

# KINEMATICAL TRANSFORMATIONS AND STRUCTURAL AGEING OF AMORPHOUS $\text{Se}_x\text{Te}_{1-x}$ SYSTEM

A. H. ABOU EL ELA and K. S. ABDU

*Physics Department, Islamic Girls College,  
Nasr City, Cairo, Egypt*

Received 30 September 1980

Revised manuscript received 20 June 1981

UDC 538.91

Original scientific paper

Differential thermal analysis studies of the binary system  $\text{Se}_x\text{Te}_{1-x}$  are reported and thermal phenomena accompanying the temperature induced changes are discussed. Glass transition mechanism is interpreted and the activation enthalpy is calculated. Thermal crystallization process has been studied and interpreted using a phenomenological model with activation enthalpy  $h^*$ . When the samples are kept at a temperature lower than the glass transition temperature ageing occurs which is related to a slow depolymerization process.

## 1. Introduction

Amorphous selenium is a lone-pair semiconductor<sup>1)</sup>, where the local change in the atomic structure is brought about by external perturbations which results in the drastic variations in physical and chemical properties. The structure of amorphous selenium has been determined as a mixture of ring molecules consisting of eight Se atoms and chain molecules connecting successively about  $10^2$  to  $10^4$  atoms<sup>2)</sup>. Recently Misawa et al.<sup>3)</sup> have shown that the ring-chain equilibrium in molten selenium can be understood in terms of a disordered chain model<sup>4)</sup> as a statistical occupation of Se atoms in cis- and trans- sites in a single molecule.

If eight Se atoms are successively located at the cis- site a ring molecule is realized, while for Se atoms located at the trans-site chain molecules are formed. Since the occupation probability for the trans-site is increased at higher temperatures, chain molecules become predominant in molten selenium with increasing temperature.

Much work has been devoted to the thermal stability of pure vitreous selenium because of its technological importance. Indication of ageing phenomena is given by the scattering of the experimental values of  $T_g$ <sup>5,6,7)</sup>. Thermal history effects were also observed on the peak of specific heat<sup>8,9)</sup> at  $T_g$ , showing that this anomaly depends on how long the sample is kept at room temperature. The evolution of the anomaly was interpreted as a relaxation towards an equilibrium state having a lower internal energy. Moreover, polymerization and depolymerization in the disordered state below the melting point was foreshadowed from the extensive study of thermodynamic equilibrium between rings and chains in the liquid state. It appeared that the temperature of polymerization  $T_0$  might be slightly higher than  $T_g$ <sup>5,10)</sup>. In principle, below  $T_0$ , the stable molecular species would be essentially  $Se_8$  rings. Therefore, it is expected that: first, the internal energy of quenched selenium will decrease with time towards the energy of depolymerized state; secondly, a sharp change of specific heat due to the initiation of the polymerization will appear at  $T_0$  when heating the depolymerized glass.

Se-Te alloys have attracted a great deal of attention and research, both components are isomorphous and the phase diagram is very simple with total miscibility. Raman spectra measurements of vitreous Se-Te alloys near pure selenium<sup>11)</sup> had indicated that tellurium enters co-polymer chains preferentially and tends to reduce the number of  $Se_1$  rings.

The aim of the present work is to investigate by means of differential thermal analysis the nature of thermal reactions, thermal history effects, and the differences that occur in the behaviour near the glass transition and crystallization of amorphous selenium and some Se-Te alloys.

## 2. Experimental

$Se_x Te_{1-x}$  samples were prepared by melting the respective weight of the elements of high purity (99.999%) in evacuated quartz tubes at 750°C for 6 h, homogenization was carried out under continuous agitation for 6 h, whereupon the resulting alloys were removed from the furnace and quenched in an ice-water bath to obtain the sample in the amorphous state. Table 1 shows the composition of the samples prepared.

TABLE 1

Sample	$Se_x$ (at. %)	$Te_{1-x}$ (at. %)
Pure Se	100	0
Te $Se_{50}$	98.04	1.96
Te $Se_{20}$	95.24	4.76
Te $Se_{12.5}$	92.59	7.41
Te $Se_{10}$	90.91	9.09
Te $Se_9$	90	10
Te $Se_4$	80	20
Te $Se_{2.5}$	71.43	28.57

Composition of  $Se_x Te_{1-x}$  samples.

Differential thermal analysis was carried out using an automatic recording thermal analyser. A small amount of the sample was placed in an evacuated quartz ampulle, while an identical quartz ampulle was used as a reference. Measurements were carried out for each sample at different heating rates. The values obtained from DTA curve reflect the entire thermal history of the sample.

### 3. Experimental results and discussion

#### (a) Glass transition

The endotherm due to glass transition occurred in all samples over a temperature range which depends on the heating rate. For higher heating rates, the endothermic peak due to the glass transition shifts towards higher temperatures and the area under the peak becomes larger. Illustrative examples for the characteristic DTA thermograms are shown in Figs. 1, 2 and 3 for pure selenium,  $\text{TeSe}_{12.5}$  and

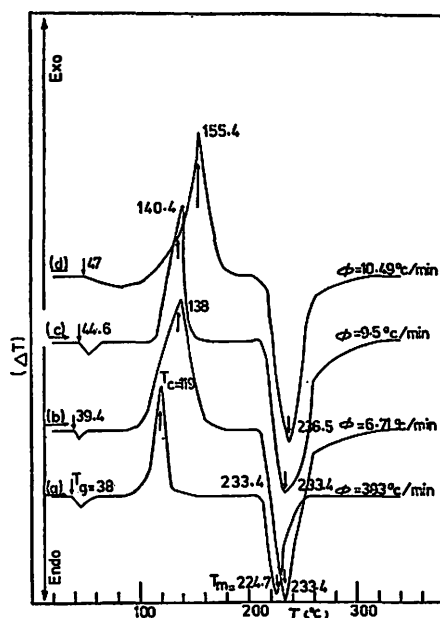


Fig. 1. Differential thermal analysis thermograms for pure selenium at different heating rates.

$\text{TeSe}_4$  at different heating rates. The characteristic temperatures on the curves are  $T_g$ , the glass transition temperature;  $T_c$ , the usual crystallization peak temperature due to the exothermic reaction; and  $T_m$ , an endothermic peak temperature due to the melting of the crystalline material.  $T_g$ ,  $T_c$  and  $T_m$  change markedly and increase for higher heating rates.

Theories on the effect of heating or cooling rate on the glass transition temperature have been proposed by McMillan<sup>12)</sup> and Moynihan et al.<sup>13)</sup>. The relation-

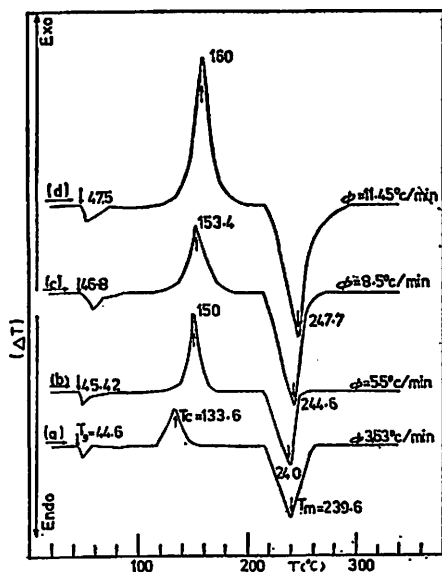


Fig. 2. Differential thermal analysis thermograms for Te Se<sub>12.5</sub> at different heating rates.

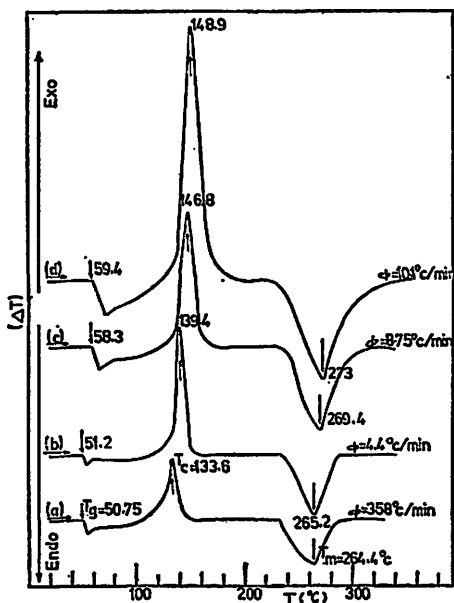


Fig. 3. Differential thermal analysis thermograms for Te Se<sub>4</sub> at different heating rates.

ship between the glass transition temperature  $T_g$  and heating rate  $\varphi$  has been derived by Moynihan et al.<sup>13)</sup> as

$$-\frac{d \ln \varphi}{d \left( \frac{1}{T_g} \right)} = -\frac{\Delta h_g}{R} \quad (1)$$

where  $\Delta h_g$  is the activation enthalpy for the relaxation time controlling the structural transformation. If  $T_g$  is defined as the onset temperature of the endotherm of the DTA curves as shown in Fig. 1, the relation between  $\ln \varphi$  and  $1/T_g$  yields a straight line from which  $\Delta h_g$  can be estimated.

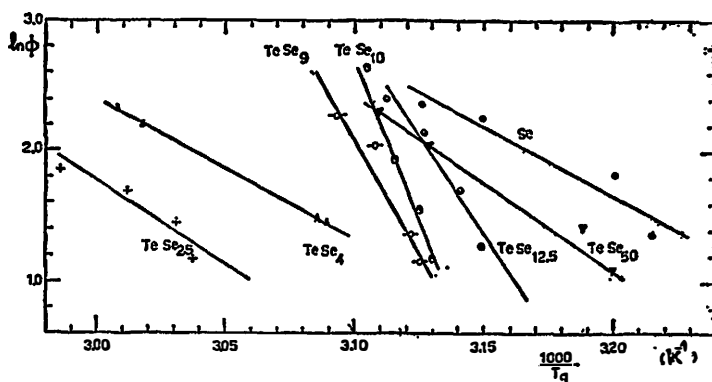


Fig. 4. The relation between  $\ln$  (heating rate) and  $1000/T_g$ .

Fig. 4 shows the relationship between  $\ln \varphi$  and  $1/T_g$  for  $\text{Se}_x\text{Te}_{1-x}$  samples, the results approximate to a straight line. The values of the activation enthalpy  $\Delta h_g$  estimated from Fig. 4 are shown in Table 2. The value obtained for pure selenium (75.36 kJ/mole) is smaller than the value obtained from the stress relaxation by Eisenberg and Tobolsky<sup>5)</sup>: 209.34 kJ/mole and 272.2 kJ/mole for the melt quenched at 270 °C and 500 °C, respectively. Though the absolute value of  $\Delta h_g$  differs from that of Eisenberg and Tobolsky, both works agree about the tendency that the lower the holding temperature of selenium before quenching the smaller the value of  $\Delta h_g$ .

TABLE 2

Sample	$\Delta h_g$ (kJ/mole)
Pure Se	75.7
Te Se <sub>50</sub>	85.8
Te Se <sub>20</sub>	360
Te Se <sub>12.5</sub>	243.6
Te Se <sub>10</sub>	283.1
Te Se <sub>9</sub>	291.5
Te Se <sub>4</sub>	91.6
Te Se <sub>2.5</sub>	145.7

The values of the activation enthalpy for glass transformation.

### (b) Crystallization process

Following the glass transition endotherm, the exotherm due to the crystallization of  $\text{Se}_x\text{Te}_{1-x}$  begins at temperatures above  $80^\circ\text{C}$ . The features of the exothermic peak due to crystallization are similar to that of glass transition. As the rate of heating increases, the exothermic peak temperature  $T_c$  shifts towards higher temperatures and the area under the peak becomes larger. Moreover, the peak shows asymmetrical change with temperature. These DTA characteristics may be explained in terms of a model<sup>14,15</sup>) in which some activation energy is given for the structural transformation and the crystallization in the bulk begins from some nucleus with a velocity proportional  $\exp(-h^*/kT)$ , where  $h^*$  is the potential barrier activation energy (Fig. 5) for the amorphous state (A) to be transformed into the crystalline (C). Microscopical observation of crystallization velocity for selenium<sup>16</sup>) shows that the value of  $h^*$  is nearly equal to the bonding between the neighbouring atoms for selenium ( $h^* \approx 1 \text{ eV}$ ) and not a surface energy or activation energy for self diffusion bonding energy. In Fig. 5  $h^* = h_0 - h$ , where  $h_0$  is a crystalline bonding energy. If the liquid  $\text{Se}_x\text{Te}_{1-x}$  sample is quenched to room temperature, the quenched sample stays in the amorphous state characterized by the amorphous bond consisting of both ring and chain structures of selenium. The change from the amorphous state to the crystalline takes place through three processes:

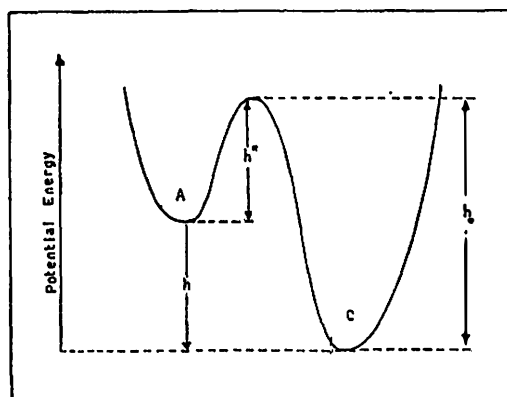


Fig. 5. Representation of the barrier model, A denotes the amorphous state, C is the crystalline state and  $h^*$  is the activation enthalpy of crystallization.  $h_0 = h^* + h$  is the bonding energy.

- i) Generation of nuclei.
- ii) Amorphous bond breaks away so that the ring structure is transformed to the short atomic chain with dangling bonds at its both ends.
- iii) One of the dangling bonds couples with the crystallization nucleus with the subsequent formation of a new active dangling bond, so that the crystalline state may be formed through the chain structure. Hence a new dangling bond is generated at the other end of the crystalline chain. Thus propagation of crystallization takes place with the movement of the crystallization front, and when an atom is released from amorphous bond state to form the crystalline, the sample

would evolve a heat of crystallization  $h^* = h_0 - h$ . Kawarada et al.<sup>14)</sup> derived a formula for the rate of crystallization, assuming that crystallization takes place from both ends of a chain and the mean unit of the crystallized chain has a length  $a_0$ . The velocity of the macroscopic crystallization process  $\left(\frac{dr}{dt}\right)$  is given by

$$\frac{dr}{dt} = a_0 p v_0 \exp [-h^*/k(\varphi t + T_0)] \quad (2)$$

and the rate of crystallization  $\frac{dN}{dt}$  in a mean unit length  $a_0$  at a time  $t$  in three dimensions will be

$$\frac{dN}{dt} = [1 - l(r)] 4\pi \left(\frac{r}{a_0}\right)^2 n p v_0 \exp [-3h^*/k(\varphi t + T_0)] \quad (3)$$

where  $r$  is the distance of crystallizing front measured from a nucleus,  $n$  is the density of nuclei,  $p$  is the probability that a dangling bond of amorphous structure is captured by the crystallizing bond of a nucleus,  $v_0$  is the vibrational frequency of neighbouring atoms,  $T_0$  is the initial temperature of the sample,  $\varphi$  is the heating rate,  $t$  is the heating time and the factor

$$v_0 \exp [-h^*/k(\varphi t + T_0)]$$

is the number of dangling bonds generated per unit time. If the crystallization starts at time  $t = 0$  from the nuclei distributed over  $n$  sites per unit length of the sample, then as soon as the front of the crystallization from neighbouring nuclei meets another front of crystallization, the growth of the structural change process comes to the end. This process is represented by the factor  $[1 - l(r)]$ , where  $l(r) = 1$  when crystallization is entirely achieved. For pure selenium with  $h^* \cong \cong 1$  eV,  $n^{1/3} = 5 \times 10^3 \text{ cm}^{-1}$ ,  $a_0 = 10^{-6} \text{ cm}$  and  $p v_0 = 1.2 \times 10^{11} \text{ sec}^{-1}$ , the crystallization velocity is  $\frac{dr}{dt} \cong 2 \times 10^{-6} \text{ cm/sec}$  at  $127^\circ \text{C}$ , which is in good agreement with the experimental value obtained by microscopic observation<sup>17)</sup>.

### (c) Structural ageing

Ageing phenomena was observed in the liquid-quenched amorphous  $\text{Se}_x\text{Te}_{1-x}$  alloy system when kept at a temperature lower than  $T_g$ . Illustrative examples are shown in Figs. 6, 7 and 8 for  $\text{TeSe}_{10}$ ,  $\text{TeSe}_9$  and  $\text{TeSe}_{2.5}$  thermograms of freshly prepared  $t = 0$  (Fig. a) and aged samples  $t = 2$  days (Fig. b) are compared. When the sample is kept at  $27^\circ \text{C}$  for 2 days after quenching, new features appear on the thermogram:

- i)  $T_g$  increases by a few degrees,
- ii) a non-symmetrical endothermic peak sets in just above  $T_g$ .
- iii) The closer the holding temperature (the temperature the sample is kept at for ageing) to the glass transition temperature  $T_g$  the more rapid the kinetics of ageing.

iv) The peak crystallization temperature  $T_c$  is slightly lowered, while the exothermic crystallization peak height is slightly increased.

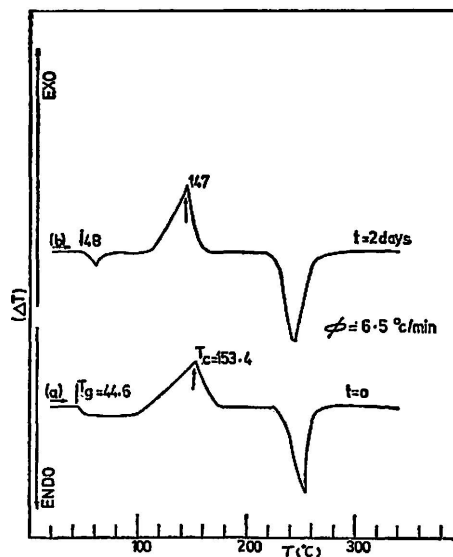


Fig. 6. Ageing phenomena in liquid-quenched amorphous  $\text{TeSe}_{10}$  alloy system. Thermograms of (a) freshly prepared ( $t = 0$ ) and (b) aged for 2 days, are compared.

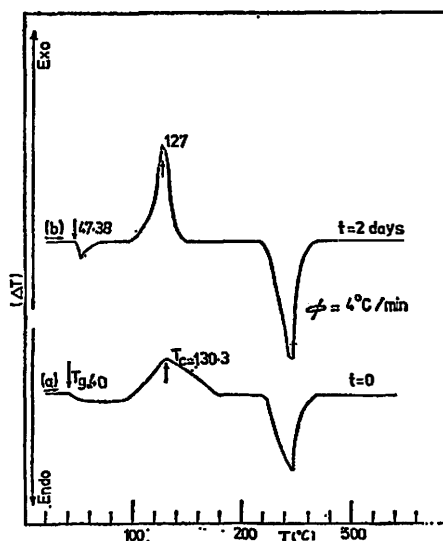


Fig. 7. Ageing phenomena in liquid-quenched amorphous  $\text{TeSe}_9$  alloy system. Thermograms of (a) freshly prepared ( $t = 0$ ) and (b) aged for 2 days, are compared.



The height of the endotherm near  $T_g$  increase to saturation within a time of about 100 hours.

Structural ageing can be attributed to the coexistence of two molecular forms of selenium of the ring and chain types, which give rise to polymerization and depolymerization-process in all its metastable forms and its alloys.

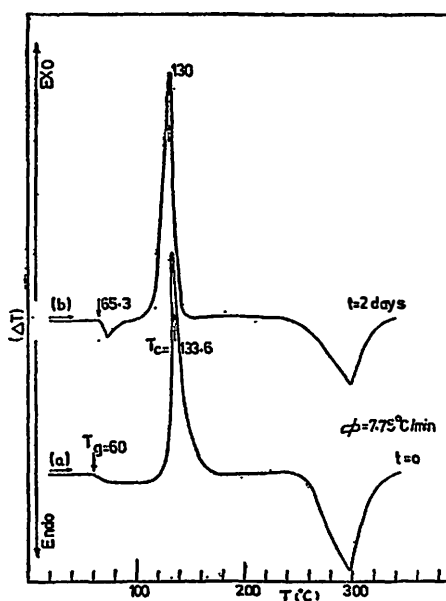
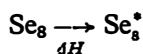


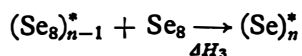
Fig. 8. Ageing phenomena in liquid quenched amorphous  $\text{TeSe}_{2.5}$  system. Thermograms of (a) freshly prepared ( $t = 0$ ) and (b) aged for 2 days, are compared.

(a) Process of depolymerization of chains: The mixture of chains and rings which are in thermal equilibrium in the liquid state becomes out of equilibrium when it is quenched to  $0^\circ\text{C}$ . At this temperature, rings should be the only stable molecules in ideally disordered phase. Because of the high viscosity below  $T_g$ , the glass tends very slowly towards this situation by local arrangements of bonds and small atomic displacements. The rate of depolymerization of chains increases with the rate of heating<sup>18)</sup> and the contribution of van der Waals forces to the internal energy is increased by the molecular reorganization, which explains the high values observed for  $T_g$  and the increased values for microhardness and density after ageing<sup>9)</sup>.

(b) Process of polymerization of rings: The endotherm near  $T_g$  indicates the initiation step and beginning of polymerization of  $\text{Se}_8$  molecules, developed in quenched selenium which can be written as<sup>7)</sup>



where  $\Delta H$  is the enthalpy of initiation. The initiation step is followed by several chain propagation steps



where  $\Delta H_3$  is the enthalpy of propagation. Moynihan and Schnaus<sup>7)</sup> had shown that the total energy of polymerization  $H_{\text{polym}}$  is given by

$$H_{\text{polym}} = N \Delta H + (W - N) \Delta H_3$$

where  $N$  is the total concentration of polymer molecules, and  $W$  is the total concentration of monomer segments incorporated into the polymer. The term  $N(\Delta H - \Delta H_3)$  represents the energy supplied to initiate the polymerization at  $T = T_0 \cong T_g$ , and the term  $W \Delta H_3$  is due to the propagation of polymerization. For pure selenium  $\Delta H \cong 96.3$  kJ/mole and  $\Delta H_3 \cong 7.54$  kJ/mole.

For  $\text{Se}_x\text{Te}_{1-x}$  samples it is expected that the values of  $\Delta H$  and  $\Delta H_3$  differs from that for pure selenium, since tellurium tends to shorten selenium chains and affect the process of polymerization.

#### References

- 1) M. Kastner, Phys. Rev. Lett. **28** (1972) 355;
- 2) S. Brieleb, Z. Physik. Chem. **A 144** (1929) 324;
- 3) M. Misawa and K. Suzuki, J. Phys. Soc. Japan **44** (1978) 1612;
- 4) Idem *Liquid Metals* 1976, Institute of Physics Conference, No. 30 (1977);
- 5) A. Eisenberg and A. V. Tobolsky, J. Polymer Sci. **61** (1962) 483;
- 6) M. Meyers and E. J. Felty, Mat. Res. Bull. **2** (1967) 535;
- 7) C. T. Moynihan and U. E. Schnaus, J. Am. Cer. Soc. **54** (1971) 136;
- 8) P. Chaudhari, P. Bearmore and M. B. Bever, Physics and Chem. Glasses **7** (1966) 157;
- 9) G. C. Das, M. B. Bever, D. R. Uhlmann and S. C. Moss, J. Non-Cryst. Solids **7** (1972) 251;
- 10) E. Grochowski and W. Brenner, J. Cryst. Growth **13—14** (1972) 843;
- 11) A. T. Ward, J. Phys. Chem. **74** (1970) 4110;
- 12) J. A. McMillan, J. Chem. Phys. **42** (1965) 3497;
- 13) C. T. Moynihan, A. J. Easteal, J. Wilder and J. Tucker, J. Phys. Chem. **78** (1974) 2673;
- 14) M. Kawarada and Y. Nishina, Japan J. Appl. Phys. **14**, **10** (1975) 1519;
- 15) A. H. Abou El Ela, M. K. El Mously and K. S. Abdu, J. Materials Science, **15** (1980) 871;
- 16) S. Hamada, T. Sato and T. Shirai, Bull. Chem. Soc. Japan **40** (1967) 864;
- 17) S. Muraoka, T. Ueno and A. Okajima, Japan J. Appl. Phys. **13** (1974) 1459;
- 18) J. Cornet and D. Rossier, Proc. 5 th Intern. Conf. on Amorphous and Liquid Semiconductors, Garmisch-Partenkirchen 1973, Ed. J. Stuke, Taylor & Francis Ltd. 1974, p. 267.

KINEMATIČKE TRANSFORMACIJE I STRUKTURNO STARENJE  
AMORFNOG  $\text{Se}_x\text{Te}_{1-x}$  SISTEMA

A. H. ABOU EL ELA i K. S. ABDU

*Physics Department, Islamic Girls College,*

*Nasr City, Kairo, Egipat*

UDK 538.91

Originalni znanstveni rad

Objavljeni su rezultati studija diferencijalne termičke analize na binarnom sistemu  $\text{Se}_x\text{Te}_{1-x}$  i diskutirani termički fenomeni pridruženi efektima induciranym promjenama temperature. Objašnjen je mehanizam prijelaza iz staklastog stanja u kristalinično i izračunata je aktivaciona entalpija za taj proces.