# Thermodynamic Properties and Kinetic Fragility of GexSe90-xSb10 Chalcogenide Glasses (Postprint)

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## Abstract

The properties of GexSe90-xSb10 (x=20, 23, 25, 30) glasses and their crystals prepared by melt-quenching were investigated using DSC. The glass transition temperature Tg of GexSe90-xSb10 glasses at different heating rates, as well as the temperature dependence of specific heat capacity and entropy for both glass and crystal phases were obtained. Based on these results, the kinetic ideal glass transition temperature T0, thermodynamic ideal glass transition temperature TK (Kauzmann temperature), and kinetic fragility parameter m of GexSe90-xSb10 were determined. The results indicate that Tg, specific heat capacity, and entropy of GexSe90-xSb10 glass and crystal all increase with increasing heating rate. Tg and T0 exhibit a trend of first increasing and then decreasing with increasing Ge content, whereas TK shows a linear increasing trend with increasing Ge content. The m, Tg/TK, Tg/Tm, and Tg/T0 values of GexSe90-xSb10 glasses are 20.7~23.2, 1.183~1.352, 0.678~0.742, and 1.006~1.019, respectively. The m values of GexSe90-xSb10 glasses are all less than 30, and the Tg/TK values are all greater than 1.1, indicating that they are typical 'strong' melts. The Tg/Tm values are all greater than 2/3, indicating relatively strong glass-forming ability.

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# Study on Thermodynamic Properties and Kinetic Fragility of GexSe90-xSb10 Chalcogenide Glasses

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## Abstract

The properties of GexSe90-xSb10 (x=20, 23, 25, 30) glasses and their crystals prepared by the melt-quenching method were investigated using differential scanning calorimetry (DSC). The glass transition temperature (Tg) of GexSe90-xSb10 glasses at different heating rates, as well as the temperature-dependent specific heat capacity and entropy of both glass and crystal states were obtained. Based on these results, the kinetic ideal glass transition temperature (T0), thermodynamic ideal glass transition temperature (TK, Kauzmann temperature), and kinetic fragility parameter (m) were determined. The results show that Tg, specific heat capacity, and entropy of GexSe90-xSb10 increase with increasing heating rate. Both Tg and T0 first increase and then decrease with increasing Ge content, while TK increases linearly with Ge content. The m, Tg/TK, Tg/Tm, and Tg/T0 values for GexSe90-xSb10 glasses are 20.7~23.2, 1.183~1.352, 0.678~0.742, and 1.006~1.019, respectively. Since m is less than 30 and Tg/TK is greater than 1.1 for all compositions, GexSe90-xSb10 glasses are typical "strong" melts. The Tg/Tm values greater than 2/3 indicate strong glass-forming ability.

**Key Words:** GexSe90-xSb10 glass, glass transition temperature, specific heat capacity, kinetic fragility

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## Introduction

Metallic glasses exhibit excellent properties distinct from conventional materials, attracting extensive research attention in recent years. The glass transition represents a major branch of amorphous materials research. Three characteristic temperatures describe the glass transition of melts: the practical nominal glass transition temperature Tg [1~4], the kinetic ideal glass transition temperature (VFT temperature) T0, and the thermodynamic ideal glass transition temperature TK (Kauzmann temperature [5]), at which the entropy of the liquid equals that of the corresponding crystal, representing the limiting temperature for the existence of supercooled melts. Only with precise data on Tg, T0, and TK and their relationships can the evolution of subcritical and critical nuclei in supercooled melts and glass matrices be determined, enabling accurate prediction of amorphous formation ability and precise compositional design of amorphous materials [6~8]. Another important parameter characterizing glass properties is the liquid fragility parameter m. Angell [9] proposed the concept of “melt fragility,” dividing melts into two categories—strong and fragile—based on the magnitude of m to describe structural characteristics of melts and dynamic behavior of glasses.

Researchers have conducted numerous studies on Tg, T0, TK, and m of metallic glasses [10~25]. Jiang et al. [17] determined the TK of Pt69.0Ni9.6P21.4 alloy by measuring the temperature-dependent specific heat capacity and entropy of both crystal and melt states. Jiang et al. [12] obtained Tg, T0, and TK for Zr46(Cu4.5/5.5Ag1/5.5)46Al8 alloy through experiments and calculations. Gallino et al. [26] investigated the specific heat capacity and viscosity of Pt-based metallic glasses using calorimetry and thermomechanical analysis, established the VFT relationship for viscosity measurements, and calculated temperature-dependent structural entropy from specific heat capacity functions. To date, Tg, T0, and TK have been obtained for many metallic glass systems including Zr-based [10~16], Pt-based [11,17,18], La-based [19~22], and Pd-based [10~14,23,24] alloys, and m values have been determined for most metallic glasses. Jia et al. [19] studied the thermodynamic fragility characteristics of La-based metallic glasses, proposed the concept of thermodynamic fragility coefficient MΔS, and pointed out a linear relationship between MΔS and m.

Chalcogenide glasses possess excellent glass-forming and fiber-drawing capabilities, good thermal stability, and outstanding optical properties. They can be molded into complex infrared optical elements in a single step through precision molding technology [27~29], making them promising candidates to replace traditional Ge and ZnSe single crystals in thermal imaging applications. Obtaining the relevant properties of chalcogenide glasses is a prerequisite for their application and development. Vázquez et al. [29] studied the Tg of GexSb0.23-ySe0.77-x+y glasses at different heating rates and determined their crystallization activation energy. Lee et al. [30] investigated the composition dependence of Tg in Ge-rich Ge-Se-Sb glasses and found that Tg is primarily influenced by Ge content. However, studies on T0, TK, and m of Ge-Se-Sb chalcogenide glasses remain limited, particularly regarding TK, for which no reports have been published. This work focuses on investigating the characteristic glass transition temperatures Tg, T0, TK, and m of GexSe90-xSb10 (x=20, 23, 25, 30, atomic fraction) glasses and their relationships.

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## 1. Experimental Methods

Raw materials of 99.999% purity Ge, Se, and Sb were used to synthesize GexSe90-xSb10 (x=20, 23, 25, 30) glasses and crystals. High-purity quartz tubes with an inner diameter of 15 mm served as reaction containers. First, the quartz tubes were cleaned with hydrofluoric acid, acetone, and deionized water, then baked in a vacuum oven at 423 K for 12 h. Subsequently, weighed amounts of Ge, Se, and Sb were loaded into the quartz tubes according to stoichiometric ratios and baked at 393 K for 6 h. Finally, the tubes were sealed under a hydrogen-oxygen flame at a vacuum level of $10^{-4}$ Pa. Both glass and crystal samples were synthesized in a rocking furnace. The glass synthesis procedure involved heating the sealed samples to 513 K and holding for 12 h, then to 903 K for 12 h, and finally to 1173 K for 12 h while rocking the furnace to ensure homogeneous mixing. The samples were then removed from the furnace and cooled in air to obtain GexSe90-xSb10 glass samples. Crystal samples were prepared by cooling the samples from high temperature to 773 K, holding for 72 h, and then furnace cooling to room temperature.

A DSC 823e differential scanning calorimeter was used to measure the heating curves of GexSe90-xSb10 glasses during heating. Temperature and heat flow were calibrated using In and Zn standards with a measurement accuracy of $±$0.02 K. Heating rates were set at 0.167, 0.333, 0.500, and 0.667 K/s, using aluminum crucibles with good thermal conductivity.

Specific heat capacity cp(T) (where T is thermodynamic temperature) was measured using the sapphire calibration method. Each sample required separate measurements of heat flow for empty crucible, sapphire reference, and sample. Heat flow measurements employed a stepwise isothermal method: heating rate Rh of 0.167 K/s, starting isothermal temperature of 373 K, temperature interval of 150 K, and isothermal hold time of 10 min. Sample mass was 20 mg with particle size of 75 mm. High-purity Ar gas was used as protective atmosphere throughout the measurements. To ensure experimental accuracy, each measurement was repeated four times.

The measured heat flow Q can be expressed as: where msam is the sample mass. At the same heating rate, the difference between measured heat flow and baseline heat flow from DSC is proportional to heat capacity (cp(T) · msam). Within a certain temperature range, this can be expressed as:

where Qbl and Qbls are baseline heat flows for empty sample crucible and empty sapphire crucible, respectively, Qsap is the measured sapphire heat flow, cp(T)sap and msap are the specific heat capacity and mass of the standard sapphire reference. From this equation:

The structure of GexSe90-xSb10 glasses was analyzed using an XRD-6000 X-ray diffractometer (XRD) with a scanning range of 10°~80° and scanning rate of 4°/min.

## 2. Results and Discussion

### 2.1 XRD Analysis

[Figure 1: see original paper] shows the XRD patterns of GexSe90-xSb10 (x=20, 23, 25, 30) samples. Three broad diffraction humps appear as diffuse peaks at 2 values of 15°, 30°, and 51°, which are typical structural features of chalcogenide glasses, confirming that the prepared GexSe90-xSb10 chalcogenide glass samples possess a fully amorphous structure.

### 2.2 Glass Transition Temperature Tg

[Figure 2: see original paper] presents the DSC curves of GexSe90-xSb10 (x=20, 23, 25, 30) glasses at different heating rates, with the glass transition temperature Tg indicated. The results demonstrate that Tg of GexSe90-xSb10 glasses is influenced by both heating rate and Ge content. At a constant heating rate, Tg initially increases with Ge content, reaching a maximum at 25% Ge, then decreases with further Ge addition. This trend aligns with the findings of Vázquez et al. [29] in GexSb0.23-ySe0.77-x+y glasses. As the heating rate increases, the Tg values for all four GexSe90-xSb10 compositions shift to higher temperatures, showing significant kinetic effects of the glass transition. This behavior relates to the decrease in relaxation time with increasing heating rate. Higher heating rates result in shorter time periods during heating, requiring higher temperatures for the glass to relax into the supercooled liquid state [31], leading to continuously increasing Tg values.

The overall average bond energy is the primary factor affecting the glass transition temperature in chalcogenide infrared glasses [32,33]. Higher average bond energy corresponds to higher Tg. The chemical bonds present in Ge-Se-Sb glasses and their bond energies [32] are: Ge-Ge (1.63 eV), Se-Se (1.90 eV), Sb-Sb (1.31 eV), Sb-Se (1.86 eV), Ge-Se (2.12 eV), and Ge-Sb (1.48 eV). According to chemical threshold theory, heteropolar bonds (Ge-Se and Sb-Se) form preferentially over homopolar bonds (Ge-Ge, Se-Se, and Sb-Sb).

The overall average bond energy can be expressed as [32]:

where Ec represents the average bond energy of the cross-linked structure, and Erm represents the average binding energy per atom outside the cross-linked structure. For Se-rich structures (x=20, 23, 25), Erm and Ec can be expressed as:

For Se-deficient structures (x=30), Erm and Ec can be expressed as:

where is the average coordination number, =mGe • NGe+ mSe • NSe+ mSb • NSb (where NGe, NSe, NSb are the atomic coordination numbers of Ge, Se, and Sb, being 4, 2, and 3 [32], respectively; mGe, mSe, and mSb are the molar fractions of Ge, Se, and Sb); Pr and Pp represent the cross-linking degrees of Se-rich and Se-deficient structures, respectively; Ehb is the average heteropolar bond energy; ESe-Se is the Se-Se bond energy; E<> is the average energy of Ge-Ge, Sb-Sb, and Ge-Sb bonds, E<>=(EGe-Ge+ESb-Sb+EGe-Sb)/3.

Ehb, Pr, and Pp are:

where EGe-Se and ESe-Sb are the bond energies of Ge-Se and Se-Sb bonds, respectively.

Substituting the bond energy values into equations (4)~(11) yields average bond energies of 2.48, 2.60, 2.68, and 2.65 eV for the four GexSe90-xSb10 (x=20, 23, 25, 30) glass compositions. The overall average bond energy in GexSe90-xSb10 glasses thus shows an initial increase followed by a decrease with increasing Ge content, reaching a maximum at 25% Ge. This trend corresponds well with the Tg behavior shown in [Figure 2: see original paper].

### 2.3 Ideal Glass Transition Temperature T0

According to the Vogel-Fulcher equation [24]:

where A, D, and T0 are fitting parameters, with T0 representing the glass transition temperature as Rh$→$0, i.e., the kinetic ideal glass transition temperature.

The Vogel-Fulcher equation was used to fit the relationship between heating rate and glass transition temperature for GexSe90-xSb10 (x=20, 23, 25, 30) glasses, as shown in [Figure 3: see original paper]. The fitting results yield T0 values of 500.10, 514.49, 562.66, and 548.85 K for GexSe90-xSb10 glasses. T0 exhibits an initial increase followed by a decrease with increasing Ge content, consistent with the trend calculated from data reported by Vázquez et al. [29].

### 2.4 Determination of Thermodynamic Ideal Glass Transition Temperature TK

[Figure 4: see original paper] shows the specific heat capacities of GexSe90-xSb10 (x=20, 23, 25, 30) glassy (undercooled melt) samples and their corresponding crystalline samples during heating. The solid and dashed lines represent curves fitted by least squares for the glassy sample specific heat capacity cp^g(T) and crystalline sample specific heat capacity cp^c(T), which can be expressed as [17]:

where a, b, c, d, e, and f are fitting parameters. The fitting parameters for the specific heat capacities of GexSe90-xSb10 undercooled melts and crystals obtained using equations (13) and (14) are listed in .

The measurement range for crystalline sample specific heat capacity shown in [Figure 4: see original paper] is above 373 K but below the melting temperature. The measurement range for glassy sample specific heat capacity is above Tg but below the crystallization temperature. The specific heat capacity of each chalcogenide glass composition increases slightly with Ge content, with an average value of approximately 117 J/(mol · K).

The entropy difference between glassy (undercooled melt) and crystalline states $\Delta$Sg-c(T) can be expressed as [17]:

where $\Delta$Sf is the entropy of fusion, expressed as $\Delta$Sf=$\Sigma$ixi$\Delta$Sfi (where xi and $\Delta$Sfi are the mole fraction and entropy of fusion of component i, respectively; the entropies of fusion for Ge, Se, and Sb components are given in reference [34]). The calculated $\Delta$Sf values for GexSe90-xSb10 (x=20, 23, 25, 30) are 26.492, 26.644, 26.568, and 26.538 J/(mol · K), respectively.

TK is defined as the temperature at which the entropy of the undercooled melt equals that of the crystal. Setting $\Delta$Sg-c(T)=0 yields TK. Taking the typical composition Ge20Se70Sb10 as an example, the calculated entropy functions for undercooled melt and crystal are shown in [Figure 5: see original paper]. The calculated TK=376.89 K represents the lowest temperature at which the Ge20Se70Sb10 undercooled melt can exist. Similarly, the TK values for GexSe90-xSb10 (x=23, 25, 30) glasses are determined to be 401.68, 418.77, and 473.41 K, respectively.

[Figure 6: see original paper] plots TK as a function of x. Linear fitting yields:

TK = 179.80 + 9.71x

This demonstrates that TK increases linearly with Ge content, indicating that higher Ge content raises the lowest temperature at which the undercooled melt can exist.

## 2.5 Kinetic Fragility

Studies [35~38] have shown that m can be expressed as:

where $\tau$(T) is the temperature-dependent relaxation time. Since viscosity is proportional to relaxation time, shear viscosity  (T) can be used as an approximation for $\tau$(T), making m represent the slope of the viscosity curve at Tg. If the Arrhenius formula [25] describes  (T), then m can be expressed as:

where R is the gas constant and E is the activation energy. Using Tg values measured at different heating rates, the corresponding E values were calculated via the Kissinger equation [39], which were then substituted into equation (19) along with Tg to compute m. lists the m values for the four chalcogenide glass compositions, yielding m values between 20.7 and 23.2 for GexSe90-xSb10 (x=20, 23, 25, 30) glasses. These values are comparable to those calculated for other Ge-Se-Sb glass compositions [40] (Ge8Sb15Se77 (m=33.7), Ge13Sb23Se64 (m=25.7), and Ge18Sb23Se59 (m=32.4)). The magnitude of m reflects the structural stability of the melt near Tg [41] and can be used to classify melts as strong or fragile. Generally, melts with m<30 are defined as "strong," those with m>70 as "fragile," and those with m between 30 and 70 as "intermediate." The GexSe90-xSb10 (x=20, 23, 25, 30) glasses studied here all have m<30, indicating they are typical "strong" melts.

The ratio Tg/TK can characterize the features of "strong" melts at Tg and qualitatively distinguish between strong and fragile melts [42]. GexSe90-xSb10 (x=20, 23, 25, 30) glasses exhibit large Tg/TK values (Tg/TK>1.1 [43]), ranging from 1.183 to 1.357. For strong melts, excess entropy depends only on structural entropy without requiring additional vibrational entropy, resulting in smaller increases in excess entropy above Tg and consequently larger Tg/TK values.

The ratio Tg/Tm can characterize the glass-forming ability of materials [4]. A smaller relative interval between Tg and Tm yields a larger Tg/Tm, making it easier for the melt to bypass the region between Tg and the liquidus temperature without crystallization during cooling, i.e., stronger glass-forming ability. GexSe90-xSb10 glasses show Tg/Tm values between 0.678 and 0.742, all greater than 2/3, indicating relatively strong glass-forming ability.

The Tg/T0 values for GexSe90-xSb10 (x=20, 23, 25, 30) glasses range from 1.006 to 1.019, consistent with results reported by Sreeram et al. [44] for Ge-Se-Sb chalcogenide glasses (Tg/T0 1). From the Gibbs-DiMarzio equation [32]:

where b is a system parameter. Since =ΣixiNi, the average coordination number for GexSe90-xSb10 (x=20, 23, 25, 30) glasses ranges from 2.5 to 2.7, yielding b values of 0.010~0.029 for these glasses.

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## Conclusions

1. The glass transition temperature Tg and kinetic ideal glass transition temperature T0 of GexSe90-xSb10 (x=20, 23, 25, 30) chalcogenide glasses first increase and then decrease with increasing Ge content, reaching maximum values at x=25. The Kauzmann temperature TK increases linearly with Ge content.
2. The kinetic fragility parameter m of GexSe90-xSb10 glasses ranges from 20.7 to 23.2 (less than 30), and Tg/TK ranges from 1.183 to 1.357 (greater than 1.1), indicating these glasses are "strong" melts. The Tg/Tm values between 0.678 and 0.742 (greater than 2/3) indicate strong glass-forming ability.
3. The system parameter b for GexSe90-xSb10 glasses was determined to be in the range of 0.010~0.029.

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## References

[1] Angell C A. Science, 1995; 267: 1924

[2] Fontana G D, Battezzati L. Acta Mater, 2013; 61: 2260

[3] Mukherjee S, Schroers J, Johnson W L, Rhim W K. Phys Rev Lett, 2005; 94: 245501

[4] Turnbull D. Contemp Phys, 1969; 10: 473

[5] Kauzmann W. Chem Rev, 1948; 43: 219

[6] Jian Z Y, Zhou J, Chang F E, Jie W Q. Acta Metall Sin, 1999; 45: 1146 (in Chinese)

[7] Debenedetti P G, Stillinger F H. Nature, 2001; 410: 259

[8] Gibson J M. Science, 2009; 326: 942

[9] Angell C A. J Non-Cryst Solids, 1985; 73: 1

[10] Cai A H, Ding D W, Xiong X, Liu Y, An W K, Zhou G J, Luo Y, Li T L, Li X S. Mater Des, 2014; 63: 233

[11] Gallino I, Schroers J, Busch R. J Appl Phys, 2010; 108: 063501

[12] Jiang Q K, Wang X D, Nie X P, Zhang G Q, Ma H, Fecht H J, Bendnarcik J, Franz H, Liu Y G, Cao Q P, Jiang J Z. Acta Mater, 2008; 56: 1785

[13] Battezzati L, Castellero A, Rizzi P. J Non-Cryst Solids, 2007; 353:

[14] Battezzati L. Rev Adv Mater Sci, 2008; 18: 184

[15] Glade S C, Busch R, Lee D S, Johnson W L, Wunderlich R K, Fecht H J. J Appl Phys, 2000; 87: 7242

[16] Evenson Z, Busch R. Acta Mater, 2011; 59: 4404

[17] Jiang Q, Xu X Y, Li J C. Acta Metall Sin, 1997; 33: 6 (in Chinese)

[18] Legg B A, Schroers J, Busch R. Acta Mater, 2007; 55: 1109

[19] Jia R, Bian X F, Wang Y Y. Chin Sci Bull, 2011; 56: 3912

[20] Lu Z P, Li Y, Liu C T. J Appl Phys, 2003; 93: 286

[21] Senkov O N. Phys Rev, 2007; 76B: 104202

[22] Jiang Q K, Zhang G Q, Yang L, Wang X D, Saksl K, Franz H, Wunderich R, Fecht H, Jiang J Z. Acta Mater, 2007; 55: 4409

[23] Fiore G, Battezzati L. J Alloys Compd, 2009; 483: 54

[24] Fan G J, Löffler J F, Wunderlich R K, Fecht H J. Acta Mater, 2004; 52: 667

[25] Zhu M, Li J J, Yao L J, Jian Z Y, Chang F E, Yang G C. Thermochim Acta, 2013; 565: 132

[26] Gallino I, Gross O, Fontana G D, Evenson Z, Busch R. J Alloys Compd, 2014; 615: S35

[27] Zhang X H, Guimond Y, Bellec Y. J Non-Cryst Solids, 2003; 326:

[28] Varshneya A K, Mauro D J. J Non-Cryst Solids, 2007; 353: 1291

[29] Vázquez J, Barreda D G, López-Alemany P L, Villares P, Jiménez-Garay R. J Alloys Compd, 2005; 390: 94

[30] Lee J H, Lee W H, Park J K, Yi J H, Shin S Y, Park B J, So B, Heo J, Choi J H, Kim H J, Choi Y G. J Non-Cryst Solids, doi: 10.1016/j.jnoncrysol.2015.04.003

[31] Soltana A S, Abu-Sehly A A, Joraid A A, Alamri S N. Thermochim Acta, 2013; 574: 73

[32] Tlchý L, Tichá H. J Non-Cryst Solids, 1995; 189: 141
[33] Guo H, Tao H Z, Gong Y Q, Zhao X J. J Non-Cryst Solids, 2008; 354: 1159
[34] Dinsdale A T. Calphad, 1991; 15: 317
[35] Angell C A. MRS Bull, 2008; 33: 544
[36] Martinez L M, Angell C A. Nature, 2001; 410: 663
[37] Ito K, Moynihan C T, Angell C A. Nature, 1999; 398: 492
[38] Angell C A. J Non-Cryst Solids, 1988; 102: 205
[39] Kissinger H E. Anal Chem, 1957; 29: 1702
[40] Rabinal M K, Sangunni K S, Gopal E S R. J Non-Cryst Solids, 1995; 188: 98
[41] Zhang C Z. PhD Dissertation, Shandong University, Jinan, 2011 (in Chinese)
[42] Guo Y F, Yavari A R, Zhang T. J Alloys Compd, 2012; 536: 91
[43] Angell C A. Physica, 1997; 107D: 122
[44] Sreeram A N, Varshneya A K, Swiler D R. J Non-Cryst Solids, 1991; 128: 294

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*Note: Figure translations are in progress. See original paper for figures.*