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CRYSTALLIZATION KINETICS OF SOME Ge-Sb-Se Glasses

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ABSTRACT

The crystallization kinetics of alloys in the Ge-Sb-Se system was investigated by means of differential thermal analysis, differential scanning calorimetry and X-ray diffraction. The calorimetric results obtained both for isothermal and continuous heating experiments were successfully interpreted with the same set of kinetic parameters. The Johnson-Mehl-Avrami-Erofe'ev equation with a rate constant following the Arrhenius behaviour gives the best fit to the experimental data. The values obtained for the effective activation energy increase from 75 to 229 kJ/mol with Sb content, except for pure selenium (81 kJ/mol). The pre-exponential factor of the rate constant increases at the same time from 1×10^{6} to 1×10^{16} s^{-1}, except for pure selenium (4×10^{8}). The kinetic exponent ranges between 1.2. and 2.5 without any clear trend against composition. Some kind of compensation effect occurs that may be attributed to the primary crystallization of Sb_2Se_3 in most of the glasses.

INTRODUCTION

Glasses of the Ge-Sb-Se system have the interesting optical property of being transparent to infrared radiation from 2 to 16 μm. As a consequence, their optical properties have been studied in detail [1]. Further studies have been carried on their electrical properties, density, microhardness, heat capacities and elastic and

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dilatometric properties [2]. All these properties have been related to the phase diagram of the system [3], however no crystallization kinetic studies were reported but only the glass forming region of the ternary system [4]. In the present paper the crystallization kinetics of some of these glasses has been studied from calorimetric measurements and is reported in the present paper.

EXPERIMENTAL PROCEDURE AND RESULTS

The preparation details of the air-quenched samples were given elsewhere [4]. The amorphous state of all the samples was checked by X-ray powder diffraction. Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) were performed using a DSC II Perkin Elmer and a STA 429 Netzsch equipment, respectively. Eleven glasses of different compositions in the subsystem $GeSe_2$-Sb_2Se_3-Se were prepared. Their compositions are given in Fig. 1 with the corresponding part of the ternary phase diagram. As shown in this figure most of these compositions lie on the region of primary solidification (under equilibrium regime) of Sb_2Se_3 crystals. DSC analysis was carried out on 10-15 mg of powdered sample and allowed to determine the crystallized fraction, , x, and the rate of crystallization, dx/dt, as a function of temperature, T, in continuous heating experiments, or time, t, in isothermal ones.

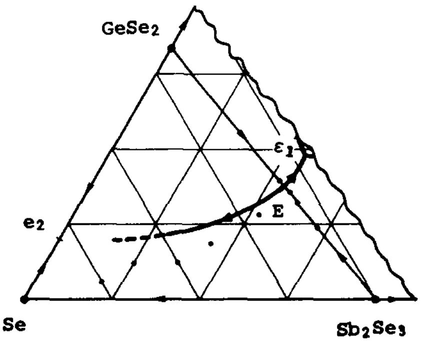

Fig. 1.- Part of the phase diagram of the Ge-Sb-Se system showing the studied compositions.

The kinetic behaviour upon crystallization was explained taking a rate of reaction given by

$$dx/dt = k(T)\ f(x)$$

where k(T) is the rate constant of the form $k(T)=k_0.\exp(-E/RT)$ with k_0 the pre-exponential factor and E the effecttive activation energy, both being independent of temperature, and f(x) follows the Johnson-Mehl-Avrami-Erofe'ev equation

$$f(x) = n(1-x)[-\ln(1-x)]^{(n-1)/n}$$

The value of E was deduced from the logarithmic plot of dx/dt as a function of 1/T at a fixed value of x. The values of $\ln(k_0)$ and n were deduced from the plot of $\ln[k_0 f(x)]$ as a function of $-\ln(1-x)$ both for isothermal and continuous heating conditions by use of the expression [5]

$$\ln[k_0 f(x)] = \ln(dx/dt) + E/RT$$

and comparison with the plot of $\ln[f(x)]$ as a function of $-\ln(1-x)$. Fig. 2 shows, as an example, such a plot for the $Ge_{7.5}Sb_{17.5}Se_{75}$ glass. The values obtained for the activation energy, E, the pre-exponential factor, k_0, and the kinetic exponent, n, are given in Table 1.

DISCUSSION AND CONCLUSIONS

As shown in Table 1, both the pre-exponential factor and the effective activation energy increase with increasing antimony content whereas the kinetic exponent shows no clear trend against composition. Therefore, there is the possibility of a compensation effect [6]. Fig. 3 shows the plot of E versus $\ln(k_0)$. There is a linear relationship between both quantities in most of the glasses.

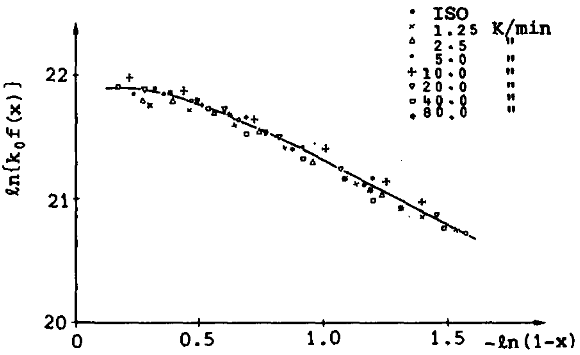

Fig. 2.- Plot of $\ln[k_0 f(x)]$ vs. $\ln(1-x)$ for the sample with composition $Ge_{7.5}Sb_{17.5}Se_{75}$. Full line is the plot for $n=1.12$

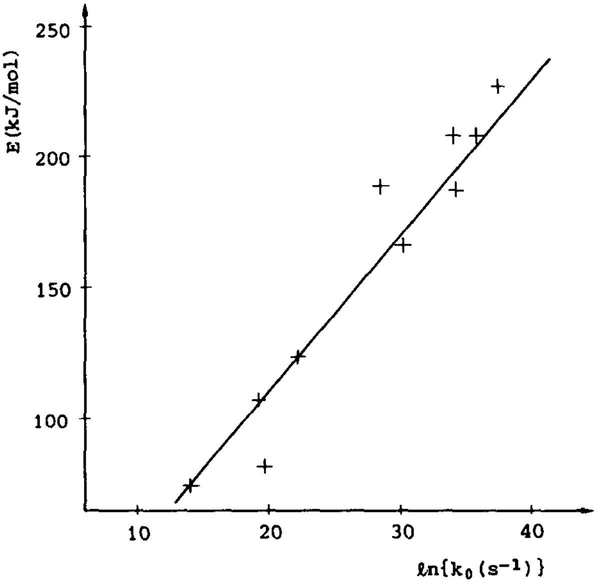

Fig. 3.- Compensation plot for the crystallization of glasses in the $GeSe_2$-Sb_2Se_3-Se system.

Table 1 .- Kinetic parameters of the samples

Sample composition Ge : Sb : Se			E kJ/mol	n	$\ln(k_0)$ k_0 in s^{-1}
0	0	100	81±3	2.5±0.1	19.7±0.5
2.5	7.5	90	74	2.2	14.0
5	10	85	107	1.6	19.6
5	15	80	122	1.5	23.5
7.5	17.5	75	123	1.2	22.2
10	20	70	166	1.5	30.2
11.25	21.25	67.5	187	1.2	34.2
15.79	21.05	63.16	189	1.4	28.5
14.1	23.08	62.82	227	1.3	37.4
12.5	25	62.5	208	1.9	34.0
9.53	28.57	61.9	208	1.9	35.8

The discrepancies occur for pure selenium and glasses with a composition near the binary eutectic, E, of the $GeSe_2$-Sb_2Se_3 system. As most of the remaining glasses have a composition in the region of primary crystallization of Sb_2Se_3 crystal, under equilibrium condition, we conclude that probably the compensation effect reflects the fact that the first crystallization product is Sb_2Se_3 in these alloy glasses.

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