

# Analysis of Activation Energies & Experimental Evidence for Energetic Phase Separation in $\text{Ge}_x\text{Se}_{1-x}$ Glassy System

Deepak Sharma<sup>1</sup>, Anand Mohan Awasthi<sup>2</sup>

<sup>1</sup>Applied Science Department, SCRIET, CCS University, Meerut, India

<sup>2</sup>UGC-DAE Consortium for Scientific Research, Indore, India

Email: [deepak22phys@gmail.com](mailto:deepak22phys@gmail.com)

Received 12 March 2014; revised 13 April 2014; accepted 19 April 2014

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## Abstract

Glass science reveals peculiar properties due to the lack of long range order and presence of heterogeneity in Chalcogenide glasses. In thermal studies, structural relaxation at the glass transition region is governed by the activation energy of the cooperative unit (zU). In the cooperative molecular dynamics, we are considering the analysis of three activation energies, namely activation energy per BMS (U), activation energy of the cooperative unit (zU) and the apparent activation energy (z<sup>2</sup>U). From the energetic dynamics of activation energy analysis across the  $\text{Ge}_x\text{Se}_{1-x}$  glass series, data represent three-phase segregation. From our data, we also observed that the value of  $U_{\text{CRR}}/RT_g$  across the  $\text{Ge}_x\text{Se}_{1-x}$  glass series is nominally changed from 34.343 to 36.19.

## Keywords

Activation Energies, Chalcogenide Glasses, Glass Transition, Heterogeneity, Molecular Dynamics, Structural Relaxation

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## 1. Introduction

Structural relaxation is an atomic level rearrangement observed in most amorphous materials and Chalcogenide glasses below the crystallization temperature. Structural relaxation has an impact on optical [1], mechanical [2], and electronic transport properties [3]-[6], and has been also reported for metallic glasses [7]. Amorphous semiconductor such as Si [8], Ge [9], and Chalcogenide glasses, their various elemental combinations are reported for application in electronic nonvolatile resistive memories based on phase change [5] [6] and in thermal transport properties. Nowadays the development of phase change memory technology led to the appearance of new

materials. Chalcogenide glass semiconductors are one of these families due to their interesting properties. Structural relaxations in Chalcogenide glasses occur through cooperative rearranging region, which grow with decreasing temperature. Earlier studies on thermal annealing have shown the presence of significant defect annihilation during the structural relaxation process where point defects such as vacancies, dangling bond, and distorted bonds disappear at traps and recombine in pairs [8]. Our recent work has demonstrated unexpected nano-metric signals reported first time by Raman scattering in present  $\text{Ge}_x\text{Se}_{1-x}$  glasses [10] in place of Boson peak feature in Chalcogenide glasses [11]. The general nature of these excess vibration acoustic vs. optic is quite debated [12]-[16]. The purpose of the current work is to report experimental observations of three-phase separation from activation energies data analysis and nominally change in the values of  $U_{\text{CRR}}/RT_g$  in thermal studies by modulating differential scanning calorimetry.

## 2. Experimental Details

Chalcogenide glasses containing S/Se or Te constitute a rich family in combination with group IV elements. Intense research activities based on these glasses are due to technological applications in resistive phase change memory devices.  $\text{Ge}_x\text{Se}_{1-x}$  glasses were prepared by melt quenching technique, preparation details of glasses are mentioned in the article [10] [17]. Amorphous nature of the sample was verified by XRD, which shows no crystalline Bragg peaks. Glassy nature of the samples was confirmed by modulated differential scanning calorimetry MDSC (2910, TA Instruments). Glass transition temperature  $T_g$  was determined from the inflexion point of baseline shift in their heat capacity data, obtained at heating scan rate of  $5^\circ\text{C}/\text{min}$ , and modulation of  $\pm 1^\circ\text{C}$  at 80 sec period [18] [19].

## 3. Results & Discussion

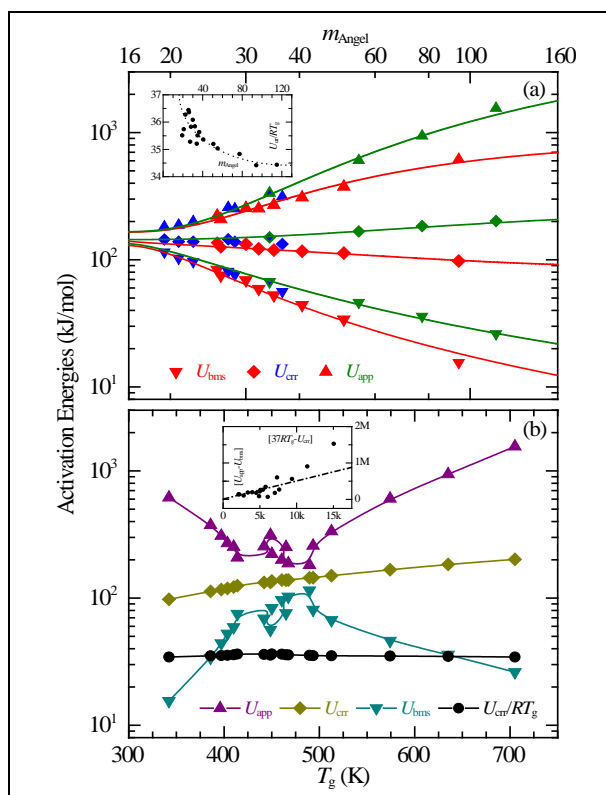
Structural relaxation at the liquid glass transition has been studied for many years. It is commonly believed that glass transition is just to avoid the crystallization process. Glassy state is an extension of liquid state in which viscosity increases above  $\sim 10^{13}$  poise; it means that solid does not flow. Glass transition would then be kinetic in nature, a gradual freezing out of equivalent configurations. The value of glass transition ( $T_g$ ) and the shape of specific heat depend on heating and cooling rates of the measurements and also on the thermal history of the sample [20] [21]. In general, it has observed with the data, position of glass transition temperature shift towards at high temperature, with high heating rates employed.

We have made numerous efforts to understand the nature of glass transition and relate  $T_g$  easily to some quantitative quantity which is  $U_{\text{CRR}}/RT_g$ . In the usual liquid regime above the melting point the isochoric activation energies are very small but the apparent activation energies grow dramatically in the supercooled regime.  $U_{\text{CRR}}$  is the activation energy per basic molecular structural unit at cooperative rearranging region. The concept of cooperative molecular motion is useful to rationalize dramatic changes in the transport properties of liquids as they are cooled towards their glass transition. Mode coupling theory (MCT) [22] attributes slowing down particle motion at low temperature which eventually causes a structural arrest of the liquid dynamics. However, there has been no direct experimental observation of this kind of cooperative motion. It is natural to suppose that cooperative motion might be associated with dynamical heterogeneity. The intermolecular spatial correlation in the glassy state is determined by the collective rearrangement inside the glass transition zone. Correlation length  $\zeta$  considered by Adam Gibb's theory [23] characterizes this cooperative rearranging region in under cooled liquids. The "Arrhenius" activation energy of the basic molecular species is defined as

$$U_{bms} = R \left. \frac{d \ln \tau}{d(1/T)} \right|_{T_0 \rightarrow 0} = RB$$

$U_{bms}$  is identified with the potential barrier formed by the interaction of the molecule with its neighbors [24] [25]. Microscopically glass former is cooled; the identity and nature of dynamical entity undergo significant changes—from being atomic and fast tunneling, to dipolar/rigid polyhedral slowly liberating molecules to loosely connect molecular-clusters, sluggishly diffusing because of free volume [26]. This implies a successive collectivization of the basic atomic motion. Therefore, the assumption of single activation energy and time-scale oversimplifies the hierarchically evolving nature of microscopic glass dynamics.

Non-Arrhenicity ensues from the imperfect de-mixing of  $\alpha$ - and  $\beta$ -relaxation modes, implying that the mole-



**Figure 1.** Behavior of three activation energies and energetic phase segregation.

cular dynamical units in the glass transition region are not independent (*i.e.*, imprecisely defined). This imprecision gets embodied in the form of Vogel-Fulcher temperature dependence of the (atomic) relaxation time. The Vogel-Fulcher form is sometimes interpreted as super-Arrhenius in following manner

$$\tau = \tau_0 \cdot \exp\left[\frac{B}{(T - T_0)}\right] \Leftrightarrow \tau = \tau_0 \cdot \exp(ZU/RT).$$

To describe the cooperative molecular dynamics one thus uses three activation energies viz., that of a basic molecular species  $U_{\text{bms}} = RB$ , cooperative unit  $U_{\text{crr}} = ZRB$ , and the apparent one  $U_{\text{app}} = Z^2RB$ . Activation energies determined for the energetic characterization of  $\text{Ge}_x\text{Se}_{1-x}$  system are shown in **Figure 1** against  $T_g$  and the glass fragility  $m_{\text{Angel}}$ . The A-G factor  $U_{\text{crr}}/RT_g$  seen nominally constant, varies within 34.41 and 36.44! The concurrences  $U_{\text{crr}}/RT_g \rightarrow \sim 37$  when  $m_{\text{Angel}} \rightarrow \sim 16$  and  $Z \rightarrow \sim 1$  (**Figure 1(b)** inset) provide  $(37 - U_{\text{crr}}/RT_g)$  as the “energetic measure” of non-Arrhenicity/spatial uniformity.

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