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NON-ISOTHERMAL CRYSTALLIZATION KINETICS OF $In_4Se_{96-x}S_x$ CHALCOGENIDE GLASSES USING DIFFERENTIAL SCANNING CALORIMETRY

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In this work thermal analysis of amorphous semiconductor $In_4Se_{96-x}S_x$ (x=0, 4, 8, 12) has been studied by Differential Scanning Calorimetry (DSC) under non-isothermal conditions at four different heating rates i.e. 5^oC/min, 10^oC/min, 15^oC/min, 20^oC/min. Two well defined crystallization exothermic and endotherm peaks are exhibited in the DSC thermogram. Glass transition temperature (T_g), crystallization temperature (T_c), activation energy for structural relaxation (ΔE_t), activation energy of crystallization (ΔE_c), crystallization enthalpy (ΔH_c) and order parameter (n), are estimated by using different methods of analysis such as Johnson–Mehl– Arvami (JMA) model, Ozawa and Kissinger under non-isothermal condition. Surface morphological analysis of annealed thin film at 90^oC have been carried out by Scanning Electron Microscope (SEM) which reflects development of grains. Energy Dispersive Analysis by X-ray (EDX) analysis shows the perfect compositional elements in alloy. On the basis of observed experimental data, it's found that T_c-T_g is maximum and crystallization enthalpy (ΔH_c) is minimum for $In_4Se_{88}S_8$ .This indicates that glass $In_4Se_{88}S_8$ is thermally most stable.

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Keywords: Chalcogenide, Crystallization, Activation Energy, Phase Change, Thin Films

1. Introduction

Amorphous semiconductors consisting of chalcogen element of group VI of the periodic table are called chalcogenide materials prepared by melt quench technique exhibit glass transition phenomenon and hence are called glasses. Chalcogenide glasses have wide applications such as in solar energy conversion, infra-red lenses, optical memory, optical recording media because of their excellent laser writer sensitivity, xerography, laser printing and infra-red spectroscopy[1-3].

When molten semiconducting crystalline material instantly cooled it changes to an amorphous state detaining its semiconducting behavior[4].Any material that has the potential to exist amorphous phase to crystalline phase is useful for technological applications such as optical storage and phase change random access memory (PC-RAM)Because they are stable many years at operating temperature. The speed at which phase change memory devices can operate depends on the crystallization kinetics of the amorphous phase. Long range order is absent in amorphous material that indicate lack of translational periodicity. Thermal analysis is a measurement which shows the change of substance in terms of physical and chemical properties with variation in temperature. The thermal changes in substance are due to exo-thermic and endo-thermic enthalpy transition reaction which caused by phase changes. Activation energy of crystallization has been determined by using Kissinger′s and modified Ozawa equations for non-isothermal crystallization[5].Se has wide applications like switching and xerography but in pure form Se has short lifetime and fragile. To make it robust, it is doped with In, Sb, S etc. Doped Se has large effect on their crystallization temperature, optical and thermal properties[6-7].In this paper we have reported the structural and thermal crystallization of In-Se-S chalcogenide glasses to see the thermal stability for phase change material.

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2. Experimental

Bulk glass alloys of different composition of the $In_4Se_{96-x}S_x$ (x=0, 4, 8, 12) were prepared from high purity constituent elements (99.999%) in stoichiometric ratio by using melt quench technique. The elements were heated to be the in an evacuated (10^{-6} torr) quartz ampoules up to 750^0C.The temperature was raised at the rate of 2^0 C/min[8].During the heating process the ampules were shaken continuously to ensure the homogeneity of the elements. The ampoules in molten state were quenched in ice cooled water. The quenched samples were taken out by breaking the ampoules. The obtained samples were grinded into powder form so that it became homogeneous materials. The thin film on glass substrate were prepared by thermal coating technique at a pressure of 10^{-6}torr.The obtained thin films are annealed at 90^oCfor the investigation of structural properties. Annealing of thin films is of technological importance and scientific interest. The DSC measurements are carried out using XHS-05B DSC Spectrophotometer.

3. Results and discussion

The elements compositions of the annealed thin films were checked using the Energy Dispersive X-ray (EDX) spectroscopy as shown in Figure 1.

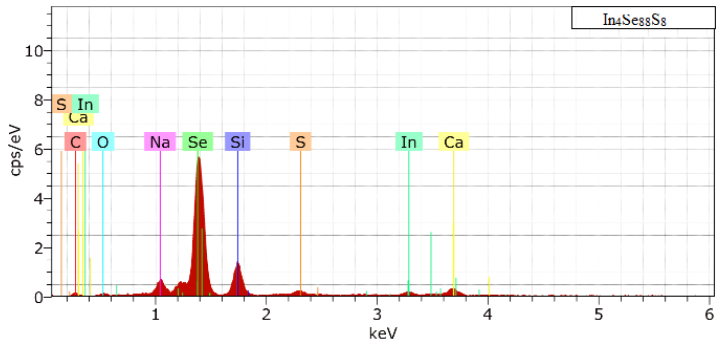

Fig. 1. Energy Dispersive X-ray (EDX) of $In_4Se_{88}S_8$

This image confirms the presence of In, Se and S. Apart from those elements already present in annealed thin film, some peaks of other elements such as Si, Na, C, O and Ca are appearing in the EDX image. This is due to making of thin film on glass substrate. These elements are already present in glass. The EDX picture of other three annealed thin films i.e. $In_4Se_{92}S_4$, $In_4Se_{84}S_{12}$, and In_4Se_{96} confirms the existence of constituent's elements in thin film.

Surface morphology of the thin films were analyzed by Scanning Electron Micro graph (SEM) apparatus JEOL (Model JSM 6380).SEM images of annealed thin films for different composition of sulphur are shown in Fig 2. SEM micrograph reflects that uniformity of the thin film on glass substrate. The average grain size of the thin film decreases with increasing sulphur contents. This leads to decrease in disorderness with addition of sulphur. Same images of the thin films change on percentage edition of sulphur content. The dark crystalline regions of various sizes are indicating nucleation dominated behaviour. The dissociation energy for Se-In, Se-Se, S-S and Se-S are 257.5 KJ/mol,239.3 KJ/mol,206.0 KJ/mol and 381.0 KJ/mol respectively[9].This shows that Se-S bonds require more energy to be dissociated which makes it robust.

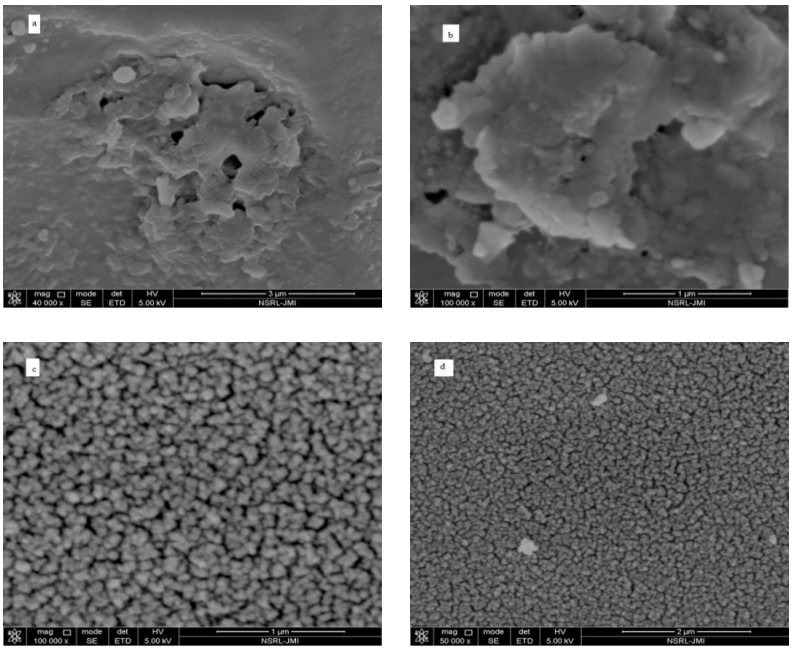

Fig. 2. SEM images of thin films (a) In_4Se_{96} (b) $In_4Se_{92}S_{4\,(c)}$ $In_4Se_{88}S_{8\,(d)}$ $In_4Se_{84}S_{12}$ at 90^0C

XRD analysis were carried out by A Regaku Ultima IV X-ray Diffractometre. The radiation source Cu $K\alpha_1$with $\lambda = 1.54$ A^0, diffraction angle in the range of 5^0 to 90^0 scan speed of 2^0/min and a chart speed of 1 cm/min were maintained for all samples. This pattern is shown in Fig 3 which reflects no sharp peak. Therefore it confirms the amorphous nature of annealed thin film.

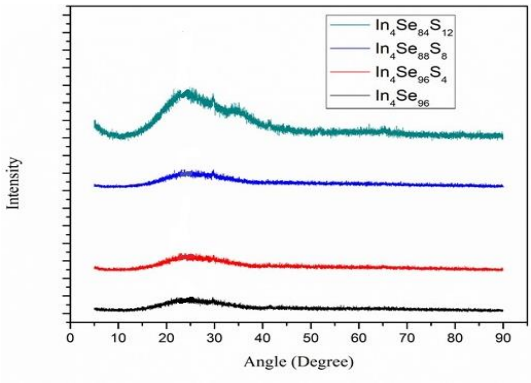

Fig. 3. XRD pattern of annealed thin film at $90^0C$of $In_4Se_{96,}$ $In_4Se_{92}S_{4,}$ $In_4Se_{88}S_{8and}$ $In_4Se_{84}S_{12}$

The thermal behavior of amorphous $In_4Se_{96-x}S_x$ (x=0, 4, 8 and 12) was investigated by using DSC in the temperature range from 25^0C to 250^0C and at different heating rates i.e. 5^0C/min, 10^0C/min,.15^0C/min and 20^0C/min. The amount of 10 milligram of each sample are heated at a constant heating rate and changes in heat flow with respect to empty aluminum pan are measured. DSC thermogram for alloy $In_4Se_{88}S_8$ are shown in Fig 4 (a) at four heating rates i.e. 5^0C/min, 10^0C/min,15^0C/min and 20^0C/min .It is cleared from the characteristics of graph that glass transition temperature (T_g) and crystallization temperature T_c vary with heating rates. Glass transition temperature (T_g) increases with increasing heating rates. DSC thermogram for all four samples at 20^0C/min are shown in Fig4 (b).Two melting points T_{m1} and T_{m2} in sample alloy $In_4Se_{84}S_{12}$ shows partial melting and recrystallization of crystallite at the moment of thermal scanning [10].

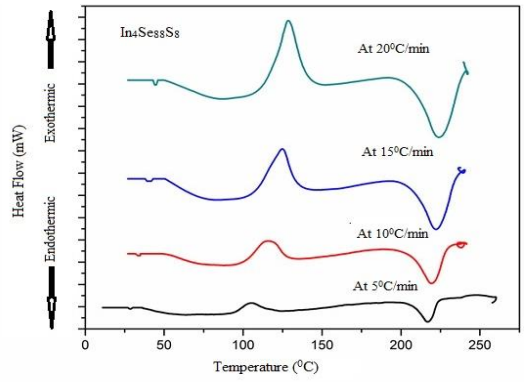

Fig. 4(a) DSC thermogram for $In_4Se_{88}S_8$ at different heating rates

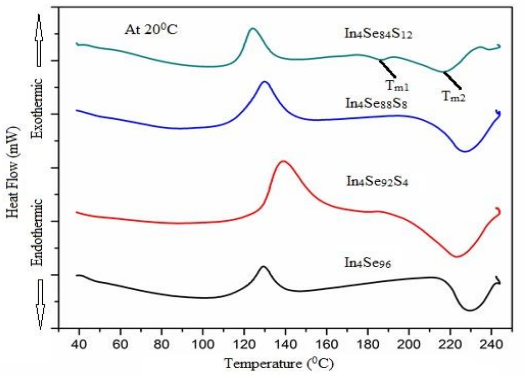

Fig. 4(b) DSC thermogram for $In_4Se_{96,}$ $In_4Se_{92}S_4$, $In_4Se_{88}S_8$ and $In_4Se_{84}S_{12}$ at 20^0C

Table 1(a). Heating rate dependence of glass transition temperature and crystallization temperature for In_4Se_{96} and $In_4Se_{92}S_4$

S.No.	Heating Rate (^{0}C/min)	In_4Se_{96}			$In_4Se_{92}S_4$		
		T_g (^{0}K)	T_c(^{0}K)	T_c-T_g (^{0}K)	T_g (^{0}K)	T_c (^{0}K)	T_c-T_g (^{0}K)
1	5	302.6	375.9	73.4	302.5	373.9	71.5
2	10	304.4	389.5	85.0	307.3	384.4	77.1
3	15	306.6	394.1	87.4	308.1	393.3	85.1
4	20	307.3	399.1	91.8	309.1	397.9	88.8

Table 1(b). Heating rate dependence of glass transition temperature and crystallization temperature for $In_4Se_{88}S_8$ and $In_4Se_{84}S_{12}$

S.No.	Heating rates (^{0}C/min)	$In_4Se_{88}S_8$			$In_4Se_{84}S_{12}$		
		T_g (^{0}K)	T_c(^{0}K)	T_c-T_g (^{0}K)	T_g (^{0}K)	T_c (^{0}K)	T_c-T_g (^{0}K)
1	5	302.1	386.2	84.1	302.4	370.3	67.9
2	10	305.9	397.5	91.6	307.6	376.6	68.9
3	15	306.4	403.3	96.9	307.8	381.9	74.1
4	20	306.5	406.2	99.7	307.9	386.2	78.2

As shown in the above Table 1(a) and Table 1(b),glass transition temperature T_g increases with increasing sulphur concentration at different heating rates.It leads to increasing of lattice rigidity. Tg represents the strength of the rigidity of the glass structure [11].Tg increases with incorporation of sulphur in In-Se system.It can be suggested that the rigidity of the investigated glassy system increases with sulphur content.On the basis of short range order concept ,the decrease in Tg can be attributed to the decrease in the dimensionality of the structural units.Tg is heating rate dependent as observed and shown in table.The results are in tune with those obtanied by J.P.Larmagnac et al. [12] and A.H.Khafagy et al.[13].The supercooled region of an amorphous alloy Tc-Tg is widely used to characterize the thermal stability of these materials.The results present in the table shows that T_c-T_g are heating rate dependants.The higher value of T_c-T_g is obtained for $In_4Se_{88}S_8$ sample , which shows the good thermal stable alloy.

Crystallization kinetics of amorphous semiconductor has been studied using Johnson-Mehl-Arvami (JMA) model[14-16]in which crystallization fraction (α) as a function of time is expressed as

$$\alpha(t)=1 - \exp[-(kt)^n] \quad (1)$$

Where α(t) is the volume fraction crystallized after time t and n isthe Avrami exponent rate constant encompassing nucleation and crystal growth factor whose temperature dependence is generally expressed by the Arrhenian-type equation[17-19]

$$f = fo \exp(-E/RT) \quad (2)$$

wherefo is the frequency factor,E is the apparent activation energy for crystallization, R is the ideal gas constant and T is the temperature in kelvin.
In a non-isothermal DSC measurements, the temperature is changed linearly with time at a rate β (=dT/dt).

$$T=T_0 + \beta t \quad (3)$$

Where T_0 is the initial temperature and T is the temperature after time t. As the temperature constantly changes with time, k is no longer a constant but varies with time in a more complicated from the Eq. (1) becomes

$$\alpha (t)= 1 – \exp[-\{k(T – T_0)/\beta\}^n] \quad (4)$$

after rearranging and taking double logrithms of Eq.(4) becomes

$$\ln[- \ln (1 – \alpha)] = n \ln k (T – T_0) – n \ln \beta \quad (5)$$

according to Eq. (5), a plot of log[- log(1 –α)] versus log β yield a straight line with slope equal to n (order parameter). Fig.5 shows the variation of ln[-ln(1 – α)] against ln β for a-$In_4Se_{96-x}S_x$ (x=0,4,8 and 12) at 100^{o}C.The value of n for the different compositions is given in Table 2. Since as-quenched sample is studied, the value of m is taken as m= n-1[20].The value of m is unity for binary sample while it is two in case of ternary samples, indicating a two-dimensional growth of ternary samples [21]

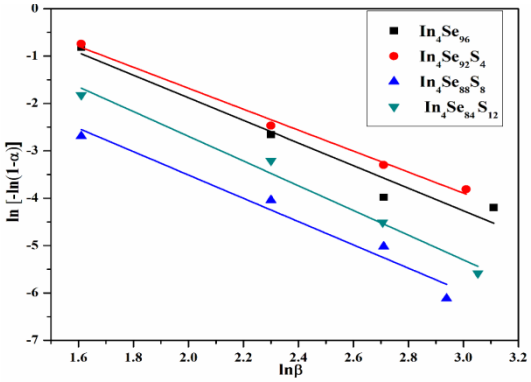

Fig. 5. Graph between heating rates and crystallization fraction

Table 2. Value of Avrami exponent for a- $In_4Se_{96-x}S_x$ (x=0, 4, 8 and 12) at 100°C.

S.No.	Sample	n	m
1	In_4Se_{96}	1.78	1
2	$In_4Se_{92}S_4$	2.21	2
3	$In_4Se_{88}S_8$	2.46	2
4	$In_4Se_{84}S_{12}$	2.60	2

The activation energy of crystallization ΔE_c can be obtained from the variation of the onset crystallization temperature T_c with heating rate by using Ozawa Equation[22-24] as

$$\ln \beta = - \Delta E_c/RT_c + C \quad (6)$$

Where C is a constant and R is a gas constant.

Fig.6 shows log β versus $1000/T_c$ curves, which come to be linear for the entire heating rate. The value of ΔE_c is calculated from the slope of each curve.

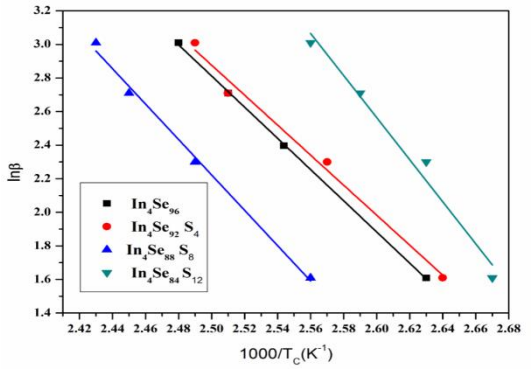

Fig. 6. Heating rate versus crystallization temperature

These values of ΔE_c for all the samples of a- $In_4Se_{96-x}S_x$ (x=0, 4, 8 and 12) is shown in Table 3. The interpretation of the experimental crystallization data is given on the basis Kissinger's, Matusia's[25-27]and modified Ozawa's equations for the non-isothermal crystallization. The activation energy ΔE_c for crystallization can also be calculated by using Kissinger's equation

$$\ln(\beta/T_c^2) = -\Delta E_c/RT_c + D \quad (7)$$

The plot of ln(β/T_c^2) versus $1000/T_c$ for all the sample are shown in Fig.7 which appears to be straight lines. The value of ΔEc may be calculated from the slope of each curve. The values of ΔE_c for all the samples of a- $In_4Se_{96-x}S_x$ (x=0, 4, 8 and 12) are shown in Table 3.

The value of ΔE_c obtained by the above two theories are in good agreement to each other

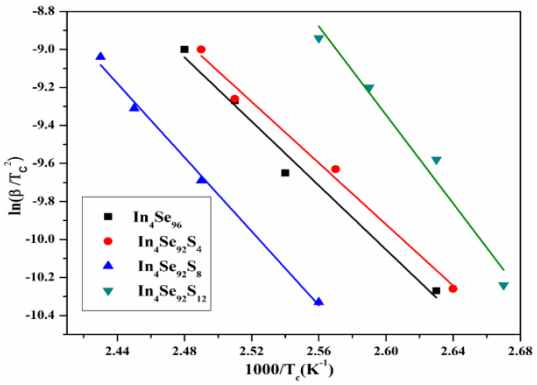

Fig. 7. Graph between $ln(\beta/T_c^2)$ vs $1000/T_c$

The heating rate (β) dependence up on the glass transition T_g in chalcogenide glasses may be interpreted in terms of thermal relaxation phenomena and it has been shown by Moynihan et al [28]that the activation energy of structural relaxation (ΔEt) [29]can be related to T_g and β by

$$d \ln\beta/d(1/T_g) = -\Delta Et/R \quad (8)$$

From the above equation we can conclude that plot of lnβ vs $1000/T_g$ should be straight line and the slope gives activation energy of structural relaxation [30]

Fig 8 shows the graph lnβ vs $1000/T_g$ for all four samples which comes to be a straight line. The value of activation energy of structural relaxation (ΔEt) can be calculated from the slope of these straight lines. Shown in Table 3.It is clear from this table that the value of ΔEc and ΔEt increases monotonically as the sulphur content increases. The present crystallization study shows that ΔEc and ΔEt increases as sulphur concentration increases which also indicates that the rate of crystallization is fast in S incorporated alloys than in alloys with small sulphur content

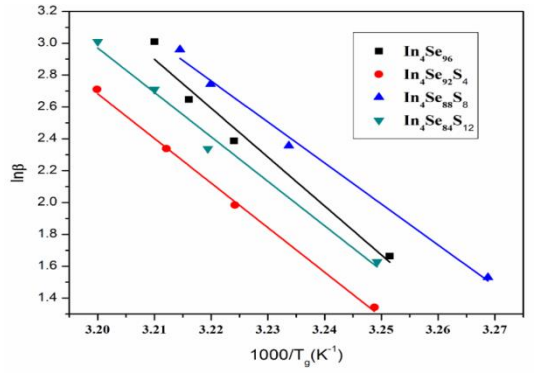

Fig. 8. Heating rate vs glass transition temperature

Table 3. Activation Energy for structural relaxation and activation energy of crystallization

Sample	ΔEt (kJ/mol)	ΔEc (kJ/mol)	ΔEc (kJ/mol)
		From Ozawa's relation (lnβ vs $1000/T_c$)	From Kissingers's equation ($ln\beta/T_c^2$ vs $1000/T_c$)
In_4Se_{96}	25.72	9.29	8.43
$In_4Se_{92}S_4$	27.98	8.93	8.06
$In_4Se_{88}S_8$	28.90	10.54	9.73
$In_4Se_{84}S_{12}$	30.61	12.53	11.65

It has been reported that chalcogenide glass rich in Se content mostly contains about 40% Se atoms in ring structure and 60% of Se atoms in polymeric chains. Selenium glass consists of a mixture of long chains and Se rings. The incorporation of In and S decreases the number of Se rings and increases the number of long Se-S-In polymeric chains and Se-S mixed rings, thus makes the Se-S-In system more rigid and a higher activation energy is needed for molecular motions and rearrangements near the Tg. As the sulphur content increases, the possibility of S-S/Se-S bond may be aroused and hence increases the density of state.

The crystallization enthalpy (ΔHc) [28-31]is evaluated for all composition using the formula

$$\Delta Hc = KA/M$$

Where K is a constant of the instrument used which is taken 1.5.A is the area of the crystallization peak and M is mass of the sample. The value of ΔHc for various composition at heating rate of 5^0C/min, 10^0C/min, 15^0C/min and 20 ^{0}C/min are shown in Table 4.from the table it is seen that the minimum heat is released for composition with 8% of S, which further confirms for the maximum stability of the glass.

Table 4. Crystallization enthalpy of the alloys at different heating rates

Sample	ΔH_c(J/g)			
	At 5 ^{o}C /min	At 10^{o}C /min	At 15 ^{o}C /min	At 20^{o}C /min
In_4Se_{96}	302.93	507.23	817.68	291.54
$In_4Se_{92}S_4$	220.74	345.70	1017.00	351.43
$In_4Se_{88}S_8$	193.52	275.66	721.21	280.16
$In_4Se_{84}S_{12}$	426.19	810.88	1197.00	512.511

4. Conclusions

Crystallisation kinetics of chalcogenide glass $In_4Se_{96-x}S_x$ (x=0, 4, 8, 12) at different heating rates under non-isothermal conditions have been studied. SEM analysis confirms the presence of constituent elements in alloy. XRD pattern confirms the amorphous nature of alloy. Ozawa and Kissinger Equations have been used to determine Activation Energy (ΔEc) of Crystallization and it is found that the value of ΔEc by both techniques are in agreement with each other. ΔEc varies with composition indicating a structural change due to addition of sulphur.

The temperature difference T_c-Tg is maximum for sample $In_4Se_{88}S_8$and crystallization enthalpy (ΔHc) is minimum for the same. This indicates that this glass is thermally most stable. The activation energy of structural relaxation (ΔEt) increases with increasing percentage of sulphur content.

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References

[1] S. Raoux, Phase Change Materials, Annu. Rev. Mater. Res. **39**, 25 (2009).
[2] D. Zhao, X. Zhang, H. Wang, H. Zeng, H. Ma, J.L. Adam, G. Chen, J. Non. Cryst. Solids. **354,** 1281 (2008).
[3] G. Dong, H. Tao, X. Xiao, C. Lin, X. Zhao, S. Gu, Mater. Res. Bull. **42,** 1804 (2007).
[4] N. Solids, N.P. Company, M. Science, M. Carlo, Monte Carlo Models Of Atomic Arrangements In Arsenic-Selenium Glasses 16 (1974).
[5] J. Sesták, G. Berggren, Thermochim. Acta. **3,** 1 (1971).
[6] C. M. Okuda, M. T. Kirimoto, L. T. Measurements, F. H. Naito, O. Prefecture, North-Holland Publishing Company **60,** 1035 (1983).
[7] A. Kumar, Physica B: Condensed Matter **183**(4), 409 (1993).
[8] M. Ganaie, M. Zulfequar, Journal of Alloys and Compounds **687,** 643 (2016).
[9] J. A. Dean, Analytical Chemistry Handbook. McGraw-Hill, 1995.
[10] F. Wang, Q. Liao, H. Zhu, Y. Dai, H. Wang, J. Alloys Compd. **686**, 641 (2016).
[11] M. Zhang, S. Mancini, JournalOf Non-Crystalline Solids **151,** 149 (1992).
[12] J. P. Larmagnac, J. Grenet, P. Michon, J. Non. Cryst. Solids. **45,** 157 (1981).
[13] A.H. Khafagy, Structural And Thermal Properties Of $Se_{85}S_{15}A_ssb_x$ Glassy System, **278,** 119 (2000).
[14] C. W. Price, Use Of Kolmogorov - Johnson - Mehl - Avrami Kinetics In Recrystallization Of Metals And Crystallization Of Metallic Glasses **38**, 727 (1990).
[15] J. Málek, Thermochim. Acta. **267,** 61 (1995).
[16] L. V. Meisel, P.J. Cote, Acta Metall. **31,** 1053 (1983).
[17] J. A. Augis, J. E. Bennett, J. Therm. Anal. **13**, 283 (1978).
[18] M. Avrami, Kinetics Of Phase Change. I General Theory, 1103 (1939).
[19] K. Harnisch, R. Lanzenberger, J. Non. Cryst. Solids. **53,** 235 (1982).
[20] Matusita, Kazumasa, Sumio Sakka, Journal of Non-Crystalline Solids **38,** 741 (1980).
[21] Mahadevan, Sudha, A. Giridhar, A. K. Singh, Journal Of Non-Crystalline Solids **88**, 11 (1986).
[22] T. Ozawa, Kinetics Of Non-Isothermal Crystallization, Polymer **12**(3), 150 (1971).
[23] T. Ozawa, Bull. Chem. Soc. Jpn. **38,** 1881 (1965).
[24] K. Matusita, T. Y. R. Komatsu, K. Matusita, T. Komatsu, R. Yokota, J. Mater. Sci. **19,** 291 (1984).
[25] H. E. Kissinger, Anal. Chem. **29,** 1702 (1957).
[26] H. Yinnon, D. R. Uhlmann, J. Non. Cryst. Solids. **54** , 253 (1983).
[27] K. Matusita, K. Miura, T. Komatsu, Kinetics Of Non-Isothermal Crystallization Of Some Fluorozirconate Glasses **88,** 283 (1985).
[28] C.T. Moynihan, A.J. Easteal, J. Wilder, J. Tucker, J. Phys. Chem. **78**, 2673 (1974).
[29] Y.Q. Gao, On The Activation Energy Of Crystallization **81**, 129 (1986).
[30] O.A. Lafi, M.M.A. Imran, K. Abdullah, Chalcogenide Glasses **395,** 69 (2007).
[31] N. Mehta, R.S. Tiwari, A. Kumar, Glass Forming Ability And Thermal Stability Of Some Se – Sb Glassy Alloys **41**, 1664 (2006).