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EFFECTS OF ALKALI METAL DOPING AND γ-IRRADIATION ON THE CRYSTALLIZATION KINETICS OF THE GLASS $Ag_7I_4VO_4$

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Abstract

The crystallization kinetics of the γ-irradiated and the unirradiated glass $Ag_7I_4VO_4$ was studied dynamically by means of DTA, and isothermally via electrical conductivity measurements. The influence of doping with alkali metal ions (Li^+, Na^+, K^+, Rb^+ or Cs^+) on the crystallization process in the glass was also investigated. The results showed that the rate of crystallization depends on the nature of the added metal ion and on the crystallization growth mechanism. The latter is a two-dimensional process for both the pure and the alkali metal-doped glasses. The effects of irradiation and additive ions on the crystallization process are discussed.

Keywords: $Ag_7I_4VO_4$, crystallization kinetics, doping effect, γ-irradiation effect

Introduction

The crystallization kinetics of glassy materials has lately received a great deal of attention for many scientific purposes [1–4]. This active interest is due, in part, to the desire for a sound theoretical understanding of the mechanism of crystal growth in different phases. Another aspect which makes the process of crystallization of higher interest is the possibility of different technological applications for crystalline and non-crystalline materials.

The crystallization of amorphous material proceeds via processes of nucleation and the growth of the nuclei formed. The crystallization rate is suppressed by reducing either or both of these processes. The crystallization process often occurs during heating, but many factors lead to a marked enhancement of the crystallization kinetics over that resulting from purely thermal effects [5]. Radiation and doping effects are some of the factors which have not been intensively investigated in glasses, except in the silicates (cf. [5, 6] and references therein). For many years, it was believed that the kinetics of crystallization of glasses can not be modified by doping, for the reason that in the amorphous state each atom can have the number of neighbours required for all its valence electrons to form bonds [5].

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The present work relates to a study of the parameters of the crystallization kinetics of the glass $Ag_7I_4VO_4$ and of the influence on these parameters of γ-radiation and of doping with alkali metal ions in place of Ag^+. This glass system has attracted considerable interest due to its high ionic conductivity [7].

Experimental

Analar grade AgI, Ag_2O, V_2O_5 and alkali metal iodides (LiI, NaI, KI, RbI and CsI) were used to prepare $Ag_7I_4VO_4$ and $M_{0.05}Ag_{6.95}I_4VO_4$ (M=Li, Na, K, Rb and Cs). All glass samples were prepared by the same method: appropriate quantities of oxides and iodides were weighed and sealed in silica glass ampoules at 10^{-5} torr. The ampoules were heated at 700°C for 30 h and the melted materials were then quenched in liquid nitrogen.

X-ray diffraction patterns of all the samples investigated were examined with a Philips pw 2103/00 diffractometer, with a Ni-filtered and Cu-target source. The glassy structure was confirmed for all quenched ingots.

The IR spectra of freshly prepared samples and of samples left in air for 7 d were identical; no water band was present, indicating the stability of the glasses in air.

The glass $Ag_7I_4VO_4$ was irradiated in air at room temperature, using a ^{60}Co gamma cell for an absorbed dose of 40.1 Mrad.

The DTA of the samples investigated was performed with a Shimadzu DT-30 thermal analyser, on samples of about 7 mg, at a heating rate of 5 K min^{-1}.

Electrical conductivity measurements were made on pellets (diameter 7 mm and thickness 2 mm), using the two-probe method. Details of the measurements are given elsewhere [8].

Results and discussion

The DTA curves of γ-irradiated and unirradiated samples of the glass $Ag_7I_4VO_4$ are shown in Fig. 1. The doped glass samples exhibited similar DTA behaviour: an endothermic peak due to the glass transition is followed by an exothermic peak due to crystallization. Both the glass transition temperatures (T_g) and the temperatures (T_c) at which the crystallizations start are given in Table 1 for the samples investigated. T_c decreases in the following sequence.

Cs-doped sample > Li-doped sample > Rb-doped sample > K-doped sample > undoped sample > Na-doped sample.

The value of T_c was also found to be decreased by the irradiation process.

A thermal analysis technique such as DTA provides a convenient means of obtaining information on the transformation kinetics of a glass. Several methods [9] have been employed for the calculation of kinetic paramters from both isothermal and non-isothermal data. In the present study, the kinetic parameters were obtained by the method of Marrota *et al.* [10] which is one of the simplest

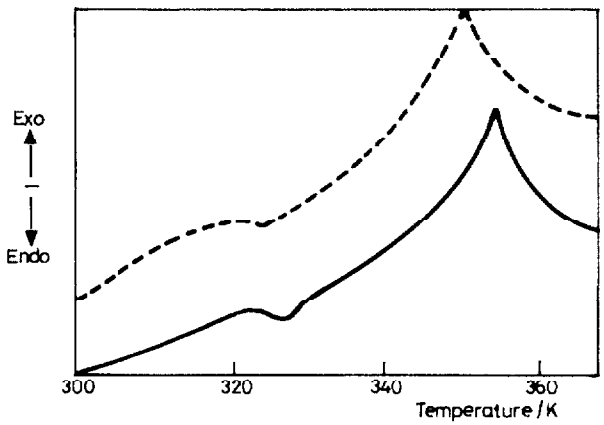

Fig. 1 DTA curves for the γ-irradiated (----) and the unirradiated (—) glass $Ag_7I_4VO_4$

Table 1 Glass trasition (T_g) and crystallization (T_c) temperatures of the glasses investigated

Glass composition	T_g/K	T_c/K
$Ag_7I_4VO_4$	328	355
γ-irrad. $Ag_7I_4VO_4$	324	351
$Li_{0.05}Ag_{6.95}I_4VO_4$	326	366
$Na_{0.05}Ag_{6.95}I_4VO_4$	331	354
$K_{0.05}Ag_{6.95}I_4VO_4$	331	359
$Rb_{0.05}Ag_{6.95}I_4VO_4$	328	364
$Cs_{0.05}Ag_{6.95}I_4VO_4$	332	367

methods used for non-isothermal data at a single heating rate. This method is based on the use of the two inflection temperatures (T_{f1} and T_{f2}) determined on a single derivative DTA (DDTA) curve (Fig. 2). The relationship between the crystallization activation energy (E) and the temperatures of the two inflection points T_{f1} and T_{f2} in the DDTA curve has the following form [10]:

$$E/R(1/T_{f1}-1/T_{f2})=1.92/n \quad (1)$$

The activation energy values of the crystallization process for the glasses investigated are given in Table 2, as estimated for a one-, two- or three-dimensional crystallization process, i.e. for n=1, 2 or 3, respectively.

To examine the kinetic parameters obtained from the thermal analysis method and also to determine the dimensionality of the crystallization process, the kinetics was studied under isothermal annealing by measuring the electrical conductivity of the sample as a function of time at temperatures (333, 343, 353 and

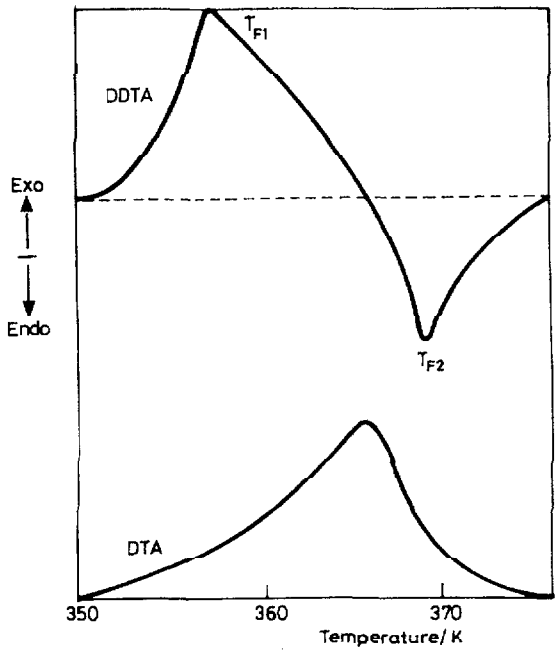

Fig. 2 DTA and DDTA curves for crystallization of the glass $Li_{0.05}Ag_{6.95}I_4VO_4$

363 K) higher than T_g. At each annealing temperature, the conductivity of the glasses investigated decreased with increase of the annealing time. Such behaviour was observed by Hariharan and Kaushik [7] for similar oxide glasses. Figure 3 shows a typical plot for the effect of the annealing time on the electrical conductivity measured at 343 K for $Ag_7I_4VO_4$. This behaviour can be explained on the basis of the increase occurring in the size of the crystallites formed in the glass during annealing. The kinetic parameters were obtained by applying the

Table 2 Crystallization activation energies (E) of the investigated glasses as estimated from DDTA for different values of the reaction mode (n)

Crystallization order (n)	1	2	3
Composition		E/eV	
$Ag_7I_4VO_4$	1.7	0.9	0.4
γ-irrad. $Ag_7I_4VO_4$	1.6	0.8	0.4
$Li_{0.05}Ag_{6.95}I_4VO_4$	1.8	0.9	0.5
$Na_{0.05}Ag_{6.95}I_4VO_4$	1.2	0.6	0.3
$K_{0.05}Ag_{6.95}I_4VO_4$	1.8	0.9	0.4
$Rb_{0.05}Ag_{6.95}I_4VO_4$	2.0	1.0	0.5
$Cs_{0.05}Ag_{6.95}I_4VO_4$	2.0	1.0	0.5

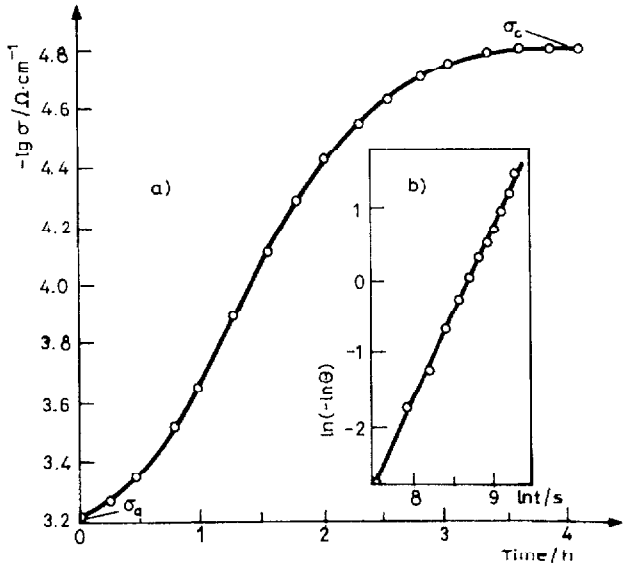

Fig. 3 Time dependence of conductivity during the glass-crystalline transformation of $Ag_7I_4VO_4$ at 343 K (a); Plot of $\ln(-\ln\theta)$ *vs.* $\ln t$ for the results of Fig. 3 (b)

empirical relation previously used by Kotkata *et al.* for chalcogenide semiconductors, (cf. [11] and references therein).

$$\theta = (\ln\sigma_c - \ln\sigma_t)/(\ln\sigma_c - \ln\sigma_a) \quad (2)$$

where θ is the amount of material left uncrystallized at time t. The terms σ_a, σ_t and σ_c are the conductivities at the beginning, at time t and at the end of the crystallization process, respectively. The Avrami equation [12] relates the amount of uncrystallized material θ with the annealing time t:

$$\theta=\exp(-kt^n) \quad (3)$$

The parameter k is a temperature-dependent rate constant, and n is a parameter which depends on the nucleation and growth modes. The values of n and k can be obtained by plotting $\ln(-\ln\theta)$ *vs.* t (Fig. 3b) according to the logarithmic form of Eq. (3).

$$\ln(-\ln\theta)=\ln k + n\ln t \quad (4)$$

At every annealing temperature, the plot of $\ln(-\ln\theta)$ *vs.* $\ln t$ was a straight line with slope n. The values of n and k at the investigated annealing temperatures are given in Table 3. The mean value of n is close to 2 indicating that the crystallization in the investigated glassy samples involves two-dimensional growth. The activation energy values for crystal growth were calculated from the tem-

perature dependence of the rate constants by using the Arrhenius equation [13], and are also given in Table 3. From Tables 2 and 3, it can be seen that the activation energies for the two-dimensional growth process calculated via the thermal technique largely coincide with those determined from conductivity measurements.

Figure 4 shows the X-ray diffraction (XRD) patterns of rapidly quenched, irradiation and annealed glassy samples (at 363 K for 6 h). In the quenching case, XRD (Fig. 4a) confirms the amorphous nature of the materials obtained, while for the irradiated and other annealed glass samples, the observed patterns suggested the formation of onyl $Ag_7I_4VO_4$ crystals (indicated by major peaks at 2θ=23.6, 25.1, 32.2 and 40° [7]).

Table 3 Kinetic parameters n, k and E for crystallization of the investigated glasses, as calculated from isothermal conductivity measurements with the Avrami equation

	Annealing temperature/K								
	333		343		353		363		
Composition	n	$-\ln k$	n	$-\ln k$	n	$-\ln k$	n	$-\ln k$	E/eV
$Ag_7I_4VO_4$	2.0	1.9	2.0	1.1	2.0	0.3	2.0	0.4	0.8
γ-irrad. $Ag_7I_4VO_4$	1.9	1.8	1.9	1.1	2.1	0.3	2.0	0.3	0.8
$Li_{0.05}Ag_{6.95}I_4VO_4$	2.0	2.2	2.0	1.3	2.0	0.4	2.1	0.4	0.9
$Na_{0.05}Ag_{6.95}I_4VO_4$	2.0	1.5	1.9	0.8	1.9	0.2	2.0	0.4	0.7
$K_{0.05}Ag_{6.95}I_4VO_4$	2.0	2.0	2.0	1.1	2.0	0.3	2.0	0.5	0.8
$Rb_{0.05}Ag_{6.95}I_4VO_4$	2.1	2.1	2.1	1.2	2.0	0.3	2.0	0.5	0.9
$Cs_{0.05}Ag_{6.95}I_4VO_4$	2.1	2.3	2.0	1.4	2.0	0.4	2.0	0.4	1.0

Our results reveal that, while the dopant alkali metal ions have no effect on the crystallization mechanism (two-dimensional, Table 3) and no detectable effect on the crystalline structure of pure $Ag_7I_4VO_4$, they do influence the rate of crystallization, in the following sequence:

$$k_{Na}>k_{Ag}>k_K>k_{Rb}>k_{Li}>k_{Cs}$$

where k_{Ag} is the crystallization rate for the pure glass and k_{Na}, k_K, k_{Li}, k_{Rb} and k_{Cs} are those for the glass doped with Na^+, K^+, Li^+, Rb^+ and Cs^+, respectively. This means that the introduction of alkali metal ions (except Na^+) leads to a decrease in the rate of crystallization.

Figure 5 shows a plot of k_d/k_u *vs.* the ionic ratio R_d/R_{Ag}, where k_d is the rate constant for the alkali metal-doped glass and k_u is that for the pure glass, R_d is the radius of the dopant ion and R_{Ag} is the radius of Ag^+. It can be seen that the rate of crystallization decreases with increase in the radius of the monovalent cation (Ag^+ or alkali metal ion), except in the case of Li^+.

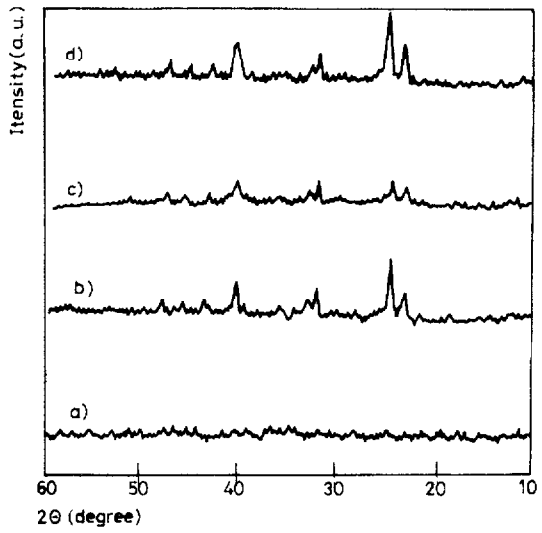

Fig. 4 XRD patterns of: (a) unannealed $Ag_7I_4VO_4$; (b) γ-irradiated $Ag_7I_4VO_4$; (c) $Ag_7I_4VO_4$ annealed at 363 K for 6 h and (d) $Na_{0.05}Ag_7I_4VO_4$ annealed at 363 K for 6 h

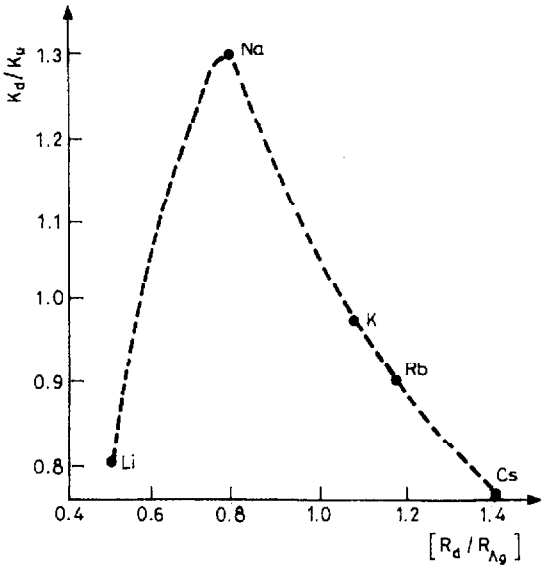

Fig. 5 Plot of K_d/K_u at 343 K *vs.* the ionic radius ratio R_d/R_{Ag}

All the above results indicate that the alkali metal dopants influence the rate of crystallization in the glass system investigated. It is well known that Ag^+ has the highest frequency (number of jumps per sec) of all the ions present in the

glass $Ag_7I_4VO_4$ [7]. Thus, if the rate of crystallization in $Ag_7I_4VO_4$ depends on the diffusion of Ag^+ in the glass, it may be expected that the partial replacement of Ag^+ by a larger alkali metal cation will cause a decrease in the rate of crystallization, as found in the present system, except for the Li^+-doped glass. The abnormal behaviour of Li^+ may be attributed to the higher reactivity of Li^+ as compared with that for the other alkali metal ions, which may lead to the formation of small concentrations of other materials or phases which could not be detected by X-ray diffraction. These materials or phases may cause a decrease in the rate of diffusion of cations and hence the rate of crystallization of the glass $Ag_7I_4VO_4$.

Conclusions

The following conclusions can be drawn from this study:

1) The partial substitution of Ag^+ by doping with alkali metal ions causes a decrease in the rate of crystallization (except in the case of Na^+).

2) The pure and the alkali metal-doped samples crystallize by a two-dimensional process.

3) A γ-irradiation dose of 40.1 Mrad has a slight effect on the crystallization process.

4) The main phase formed on heat treatment is $Ag_7I_4VO_4$.

5) The rate of crystallization decreases with increasing in the radius of the alkali metal ions (except in the case of Li^+). This may be due to the effect of the rate of diffusion of the alkali metal ion on the crystallization rate.

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