PHASE TRANSFORMATION STUDIES ON SOME SELENIDE GLASSES

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The phase transformation amorphous-crystalline of the glassy system Se_{90} Ge_{10-x} In_x (x=2, 4 and 6) has been studied. The change in the dielectric constant and dielectric loss tangent at various temperatures above the glass transition temperature and at frequency range 70 Hz - 100 KHz using the step wise method was used. Avrami, s equation was used to obtain the crystallization factors n, K and E. The results show that the order of reaction (n) decreases with crystallization temperature while the crystallization rate constant (K) increases. The activation energy (E) of transformation deduced from both the dielectric constant and dielectric loss tangent increases as the indium content increases.

Introduction

Chalcogenide glasses which contain one or more of the elements Se, Te or S are of great interest because of their possibilities for preparing both electrical [1] and optical [2] memory devices. As it well known, the working principle of such a device is the partial crystallization of the materials caused by rising the temperature by means of a currnet pulse or an intense light beam . Knowledge of crystallization kinetics and morphology is the basis for the applied research of such materials.

The crystallization of an amorphous materials proceeds by the processes of nucleation and growth. . The nature of these processes has been ascertained by analysis of the isothermal rate curves [3,4]. The growth of the nuclei requires transfer of atoms from the materials in the interface onto those nuclei of the product phase. This process was accompanied by the change of many physical properties of the glassy alloy [5,6].

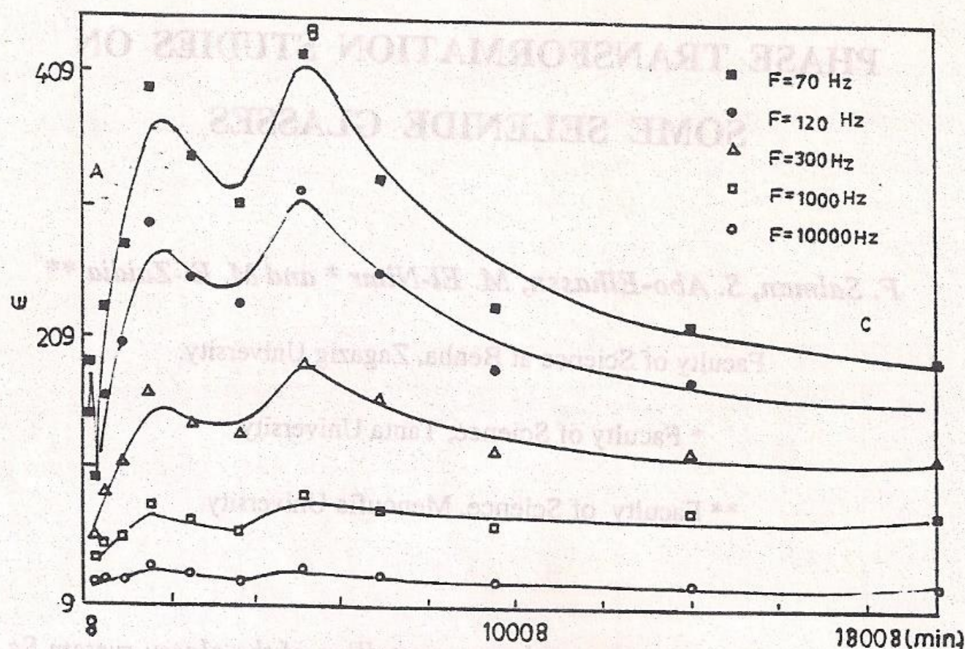

Fig. 1 : The effect of annealing time on the dielectric constnant of Se_{90} Ge_{10-x} In_x (x= 2) at annealing temperature = 120°C and at different frequencies.

The aim of this work is to study the crystallization process of the glass system Se_{90} Ge_{10-x} In_x (x=2, 4 and 6) by means of the change in dielectric properties under isothermal conditions.

Experimental Work :

The starting materials used were Selenium, Germanium and Indium. The necessary amount from each element of the mixture was weighed, loaded in a clean silica tube and sealed under vacuum (10^{-3} torr). The silica tubes were heated at 900°C into preheated furnace for 8 hours. The melt inside the tube was shaken several times during heating to ensure homogenity . After synthesis, the tube was rapidly quenched in ice water to obtain the sample in a glassy state which ensured by X-ray. The glassy samples were powdered and pressed at pressure (10^2 dyne/cm^2) to the disc form. The change in the dielectric constant and dielectric loss tangent as a function of time at crystallization temperatures 120, 130, 140 and 150 °C was recorded. The capacitance and the phase difference have been measured using lock In-amplifier Model (SR 510) with a frequency range 70Hz - 100KHz.

Results and Discussion :

Figs. (1,2) show the effect of increasing the time of crystallization on both the real part of the dielectric constant ε and the dielectric loss tangent (tan δ) of the glassy sample Se_{90} Ge_8 In_2 at differet frequencies during the annealing at 120°C These curves

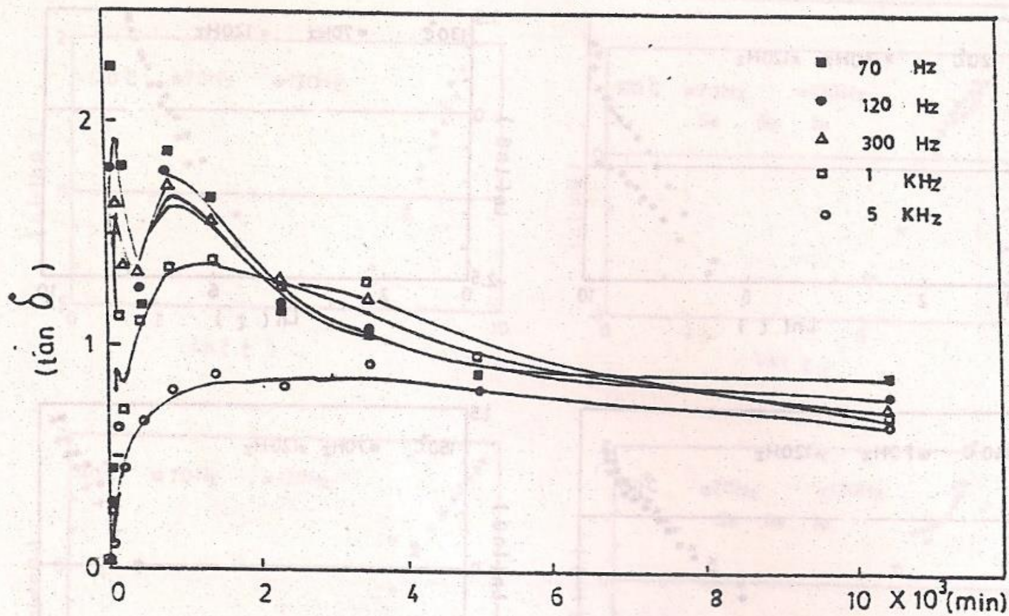

Fig.2 : The variation of dielectric loss tangent with annealing time for Se_{90} Ge_{10-x} In_x in the amorphous state and annealed at 120°C.

show that both ε and tan δ start to decrease as the time of annealing increases to reach minimum constant values. These features were detected clearly at frequencies below 1 KHz. Accordingly, curves of Figs. (1) and (2) can be divided into two periods :

i) Period (A - B) : In this region nucleation process of inhomogeneity regions proceeds by means of fluctuation. Such fluctuation dissipates spontaneously after a short time and finally disappears altogether; another part of them manages to reach the critical size.

ii) Period (B-C) : This period is characterized by a decrease in ε and tan δ as the time of annealing increases to reach constant minimum values as the sample becomes in polycrystalline phase.

The analysis of the crystallization kinetics was carried out using Avrami's equation[7] :

$$1 - \alpha = \theta = \exp(-Kt^{n}) \quad (1)$$

where K is the crystallization rate constant containing nucleation and crystall growth rate constants, n is an integer constant and α is the crystallized fraction at time t given by :

$$\alpha = p_t - p_g / p_e - p_g \quad (2)$$

where p_g and p_e are the measured physical properties at the begining and ending of

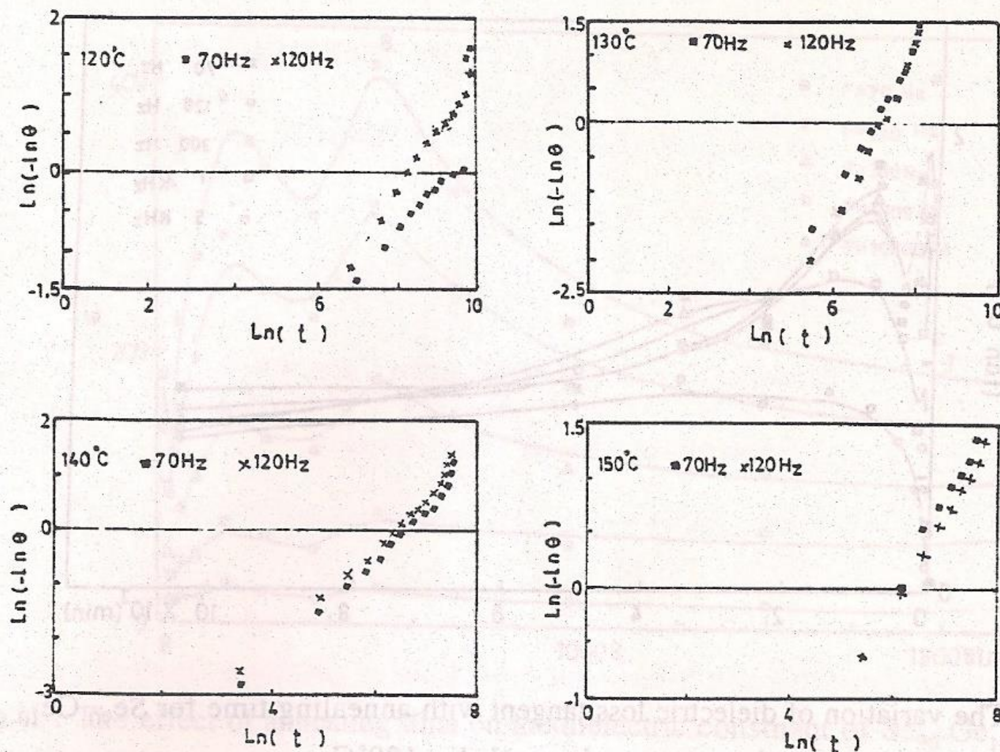

Fig. 3 : The variation of ln (-ln θ) with ln (t) at different annealing temperatures for $Se_{90}\ Ge_{10-x}\ In_x$ fordielectric constant ε.

the crystallization process respectively. P_t is the physical properties at time t between p_e and p_g. Equatiojn (2) can be applied to calculate the kinetic parameters of the amorphous - crystalline transformation during the period B-C of the Figs. (1,2). The analysis of the crystallization process.

The crystallized fraction α was computed for every sample at every crystallization temperature at different annealing times. The values of n were obtained from the slope of the plot ln (- ln θ) against ln (t) (Fig. 3 and 4). All values of n associated with ε and tan δ are tabulated in tables (1) and (2) respectively. It is clear that n decreases as the crystallization temperature increase for each sample. However, n is found to be almost more than unity. This may be attributed to a lower nucleation density such that unidirectional growth develops as the crystallization temperature increases.

Lowering of Avrami index (n) probably indicates that the nucleation sites are saturated in the final stages of crystallization.

Also it can be noticed from tables (1&2) that as the indium content increases the fractional values of the reaction order (n) seems to increase in the temperature range below 140°C, while at higher values of crystallization temperature the values of (n) appear to decrease. The increment in (n) may be attributed to that at low temperature range the nucleation mechanism is a temperature independent (i.e. heterogeneous in

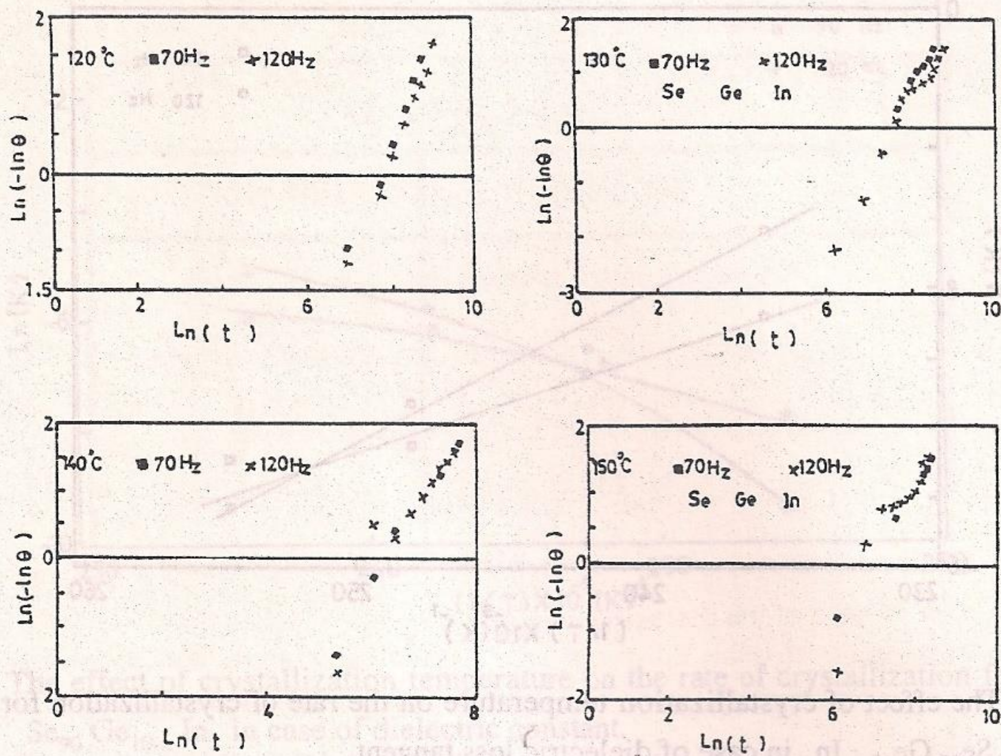

Fig. 4 : The variation at ln (-ln θ) with ln (t) at different annealing temperature and constant frequency for Se_{90} Ge_{10-x} In_x dielectic loss tangent (tan δ).

nature while as the temperature of crystallization increases the nucleation mechanism tends to be homogeneous i.e. unidirectional mechanism.

The crystallization rate constant K at any time for both ε and tan δ calculated from Figs.(3) and (4), is related to the crystallization temperature T by the equation :

$$K = K_o \exp(-E_c / RT) \quad (3)$$

where R is the universal gas constant and E_c is assumed to be the total temperature-independent activation energy of crystallization process and Ko is a constant. The relation between ln (k) and (1/T) for the system Se_{90} Ge_{10-x} In_x (x=2, 4 and 6) at frequencies 70 Hz and 120 Hz from both dielectric constant and dielectric loss tangent are given in Figs. (5 and 6). It is clear that the crystallization rate constant K increases as the crystallization temperature increases. This may be attributed to the growth of the crystalline phase on the expense of the old amorphous one.

The activation energy of crystallization of the system were calculated by the least square method and tabulated in tables (3) and (4) for both ε and tan δ respectively. From these tables it is clear that as the indium content increases the activation energy of crystallization increases. Such increase of E reflects the enhancement effect of the Indium in hindering the crystallization of germanium and selenium . As the Indium