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CRYSTALLIZATION KINETICS (ISOTHERMAL) AND TIME TEMPERATURE TRANSFORMATION (TTT) of $Ag_xTe_5Se_{95-x}$ ALLOYS

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Samples with composition $Ag_xTe_5Se_{95-x}$ (where x = 2, 4, 6) were prepared by the melt quenching technique. The glassy nature of the prepared samples has been proved through X-ray diffraction (XRD). Hydrostatic density of the as prepared samples is found to increase with Ag content. Such increase goes well with the decreased value of the calculated unshared Lone-pair-concentration. The change of the electrical conductivity with temperature during heating-cooling cycle was also investigated. A sharp increase of the electrical conductivity and a corresponding decrease of the activation energy of conduction are detected as increasing x from 2 to 6, either in the glassy, crystalline or liquid state. The conductivity dependence on time of crystallization in amorphous-crystal transformation was used to calculate the activation energy of crystallization and reaction order (n). It was found that the replacement of Se by Ag decrease the values of activation energy of crystallization. Also, the reaction order n = 2 means that the crystallization process is two dimensional growth. Also, from isothermal results, the time-temperature trans-formation (TTT) curves have been constructed. The value of cooling rate required to avoid a given volume fraction to crystallize was found to increase with increasing Ag content which means that the sample Ag_6 Te_5 Se_{89} need faster cooling rate to prevent the crystallization process. Interpretation of results in terms of the average coordination number, lone-pair concentration and cohesive energy is given.

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1. Introduction

Recently, great attention has been given to chalcogenide glasses mainly due to their wide range of applications in solid state devices both in scientific and technological fields. Optical data storage based on laser induced amorphous to crystal (a-c) phase transformation of chalcogenide glasses is an area with on – going research activity [1-4].

Ag-doped chalcogenide glasses have become attractive materials for fundamental research of their structure, properties and preparation [5-9]. They have many current and potential applications in optics and optoelectronics such as photo doping, optical imaging, photo lithography and phase change (PC) optical recording [10–16].

The principle of phase change PC optical recording is straight forward. It is based on the concept that some physical property of microscopic area of recording layer on disc surface is altered. In this technique, spots of a crystalline material are melted momentarily by start laser pulses for recording and the recorded marks are erased through annealing process during which long laser pulses heat the amorphous spots to return in to crystalline phase. The photo structural changes in the optical properties (reflection coefficient, absorption coefficient, transmission coefficient) of chalcogen alloys due to amorphous to crystalline and crystalline to amorphous phase transformations are then used for erasing and recording of pits in the chalcogenide layer.

Chalcogenide glasses containing Ag, generally, exhibit single glass transition and single crystallization temperatures, which is an important condition for rewritable disks. Thin films of

chalcogenide glasses containing Ag have found application in erasable PC optical recording [13-16]. Different Ag doped chalcogenide alloys have been developed as recording layer and their good practical performance has been reported [13-16].

In PC technology, the laser pulse duration used to erase a written spots is usually several hundred nano-seconds. Hence, the phase transformation in PC recording layer material should be very fast so that erasing is possible in such a time scale. For this reason, the study of a-c phase transformation is very important for the development of some new chalcogenide glasses as better PC recording materials.

The electrical, optical and structural properties of Ag doped chalcogenide glasses have been studied by various workers [10-12], but there are only a few studies reported on crystallization kinetics in these materials [17-19].

The present study reports the effect of replacement of Se by Ag in $Ag_x\ Te_5\ Se_{95-x}$ (where x =2,4,6) system. The study includes measurements of X-ray diffraction, density. The effect of Ag doping has been also followed through the dc electrical conductivity during heating cooling consecutive cycle. The conductivity dependence on time of crystallization in amorphous crystal transformation will be used to investigate the crystallization kinetics of the studied samples isothermally at different temperature, for each composition. Also, from isothermal electrical conductivity data the time temperature transformation (TTT) curves are constructed to determine the cooling rate required to avoid a given volume fraction to crystallize. Interpretation of the results in terms of the lone-pair concentration, expected chemical bonds and cohesive energy is given.

2. Experimental

Glassy alloys of $Ag_xTe_5Se_{95-x}$ (x = 2, 4 and 6) were prepared by melt quenching technique. High purity materials (99.999%) were weighted according to their atomic percentages and were sealed in silica ampoules under the vacuum of 10^{-5} torr. Each ampoule was kept inside the furnace at an appropriate temperature (where the temperature was raised at a rate of 3–4ºC/min). The ampoules were rocked frequently for 10 hrs at the maximum temperature to make the melt homogenous. The molten samples were then rapidly quenched in ice water to produce a glassy solid. The glassy nature of quenched ingots was confirmed by using Philips X-ray diffractometer type (PW1373) with CuK_α radiation and a Ni filter. The change of the electrical conductivity during the disorder phase transitions of amorphous $Ag_xTe_5Se_{95-x}$ alloys had been recorded continuously as a function of time by using pyrex tube supported with two fixed tungsten electrodes.

3. Results and Discussion

3.1. X-ray diffraction

Powder (XRD) patterns of the prepared glasses are shown in Fig.(1). The figure declears that all the studied samples are in amorphous state, where there is no any characteristic diffraction peaks.

3.2. Hydrostatic density:

The density of the as-prepared glasses of the system $Ag_xTe_5Se_{95-x}$ was determined by the hydrostatic weighting method. The results show that the density increases by increasing Ag content from 4.982 to 5.211gm/cm^3 as shown in table (1). The density was calculated from Myuller's formula [20].

$$\rho_{cal} = 1 / \Sigma a_i / \rho_{ci} \quad (1)$$

where a_i is the fraction of the i^{th} structure unit and ρ_i is the density of the i^{th} structure unit. Table (1) illustrates the values of both the experimental and the calculated density for all the glasses under investigation. It is clear that the replacement of Se by Ag in $Ag_xTe_5Se_{95-x}$ causes an increase in

both ρ_{cal} and ρ_{exp}. This indicates the additive nature of density as a character of glassy structure. It is also noted that the calculated values of the density are larger than the experimental one. This is due to chemical and topological defects of the glassy network.

Table (1): The density ρ, the average coordination number z, lone pair concentration LP, cohesive energy C.E., the activation energy of crystallization E_{ac}, the reaction order (n) and the cooling rate required to avoid a given volume of fraction to crystallized for all the studied samples

Composition	ρ_{exp}(gm/m^3)	ρ_{calc}(gm/m^3)	Z	LP	Eac (eV)	n	Cooling rate (deg./s)	C.E.
$Ag_2Te_5Se_{93}$	4.432	4.982	2.04	3.86	1.67	1.94	1.97	1.86
$Ag_4Te_5Se_{91}$	4.576	5.096	2.08	3.72	1.57		2.48	1.84
$Ag_6Te_5Se_{89}$	4.711	5.211	2.12	3.58	1.46		3.14	1.81

3.3. Average coordination number and unshared lone-pair electrons:

Loffe and Regal [21] suggested that the bonding character in the nearest-neighbor region characterizes the electronic properties of semiconducting materials. The average coordination number Z in a binary alloy $A_x B_{1-x}$ is defined by:

$$Z = xN_A + (1 - x)N_B \quad (2)$$

Where N_A and N_B are the coordination number of elements A and B. In ternary and higher order compounds $A_\alpha B_\beta C_\gamma$ is generalized as [21]

$$Z = (\alpha N_A + \beta N_B + \gamma N_C)/(\alpha + \beta + \gamma) \quad (3)$$

The values of Z for the examined glasses are listed in table (1). From the table, it is evident that the replacement of Se by Ag causes an increase in the values of the average coordination number Z, this means a corresponding increase of the degree of cross linking of the glassy lattice. Such increase of the average coordination number may be the result of a decrease of the concentration of unshared Lone-pair electrons (LP). The LP value is calculated according to Zhenhua [22] who stated that

$$LP = V - Z \quad (4)$$

Where V is the valence electron concentration and the values of LP concentration for the examined samples are listed in table (1). As expected the unshared LP concentration decreases with increasing Ag content. Such result goes well with the increase of the hydrostatic density of the system under study with the addition of Ag.

3.4. The chemical bond determination

The chemical bond approach is a method that has been used to examine the structure and the properties of various types of chalcogenide glass. In view of this method: (a) the atoms of one type combine more favorably with atoms of different types, (b) the bonds are formed in the sequence of decreasing bond energy until all the available valences of the atoms are filled and (c) each constituent atom is coordinated by (8-N) atoms, where N is the number of the outer shell electrons.

The bond energies E_{AB} for heteropolar bonds have been calculated by Pouling [23] using the relation

$$E_{AB} = 0.5 (E_{AA} + E_{BB}) + 23 (\chi_A - \chi_B)^2 \quad (5)$$

where E_{AA}, E_{BB} and χ_A, χ_B are homopolar bonds energies and electronegativity, respectively, for A and B atoms. The homopolar bond energies values used are (20.50 Kcal/mol) for Ag, (31.70 Kcal/mol) for Te and (43.81 Kcal/mol) for Se [23]. The electron negativity values used are 1.9 for Ag, 2.1 for Te and 2.4 for Se [23]. The types of bonds expected to occur together with their bond energies as calculated using equation (5) are Se-Ag (37.90 Kcal/mol), Se-Te (39.82 Kcal/mol) and Se-Se (43.81 k cal/mol).

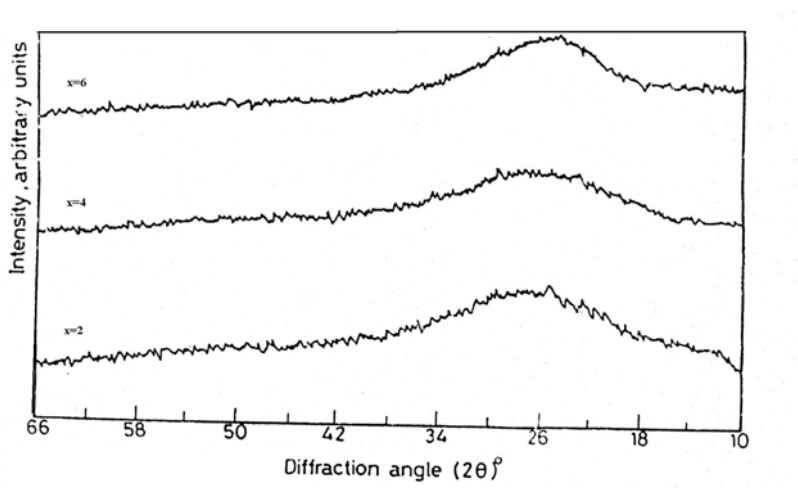

Fig. (1) : X-ray diffraction patterns for $Ag_x Te_5 Se_{95-x}$ (where x =2,4,6).

Assuming that the bond energies are additive, it is possible to estimate the cohesive energy (C.E), by summing the bond energies over all bonds expected in the material. The (C.E) for all the samples was calculated from the following equation [24].

$$C.E = \Sigma C_i D_i / 100 \quad (6)$$

where C_i and D_i are the number of the expected chemical bonds and the energy of each corresponding bond, respectively.

As can be seen from table (1), the replacement of Se by Ag causes a decrease in the values of the cohesive energy for all the studied samples.

3.5. Heat effect on the electrical conductivity of $Ag_xTe_5Se_{95}$ alloys:

To follow the change of the electrical conductivity with temperature (during heating-cooling cycle), the as prepared samples were sealed under vacuum in pyr-ex tubes with two fixed tungsten electrodes. The tubes were then heated at 623K for 6 hours and then quenched in cool air to ensure good contact between the sample and the electrodes and to preserve their glassy texture. The experimental results of the variation of the dc conductivity with temperature are displayed for $Ag_xTe_5Se_{55-x}$ alloys in Fig. (2).

The curve abcdef represents the change in conductivity during heating while the feghi is that during cooling. These obtained curves can be interpreted as follow:

The part ab represents a linear relationship corresponding to conduction in the amorphous state according to the general equation

$$\sigma = \sigma_0 \exp [-\Delta E/KT] \quad (7)$$

where σ is the conductivity, σ_0 is the pre-exponential factor, ΔE is the activation energy of conduction, K is the Bohzmann's constant and T is the absolute temperature.

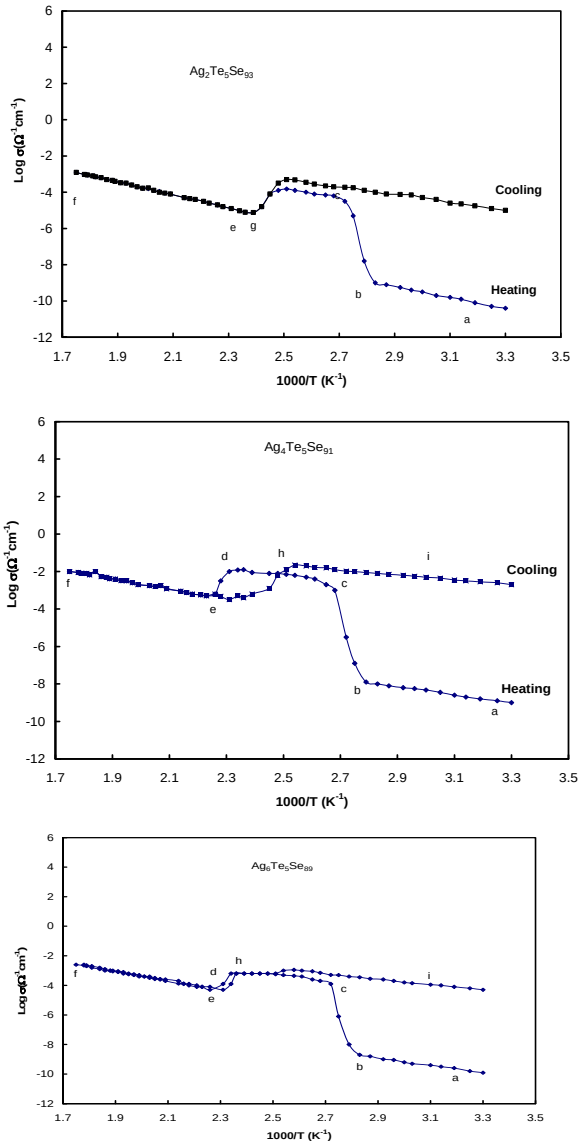

Fig. (2): The dependence of log σ as a function of temperature for all the studied samples

A continuous rapid increase in log σ is observed at point b till point c, this increase in the conductivity may be attributed to the appearance of the crystalline phase which characterizes the conduction during the part cd. Further increase of temperature causes the change of log σ over the line ef as a result of conduction in liquid state.

Table 1. Electrical parameters of the studied samples

Composition	**Liquid state**		**Amorphous state**			**Crystalline state**		
	ΔE(eV)	$\log\sigma_o$	ΔE(eV)	$\log\sigma_o$	$\log\sigma_{20}$	ΔE(eV)	$\log\sigma_o$	$\log\sigma_{20}$
$Ag_2Te_5Se_{93}$	0.71	3.30	0.60	-0.56	-10.8	0.42	-1.53	-5.20
$Ag_4Te_5Se_{91}$	0-.63	2.90	0.54	-0.98	-10.20	0.36	-1.36	-4.50
$Ag_6Te_5Se_{89}$	0.55	2.80	0.44	-1.79	-9.30	0.27	-0.54	-2.90

Values of the activation energy calculated from the slope of log σ and (1/T) for the glassy, crystalline and liquid states are given in table (2). The table shows also values of the conductivity measured at room temperature σ_{20} and those of the parameter σ_0 for the glassy and crystalline state.

During the subsequent cooling cycle feghi of the sample, the rapid increase in the conductivity at the point g is attributed to the crystallization from the liquid state. The part hi represents the change in log σ during the crystalline state. Many results can be extracted from table (2). Firstly, for each state (glassy, crystalline or liquidous), introducing Ag as a metal dopant increases the conductivity value by many orders of magnitude. There is also a corresponding decrease of the ΔE values. Secondly, the values of ΔE for each composition are nearly the same in the amorphous and liquid states since they correspond to the same disordered network. Thirdly, a sharp increase of the value of the conductivity as expected is detected for each composition as it undergoes a transition from the amorphous to crystalline state.

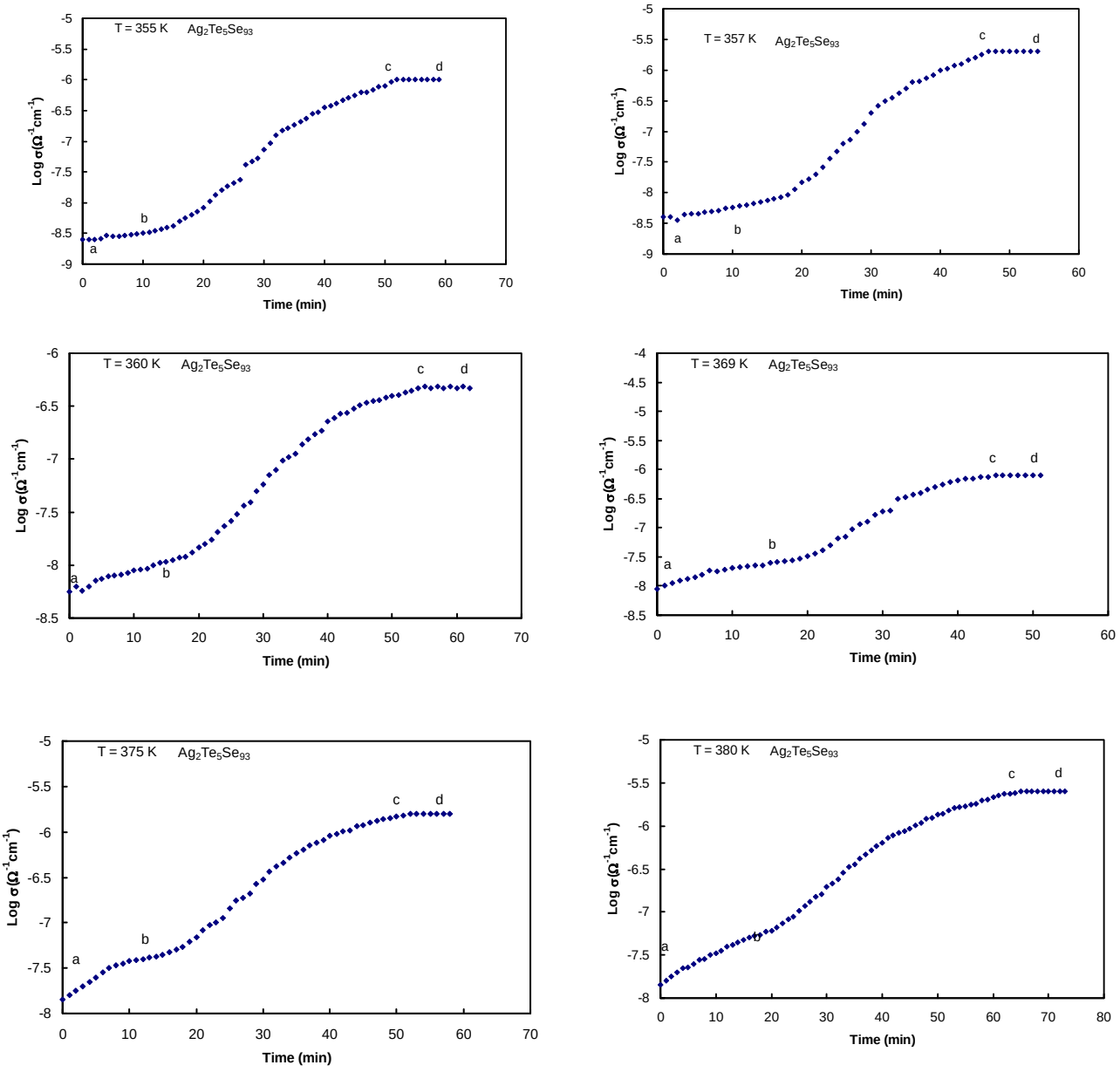

Fig. (3): The vitiation of log σ versus time for the sample $Ag_2Te_5Se_{93}$ which annealed isothermally at different temperatures

From Table (2), it is clear that the replacement of Se by Ag in $Ag_xTe_5Se_{95-x}$ leads to decrease in the values of the activation energy of conduction ΔE for these three states which is due to the replacement of Se-Se bonds (bond energy 43.81 Kcal/mol) by Se-Ag bonds which have a lower bond energy (37.91) Kcal/mol). Hence the cohesive energy of the system and the conduction

is easier, hence, ΔE will decrease. With reference to the above curves, it is easy to know the glass transition temperature Tg. It is represented by the point b, which corresponds to the beginning of rapid increase in log σ. Also, the melting point T_m is represented by point e. The value of T_g and T_m for all the studied samples are given in table (2).

3.6. Crystallization kinetics [isothermal] by using the electrical conductivity method:

If the amorphous material is subjected to isothermal annealing, crystalline phase, begin to grow around some nuclei center formed sporadically or originally present due to defects in the glass matrix. Any physical quantity which changes measurably upon crystallization can be taken as a characteristic parameter to evaluate the extent of crystallization as a function of time. D.c. conductivity had been used as a parameter to study the crystallization kinetics in many of chalcogenide glasses [25, 26].

The change of electrical conductivity during the disorder-order phase transitions of amorphous $Ag_xTe_5Se_{95-x}$ alloys had been recorded continuously as a function of time by using the two dipped electrodes.

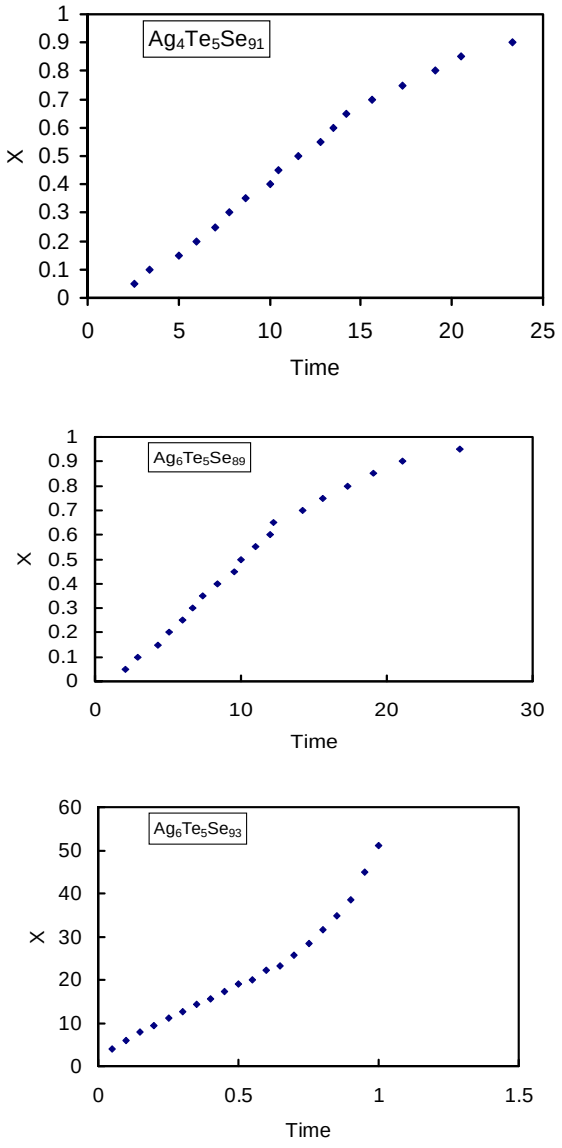

Fig. (4). The relation between X and time for the sample $Ag_2Te_5Se_{93}$ which annealed isothermally at 380K

Fig. (3) represents the variation of log σ with the time for the sample $Ag_2Te_5Se_{93}$ annealed isothermally at different temperatures as representative case.

During the crystallization process each isothermal run can be divided into three stages: the first stage (a-b) which indicates a gradual increase in the conductivity with time due to the normal heating of the sample. The second stage (b-c) shows the sharp increase in conductivity by several orders of magnitude and which attributed to the rapid growth of the crystalline state. Such process is accompanied by liberation of heat energy associated with the transformation from non equilibrium one. The time spent in such transformation was found to be a function of annealing temperature and sample composition. The third stage, beyond point c, electrical conductivity reaches a certain constant value. Such latter value refers to the end of the possible structural transformation process

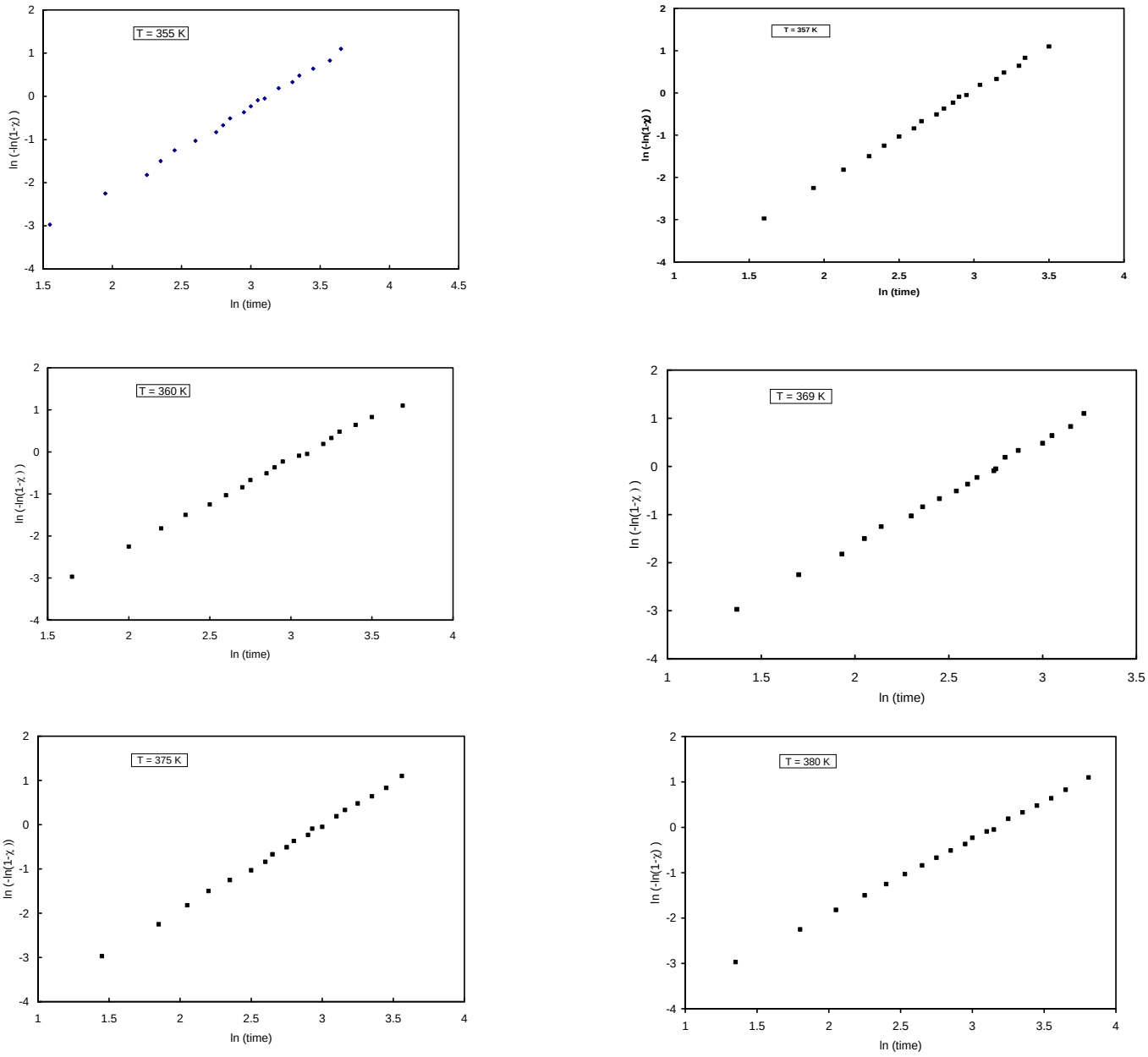

Fig. (5): The relation between ln(-ln (1-χ)) versus ln time for the sample $Ag_2Te_5Se_{93}$ which annealed isothermally at different temperatures

In the present study, the kinetic of the transformation process from the metastable state (amorphous) to the stable one (crystalline) has been calculated by considering the electrical conductivity at any intermediate point between b and c in Fig. (3), during the isothermal transformation as a characteristics quantity for a material containing two phases (amorphous and corresponding crystalline phase).

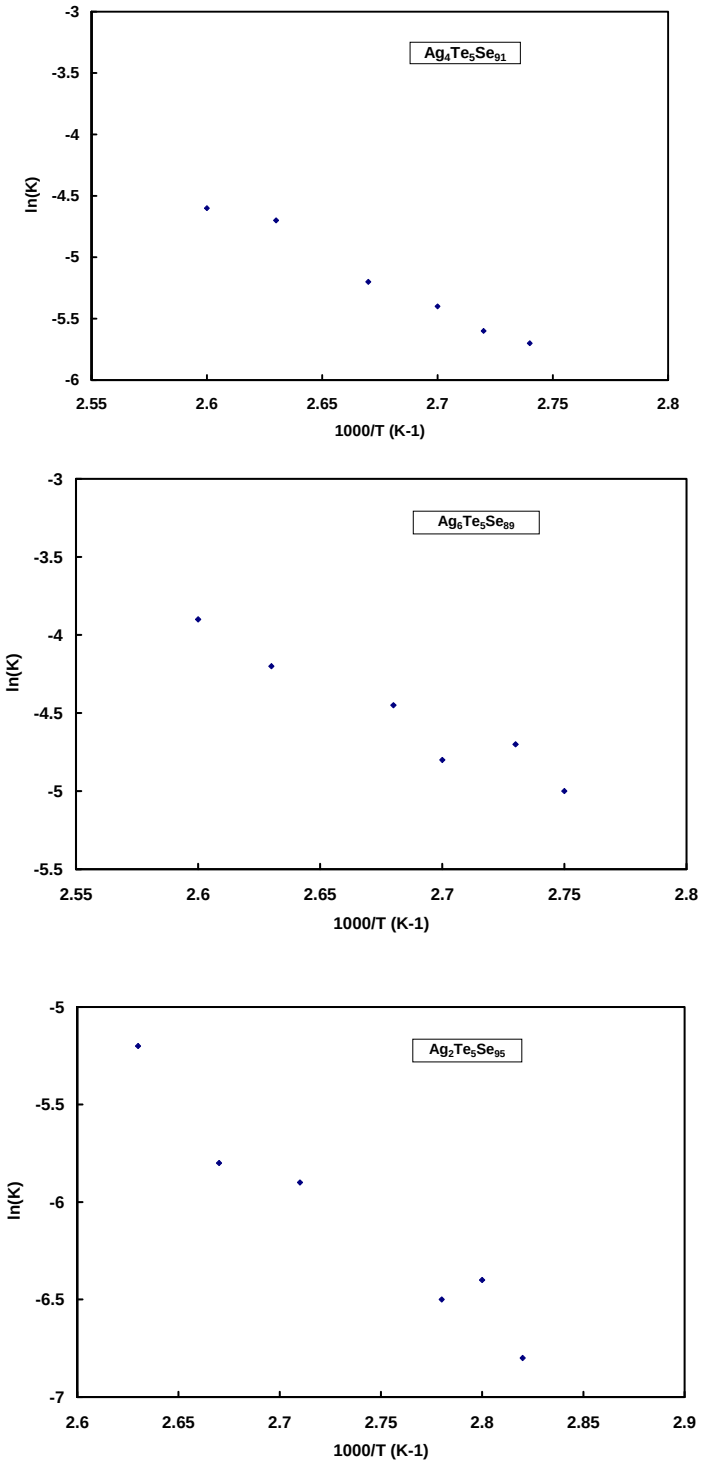

Fig. (6). The relation between ln k and 1/T for all the studied samples

The variation in the extent of crystallization χ with the time can be computed from the empirical formula.

$$1- x = \theta = (\log \sigma_\infty - \log \sigma_t) / (\log \sigma_\infty - \log \sigma_o) \quad (8)$$

Where θ the fraction is left uncrystallized at time t, σ_o and σ_∞ are the conductivities at the beginning and the end of the transformation process, respectively. These correspond to points b and c on the curves of Fig. (3). σ_t is that at any time t between b and c. So, a plot of χ against t gives a measure of the crystalinity as a function of time. Typical curves for such function are set out in Fig. (4) for all the studied samples annealed isothermally at 380 K. It is clear that the curves are sigmoid in shapes for all the samples under investigations.

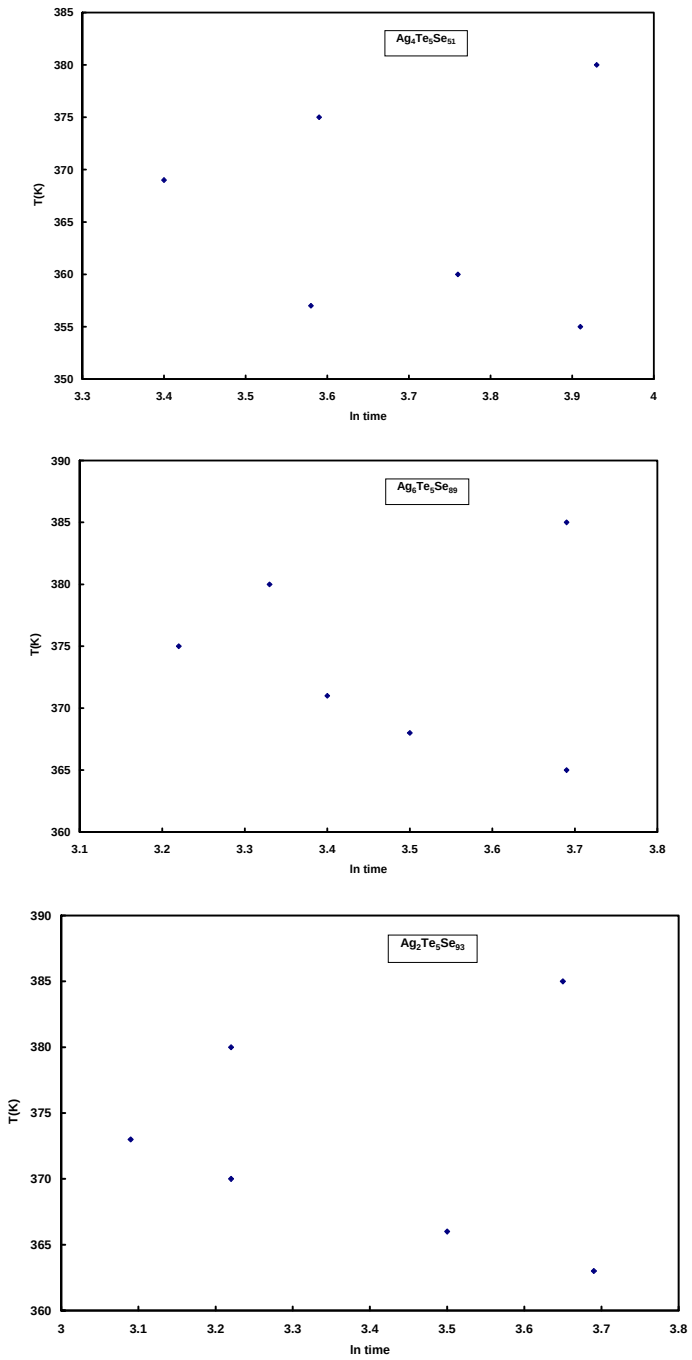

Fig. (7). Time-treatment – transformation (TTT) diagram for 10% crystallization for all the studied samples.

Avrami equation can be written in the form.

$$\ln[-\ln(1-\chi) = \ln K + n \ln t \quad (9)$$

So, the plot of ln [-ln(-1-χ)] versus ln time gives straight lines, the slopes will give n and the intersect gives the value of ln K. Fig. (5) show this relation for all the studied samples annealed isothermally at different temperatures.

The average deduced values of n for all the studied samples are shown in Table (3). It is clear that the average values of n are nearly equal 2 which mean that the crystallization is two dimensional process [27].

The activation energy of the crystallization process during amorphous/crystal transformation E_{a-c} may be calculated from the dependence of the crystallization rate K on the temperature using Arhenius equation.

$$K = K_o \exp [-E_{ac}/RT) \quad (10)$$

Where K is the rate of the crystallization constant, R is the universal gas constant and K_o most often called the frequency factor. ln K are plotted in Fig. (6) as a function of 1/T for all compositions studied. Such plot should be a straight line, in which its slope defines the activation energy of crystallization. The value for the activation energy of crystallization is listed in table (3). From the table, its cleared that the replacement of Se by Ag in $Ag_xTe_5Se_{95-x}$ where [x = 2,4,6] leads to decrease the values of the activation energy of crystallization. It is clear that E_{ac} decreases as number of Lp electrons decreases, see table (1) and according to Zhennha[22], the increase in number of Lp electrons means increase in the tendency of glass formation, so, the glass $Ag_6Te_5Se_{89}$ need a lower energy to crystallize.

3.7. Time-Temperature–Transformation (TTT):

Time temperature transformation (TTT) diagrams have been widely used in industry as a guide to heat treatment procedures and they are of good importance in metallurgy because they may be used to predict the amount of an alloy that will occur during isothermal heat treatment.

If the isothermals are found experimentally at a number of different isothermal transformation diagrams may be draw. This figure is also known as a time-temperature transformation (TTT). It gives the relation between the temperature and the time for fixed fractional amount of transformation to be attained.

In considering the time temperature transformation curves a particular fractions to be formed a given temperature was calculated and the calculation was repeated for other temperatures. The sigmoidal crystallization curves Fig. (4) obtained using the isothermal d.c. conductivity is used to calculate the time required for 100% crystallization for various temperature.

From the isothermal results, the TTT curves retained for all the studied samples are shown in Fig. (7). The nose in a TTT curve, corresponding to the least time for the given volume fraction to crystallize, results from a competition between the driving force for crystallization, which increase with increasing temperature and the atomic mobility, which decrease with decrease temperature.

The cooling rate R_c required to avoid volume fraction to crystallize can be calculated using [28].

$$R_C = (T_m - T_n)/t_n \quad (11)$$

Where T_m is the melting temperature, T_n are temperature and time at the nose of the TTT curve. Table (3), represents the value of R_C for the studied samples. From the Table, it is clear that the value of cooling rate required to avoid the crystallization was found to increase with increasing Ag content, which means that the sample $Ag_6Te_5Se_{89}$ need factor cooling rate to prevent the crystallization process.

4. Conclusions

-By increasing Ag content, both the density and the average coordination number increase, while, both the lone pair electrons and cohesive energy decrease.
-The activation energy of conduction in both amorphous, liquid and crystalline states decrease with increasing Ag content.
-The activation energy of crystallization as being determined by electrical conductivity [isothermally] is found to decrease with increasing Ag content.
-The value of cooling rate to avoid the crystallization was found to increase with increasing Ag content.

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