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THERMOGRAPHIC INVESTIGATIONS OF THE CRYSTALLIZATION OF GLASSES FROM THE Se-S-Ag SYSTEM

Maria I. Mitkova*, Zorka Boncheva-Mladenova, Higher School of Chemical Technology and Metallurgy, Sofia, Bulgaria

ABSTRACT

The activation energy of crystallization of glasses from the Se-S-Ag system are estimated on a basis of DTA meassurements carried out by a different beating rates.

INTRODUCTION

The glassy phases in the system Se-S-Ag take up a very limited area /1/ in the threeangle diagramme. This suggest that they have a great cristallization ability, which permits the application of non-isothermal techniques for the investigation of phase transitions in them. Although the problem of finding out the dependence of the activation energy on the temperature is complicated enough, at certain points of the DTA curve the activation energy of cristallization could be estimated accurately enough. This problem is discussed in the worcs of Kissinger /2/ and Usvitzkii /3/ about processes from the first order. Then the following dependences are valid:

$$1/T_{in} = C_{1in} - C_{2in} \ln b \qquad (1)$$

$$1/T_m = C_{1m} - C_{2m} \ln(b/T_m^2) \qquad (2)$$

where T_{in} and T_m are initial and maximal temperatures of the exothermal crystallization peaks, C_{1in} and C_{1m} are constants, depending on the temperature, b is the heating rate and $C_{2in} = \frac{k}{E_a}$, $C_{2m} = \frac{k}{E_a}$; k is Boltzmann constant and E_a - the respectively activation energy.

EXPERIMENTAL

Specimens have been investigated, sythezed by the previously described methods /1/. Approximately 2g samples were ground to size less then 75 μm and placed in evacuated thermographic ampules. The heating rates were 2,5; 5; 10 and 20°/min.

X-ray powder diffraction patterns confirmed the non-crystalli-

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nity of the samples. The composition of the crystallized phases was investigated also by an X-ray technique.

The habit of the crystallized phases was observed with a electrone microscope.

RESULTS AND DISCUSSION

The characteristic temperatures on the DTA curves are T_g, T_c and T_m - giving information respectively about the transition, crystallization and melting of the material. A crystallization peak usually occurs on the thermograms after a slope changing of the DTA curve, showing the T_g, but with the samples of high contents of selenium, despite the appearance of a single crystallization peak, there is a slight sign of two unresolved melting peaks. This show that the single crystallization peak may consist of two superimposed coincident peaks.

The crystallization peaks increase, with the increase of the amount of silver and sulphur content in the specimens, which implies a greater crystallization ability of these compositions. The peaks are nerrower - an indication of a faster crystallization. All characteristic temperatures increase when increasing the concentration of silver and sulphur and T_m grows to the highest extent and the difference between the T_g and T_c decreases. This tendency is probably connected with the structure of the investigated glasses in which sulphur and selenium are connected in copolymere chains striving to reduce the number of 8-atoms seleniu rings /4/ which leads to an increase of T_g. On the other hand silver is located among the chalcogenide chains, forming bridges between them. Thus creating a netlike structure of the glasses, which also deter-

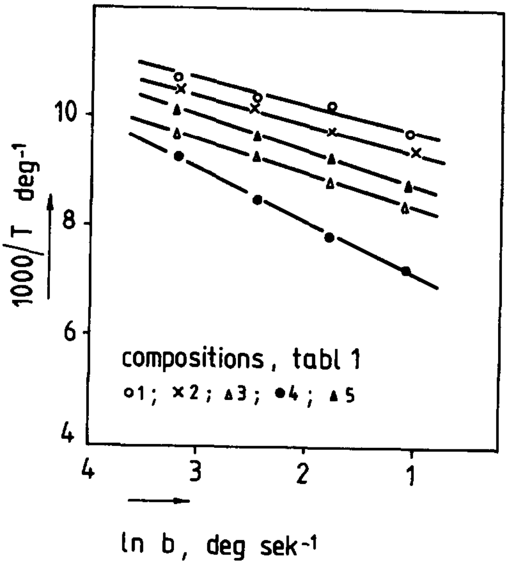

Fig. 1. Dependence of the initial crystallization temperature on the heating rate

imines the higher T_g. Since T_c dependes not only on T_g, but on the equilibrium liquidus temperature and the mechanism of crystallite nucleation in a particular sample, as well one can deduce, that both the nucleation rate and the growth rate of crystals in the metastable liquid phase just above T_g increase as the difference between T_g and the liquidus temperature increases.

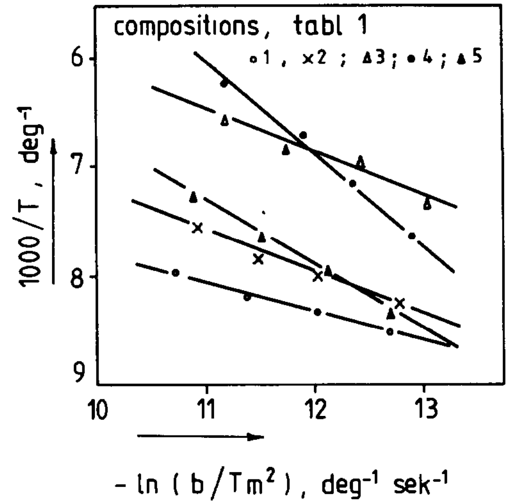

Fig. 2. Dependence of the maximal crystallization temperature on the heating rate

The characteristic temperatures are considerably lower when the DTA heating rate is slower. Fig. 1 and Fig. 2 show the dependences of the T_{in} of the crystallization peaks on the heating rate. The good location of the experimental results on the straight lines is a proof that the crystallization process obeys first order kinetics. This result is in accordance with certain diffusion limited growth processes /5/.

The activation energy of the initial stage of crystallization, i.e. at the moment starting from T_{in} and the energy, corresponding to the maximum of the exothermic peak, are determinate graphically, using a computer programm for the estimations - table 1.

The values of the crystallization energy depend on the composition of the samples but roughly speaking, they are quite low. One of the reasons for these is that T_c does not necessarily correspond to the temperature of the maximal crystallization rate, as indicated by Reed /6/. Moreover, E_a depends on the temperature before quenching /7/, which is relativelly high - 500°C in our case. Both types of activation energy have lower values when the sulphur and silver content in the glasses increase the latter having a considerably greater influence due.to its metal nature and the changes it cames in the structure of the samples.

Tabl. 1

N	composition atomic %			E_{in} ccal/mol	E_m ccal/mol
	Se	S	Ag		
1.	90	5	5	$2,43_{04}$	$8,71_{61}$
2.	85	5	10	$2,02_{05}$	$5,75_{12}$
3.	80	5	15	$1,01_{71}$	$5,21_{38}$
4.	75	5	20	$0,96_{38}$	$2,52_{48}$
5.	85	10	5	$1,71_{93}$	$3,25_{85}$
6.	80	10	10	$1,71_{75}$	$3,09_{75}$
7.	75	10	15	$0,61_{89}$	$2,23_{88}$
8.	70	10	20	$0,51_{68}$	$2,15_{26}$
9.	80	15	5	$0,98_{68}$	$3,89_{15}$
10.	75	15	10	$0,46_{23}$	$2,23_{62}$
11.	70	15	15	$0,26_{28}$	$2,09_{73}$
12.	65	15	20	$0,18_{39}$	$1,55_{09}$
13.	75	20	5	$0,72_{15}$	$2,77_{57}$
14.	70	20	10	$0,40_{11}$	$2,83_{98}$
15.	65	20	15	$0,11_{55}$	$1,51_{23}$
16.	60	20	20	$0,10_{42}$	$1,50_{77}$

The X-ray phase analyses proved, that in all cases the phase that cristallized during the DTA is Ag_2S. The diffraction patterns of specimens rich in selenium (from 80 till 90 at.%) show a progressive presence of trigonal selenium, whus typical crystallization form in cylindrites was observed with electrone microscopic investigations.

Our investigations show, that glasses from Se-S-Ag system have a very low crystallization activation energy and they change their composition at crystallization. This is an indication that crystallization could be cause by non-drastic influences, leading to grate changes in the properties of the glasses.

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