part of O$_L$ gets associated with less electronegative Mo and consequently modifies O-Mo bonds. Both O$_{Mo(V)}$ and
$O_{\text{Mo(V)}}$ peaks shift towards lower binding energy (~0.21 eV for $O_{\text{Mo(IV)}}$ and ~0.51 eV for $O_{\text{Mo(V)}}$) with significant decrease in relative intensity. Besides, Mo$^{4+}$ and Mo$^{5+}$ peak positions and intensity remain unchanged throughout the composition range. Thus, the oxidation of Ag and subsequent reduction of $O_{\text{Mo(IV)}}$ and $O_{\text{Mo(V)}}$ doesn’t affect $O_L$ and Mo species, respectively. This situation suggests electron sharing, hence bond formation that can be interpreted as $[-\text{Mo}–\text{O}–\text{Ag}–\text{O}_L–]$. The oxidation states of Mo and $O_L$ does not get affected at the expense of the formation the ($O–\text{Ag}$) bond. $[-\text{Mo}–\text{O}–\text{Ag}–\text{O}_L–]$ is the covalent structural unit of this glass that properly forms in Region-II. These units are either absent or partially formed in Region-I that might cause the clustering and hence negative $C_p$PCR. Besides, the decrease in relative intensity of $O_{\text{Mo(IV)}}$ and $O_{\text{Mo(V)}}$ suggests that more Mo is being shared with less O i.e. formation of complex oxides of Mo. These conclusions, together suggest, overall increase in covalent bonds, hence BO, during the transition from Region-I to Region-II. Previous discussion on negative heat capacity, along with the present one concludes where and why the rigidity percolation should occur in this FIC glass.

C. $\Delta H_{\text{nr}}$ and Intermediate Phase

Figure-5 shows $\Delta H_{\text{nr}}$ profile over the whole composition range. The data acquisition technique has been rigorously discussed earlier by Micoulaut et al. [17]. The heat capacity study confirms the presence of NSPS within $20 \leq x \leq 30$. The gradual formation of $[-\text{Mo}–\text{O}–\text{Ag}–\text{O}_L–]$ bonds within the system incorporates with the decreasing profile of $\Delta H_{\text{nr}}$ with MoO$_3$ concentration. Beyond NSPS, the system becomes necessarily and sufficiently covalent to exhibit the rigidity percolation.

The significance of rigidity phases is well studied [8-14, 16-19]. In this work, we also pursue the same context of the significance. The FP is found to be within $31.25 \leq x \leq 32$. Beyond FP, the system starts becoming rigid. The SRP appears beyond $x \geq 35.5$. Between these two regions, for $32.25 \leq x \leq 35$, square well like global minima appears, where $\Delta H_{\text{nr}}$ becomes very less, implying $\Delta S_c \sim 0$. This mechanically rigid but stress free region is IP. Thus, these results confirm the presence of rigidity percolation and NSPS in this FIC, conditional glass forming system, $(\text{AgI})_{75-x}(\text{Ag}_2\text{O})_{25}(\text{MoO}_3)_x$. These results can be corroborated further with various features of this system to improve applicability and understanding.
4. Conclusion

In this work, we have investigated the rigidity percolation phenomena in a FIC, conditional glass forming system. The appearance of rigidity percolation in ion conducting oxide glass system is not as apparent as in case of covalent chalcogen based glasses. The rigidity percolation fundamentally requires short range, covalent bonding where $n_1$ plays most significant role; in case of long range, ionic bonding, the percolation gets perturbed by higher order coordination. Besides, the glass formation in conditional glass formers is not as smooth as other covalent glass formers like SiO$_2$, GeO$_2$, P$_2$O$_5$. There are significant differences between conditional and other glass formers from chemical and topological aspects. The non-directional ionic bonds make the system fragile and the temperature dependence of viscosity deviates from Arrhenius behavior.

In order to know, at which threshold, this fluctuating behavior transforms into a stable profile, we examined the nature of heat capacity and interestingly, it changes sign during this transformation. The thermodynamic aspects of negative heat capacity suggest heterogeneous clustering within the system. This observation of negative heat capacity corresponding to heterogeneity of the system has been identified as a novel method for detecting NSPS. The XPS study reveals the formation of [–Mo–O–Ag–O$_L$–] bonds to give rise to the required covalent nature of the system. These two conclusions together establish the reasonability of the existence of rigidity percolation. Finally, the
measured value of ΔH_m, while plotted against composition, exhibits well like global minima for 32.25 ≤ x ≤ 35. This denotes the IP where the system is rigid but stress free and ΔS_c~ 0.

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