

# Studies of Different Theoretical Models for Glass Transition Kinetics and Physical Properties of Chalcogenide Glasses

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## Abstract

In this review article I have been discussed the glass transition kinetics and physical parameters of chalcogenide glasses (ChGs) by using melt quenching technique. For glass transition (Gt) kinetics we have been studies various parameters like glass transition temperature Kissinger, Ozawa, and **Matusita's** models for the calculation activation energy ( $E_g$ ) for glassy and crystallization region. In addition, constraint theory and topological models are employed to correlate network rigidity with thermal behavior, while statistical and atomistic considerations are used to assess variations in physical properties with composition. Using different theories we can evaluate many physical parameters for chalcogenide glasses like average coordination number  $\langle z \rangle$ , number of constraints, density, molar volume, loan pair electrons (LP), compactness etc. In this review article I have been discussed different approaches for glass transition kinetics and physical properties of chalcogenide glasses.

Keywords : Glass transition kinetics, Activation energy, Kissinger modal, Loan pair electron, Density

## 1. Introduction

Chalcogenide glasses (ChGs) have piqued the interest of scientists and engineers over the past decade due to their numerous applications in, electronics, and optoelectronics [1-3]. Research on the physic-chemical properties of ChGs can shed light on how they are transported. In particular, structural information is often predicted by analyzing the dielectric properties of ChGs. Understanding the conduction process in these materials is also aided by these experiments. Additionally, the kind and origin of the various losses that occur in the materials are effectively shown by the interaction between temperature, frequency, and the dielectric properties [4, 5]. Selenium is a good option for use in phase switching memory devices due to its strong glass-forming ability(GFA) and strength beside unstructured crystallization [6, 7].Because it can transition between (c-a) crystalline and amorphous phases while subjected to exciting fields and warmth variations, amorphous selenium, in particular, is a marketable material among chalcogens and is widely used in Phase Change Memory devices [8]. However, because of their high photosensitivity, longer mover existence (usually more than 500 ps), and capacity to display, its double metal or metalloid derivatives show better thermal performance than pure selenium. Depending on the different alloying and doping compositions, both types of switching behaviors are commonly referred to as threshold switch and memory switching [9,10]. In this review article I have been discussed differently parameters for kinetics of glass transition kinetics and physical parameters of glassy alloys.

## 2. Experimental

High-purity (99.999%) elements (chalcogen elements with other elements like Se Te with Sn, Cd, In,Zn etc) were weighed in their required at. wt% using a high-precision electronic balance. The weighed glassy alloys were sealed in ampoules (quartz) of 8 cm length and 12 mm internal diameter after evacuating them to a pressure of approximately  $10^{-5}$  Torr, thereby preventing any possible oxidation or contamination during high-temperature processing. The sealed ampoules were placed in a furnace and heated at a controlled rate of 3–4 K/min up to desired temperature where they were maintained for 12 hours. During the melt procedure, the ampoules were periodically rock to make sure uniform mixing and homogeneity of the molten material. After homogenization, the melts were quickly quenched in very cold water to get the samples in the amorphous (glassy) state. The glassy character of the as-prepared samples was

confirmed by X-ray diffraction (XRD). Thermal characterization of the samples was conducted out by means of differential scanning calorimetry (DSC) with a Shimadzu DSC-60 instrument. Approximately 5-10 mg of crushed sample was to be found in standard aluminum pans and heated at heating rates ranging from 5 to 20 K/min. DSC measurements were performed to analyze the thermal behavior, including phase transitions and crystallization kinetics under non-isothermal conditions. The heat-flow sensitivity of the instrument was  $\pm 0.01$  mW, while the temperature accuracy, as determined by the microprocessor-controlled thermal analyzer, was  $\pm 0.1$  K. It has been reported some papers to confirm the glassy nature of chalcogenide glasses.

## 2. Kinetics of Chalcogenide glasses for glassy region

### 2.2. Augis and Bennett Model

Augis and Bennett [11] created a precise model based on the following substitution of  $u$  for  $Kt$  in (1):  
$$\ln[\alpha/(T_p - T_0)] \cong -E_c/RT_p + \ln K_0. \quad (1)$$

### 2.2. Kissinger's model

According to Kissinger [12], the equation can be written as

$$\ln\left(\frac{\alpha}{T_{gp}^2}\right) = -\frac{E_g}{RT_{gp}} + \text{constant} \quad (2)$$

Using this equation the values of ( $E_g$ ) can be calculated by plotting graph between  $\ln\left(\frac{\alpha}{T_{gp}^2}\right)$  and  $1000/T_{gp}$ . The slopes give the value of ( $E_g$ ).

## 3.0 Result and Discussion

### 3.1 Variation of Glass transition Temperature

The following connection was used to assess the  $\langle Z \rangle$  of the glasses under study:

$$\langle Z \rangle = \frac{(\alpha Z_A + \beta Z_B + \gamma Z_C + \delta Z_D)}{(\alpha + \beta + \gamma + \delta)} \quad (4)$$

From the literature  $Z_A$ ,  $Z_B$ ,  $Z_C$  and  $Z_D$  are (coordination number) of A, B, C and D separately and  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ , are the at.wt. %, of elements in that order in the glassy alloys.

The relationship is followed by the fluctuation of ( $T_g$ ) with changing average coordination number.

$$\ln T_g = -aZ + b \quad (5)$$

$Z$  is the average coordination number [16] per atom, which is determined via covalent bonding. The structural alterations brought about by the adding up of In atoms can be used to explain the rising trend of ( $T_g$ ) with increasing In impurity[13]. Two molecular type, winding chains, which comprise helical chains of trigonal Se and  $Se_8$  ring molecules of monoclinic Se, are included in the well recognized structural model for amorphous Se [17–21]. When tin is added to a Se-Te system, the concentration of rings and chains are formed [13]. Indium is likely dissolved in the Se rings and forms bonds with Se.  $T_g$  rises with increasing In impurity because ( $T_g$ ) rises [22] with growing chain length and falls with rising ring concentrations.

The empirical relative use to examine the reliance of  $T_g$  on  $\alpha$  is of the form:

$$T_g = A + B \log \alpha \quad (6)$$

where A and B are constants. The  $T_g$  at a heating rate of 1 K/min is shown by the value of A. Numerous researchers have discovered that the slope B in equation 3 is correlated with the melt's cooling pace; the lower the melt's cooling rate, the lower the value of B. B's physical relevance appears to be connected to how the glass transition area responds to configurational changes.

### 3.4 Activation energy of glass transition ( $E_g$ )

The alternative method involves evaluating the  $E_g$  for the glass transition using the Kissinger formulation [23] (e.g. It has been demonstrated [26–27] that the glass transition activation energy  $E_g$  may be evaluated using the same

equation, which can be expressed as  $\ln\left(\frac{\alpha}{T_g^2}\right) = -\frac{E_g}{RT_g} + \text{const} \tan t$  (7)

The literature frequently uses the notion of structural reduction, which was established by Moynihan and other researchers [28–30], to evaluate ( $E_g$ ) from the heating rate dependence of glass transition temperature.

$$\ln \alpha = -\left(\frac{E_g}{RT_g}\right) + \text{const} \tan t \quad (8)$$

### 3.2 Fragility index (F) and reduced glass transition temperature ( $T_{rg}$ )

The fragility is designed by means of the following equation (9) [31]:

$$F = E_g / (T_g \ln 10) \quad (9)$$

Kauzmann proposed a theoretical relationship between ( $T_g$ ) and ( $T_m$ ) [32]. He claims that the ratio  $T_{rg} = (T_g / T_m)$ , sometimes known as the "two-thirds rule," is a constant that is almost equal to 2/3. The lowered glass transition temperature is known as  $T_{rg}$ .

### 3.3 Stability parameter

The following equation also defines the thermal stability parameter in the literature [33]:

$$S = \frac{(T_p - T_c)(T_p - T_g)}{T_g} \quad (10)$$

In this case,  $T_p$  stands for the peak crystallization temperature and  $T_c$  for the commencement crystallization temperature, or the temperature at which the crystallization peak begins. The resistance to devitrification following glass production is reflected in the thermal stability parameter.

### 3.5 Evaluation of density ( $\rho$ ), molar volume ( $V_m$ ) and compactness ( $\delta$ )

One physical metric used to assess the rigidity of the system is density. This has to do with the system as well. It may

be calculated using the following relation [34]:  $\rho = \left( \sum \frac{m_i}{d_i} \right)^{-1}$  .....(11)

The density value derived in Eq. (11) and the relation [34] are used to calculate the molar volume:

$$V_m = \frac{\sum x_i M_i}{\rho} \quad (12)$$

Compactness ( $\delta$ ) can be used to determine the given formula [35, 36]:

$$\delta = \frac{\sum \frac{c_i A_i}{\rho_i} - \sum \frac{c_i A_i}{\rho_i}}{\sum \frac{c_i A_i}{\rho_i}} \quad (13)$$

The lone-pair electron (LP) has been intended by given formula [34]:

$$LP = V - <Z> \quad (14)$$

### 3.6 Stoichiometry deviation R

The method for determining the R values of  $Se_aTe_bSn_cIn_d$  quaternary alloys has been explained in [35].

$$R = \frac{bN_p + dN_Q}{aN_R + cN_S} \dots \dots \dots (15)$$

Here  $a$ ,  $b$   $c$  and  $d$  are the atomic volume fractions and  $P, Q, R$  and  $S$  are the correspond to coordination numbers

## 4.0 Conclusions

The different theoretical models were successfully applied to study the thermal kinetics and physical properties of chalcogenide glasses. The results show that changes in composition significantly influence network structure, bonding, and rigidity, which in turn govern the physical and thermal behavior of the glasses. Increased average bond energy and coordination number enhance thermal stability, glass transition temperature, and resistance to crystallization. These findings provide useful guidance for designing chalcogenide glasses with improved thermal and physical performance.

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