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Crystallization kinetics in materials with a two-phase formation from an amorphous phase

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The aim of this article is to propose a simple analytical model that is capable of describing the isothermal crystallization process in materials with the formation of two crystalline phases from the same parent amorphous phase, as illustrated with an example for Ge:Sb:Te thin films. This model explains deviations from the well-known Johnson–Mehl–Avrami-Kolmogorov (JMAK) kinetics theory. The model predictions were compared with experimental results obtained from X-ray measurements on the chalcogenide glasses with composition of $Ge_2Sb_2Te_5$ (where the formation of a stable crystalline phase is preceded by the formation of a metastable phase) and in $Ge_1Sb_2Te_4$ films doped by 12% atomic of oxygen (where two stable crystalline phases are formed from the same parent amorphous phase). This model allows representing similar transformation curves as those obtained from the experiments and is capable of predicting the deviation from the classical linear dependence in the JMAK plot.

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1. Introduction

Isothermal methods of analysis are widely used to study crystallization kinetics in amorphous materials. The experimental data is frequently interpreted in terms of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) nucleation-growth model [1-3]. According to the JMAK theory, in materials with random nucleation and isotropic growth, one phase is transformed within another (one stage transformation) in an infinite specimen and the plot of ln[-ln(1-x)] versus ln(t) describing the process should be linear; however, in some chalcogenide glasses the crystallization processes start with the formation of metastable phases or are accomplished due to the formation of a two stable phases from the same parent amorphous phase [4-8]. Such processes cannot be simply described by JMAK theory and the plots of ln[-ln(1-x)] versus ln(t) are not linear, which implies that the classical Avrami's exponent *n* does not remain constant during the crystallization process.

Some authors [8, 9] have presented a theoretical description of the overall crystallization processes when the appearance of a stable crystalline phase is preceded by the formation of a metastable phase or proposed to reformulate and generalize the JMAK model for the case where more than one reaction occurs at the same time and in the same parent amorphous phase [10-13]. These theoretical considerations are difficult to apply for fitting the experimental results, but they have shown that the JMAK concept can be adapted for the case where more than one reaction occurs in the same parent amorphous phase [9, 12, 13].

The aim of this article is to propose a simple analytical model that can describe the isothermal crystallization process in materials with the formation of a two crystalline phase (metastable and stable or two stable) in the same parent amorphous phase, using as an illustration, the example of Ge:Sb:Te thin films.

2. Experimental

$Ge_2Sb_2Te_5$ thin films (with thickness from 200 to 300 nm) were prepared on glass and silicon substrates by DC magnetron reactive sputtering in atmosphere of argon from bulk targets. $Ge_1Sb_2Te_4$ films containing 12 at.% of oxygen were prepared by DC magnetron reactive sputtering in the presence of oxygen and argon gases. The films compositions were monitored by energy dispersive spectroscopy (EDS).

In situ X-ray diffraction measurements were carried out during isothermal annealing using a Rigaku Dmax/2100 Vertical X-ray diffractometer with a Cu tube.

The temperature was controlled with a Watlow´s Series 982 controller. This instrument was programmed to increase the temperature at a constant heating rate of 5 ^{o}C/min until reaching the desired temperature for isothermal annealing.

The volume fractions of the crystalline phases was determined using X-ray measurements, through diffraction intensities generated by the amorphous (I_A) and crystalline (I_C) phases with the background and noise suitably removed. The percentage of crystallinity or volume fraction was then given by the ratio $I_C/(I_C + I_A)$ [14].

3. Experimental results

Fig. 1 shows the X-ray diffraction spectra for $Ge_2Sb_2Te_5$ films taken at 102 °C (temperature of crystallization, Tc, is about 135 °C) during isothermal annealing at the times indicated on the graph. This figure also shows the patterns corresponding to $Ge_1Sb_4Te_7$ films, fully crystallized at 170 °C. The pattern corresponding to the sample annealed during 15 minutes shows wide bands, which are characteristic of the amorphous material. The patterns of this sample annealed during 75, 120, and 180 minutes show weak peaks, with positions corresponding to an fcc phase of $Ge_1Sb_4Te_7$ composition. After annealing longer than 180 min, the positions of the peaks begin to change to those corresponding to an fcc phase of $Ge_2Sb_2Te_5$ composition (pattern for an isothermal annealing during 540 minutes). Thus, in $Ge_2Sb_2Te_5$ films the formation of a stable crystalline phase is preceded by the formation of a metastable to $Ge_1Sb_4Te_7$ phase.

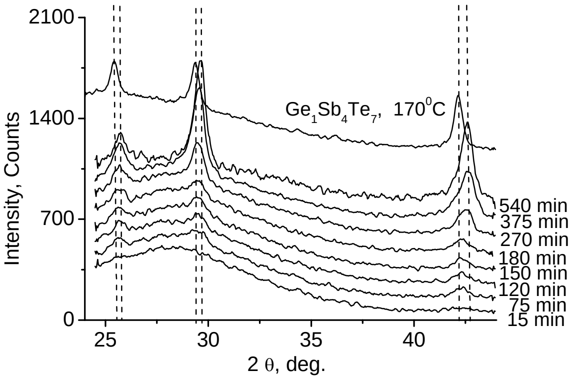


Fig.1. X-ray diffraction patterns for a $Ge_2Sb_2Te_5$ sample during isothermal annealing at a temperature of 102 ^{0}C, to the final times indicated on the plots. Upper pattern corresponds to a $Ge_1Sb_4Te_7$ film annealed during 10 min at 170 ^{0}C. Vertical lines show the position of the $Ge_1Sb_4Te_7$ peaks.

Fig. 2 shows the X-ray patterns, measured at 122 °C (Tc=132 °C), for $Ge_1Sb_2Te_4$ with 12 atomic % of oxygen. After 25 minutes of annealing time, the first crystalline fcc $GeSb_2Te_4$ phase appears. According to previous results [15, 16], it was concluded that a small amount of Ge in the film is oxidized during deposition, forming an amorphous germanium oxide phase, not detectable by the X-ray analysis. This is possible because Ge is more reactive than Sb and Te; however, the composition of these films is different to the $Ge_1Sb_2Te_4$ stochiometric phase. Therefore, during isothermal annealing, the excess Sb and Te atoms form the second crystalline phase (patterns at the 120 and 240 minutes) was identified as crystalline Sb_2Te_3. The position of the Sb_2Te_3 peaks is marked with dash vertical lines.

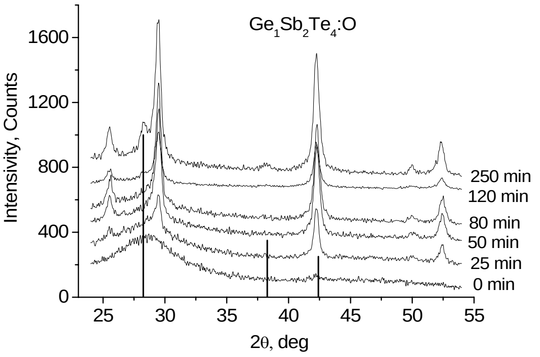
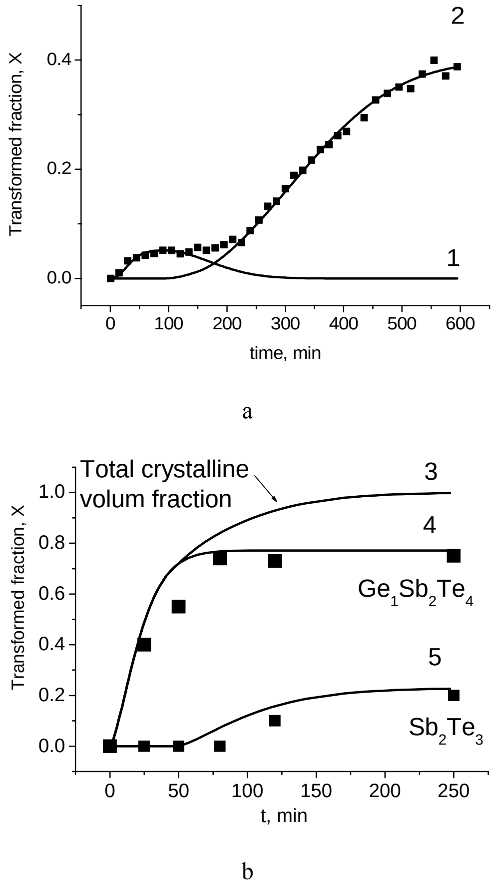


Fig. 2. X-ray diffraction patterns for a $Ge_1Sb_2Te_4$ film with 12 at % of oxygen during isothermal annealing at 122 °C, to the final times indicated on the figure. Vertical lines indicate the position of the Sb_2Te_3 crystalline phase.

Fig. 3 shows the evolution of the volume fraction of crystalline material in $Ge_2Sb_2Te_5$ films (Fig.3a) and $Ge_1Sb_2Te_4$ with 12 atomic % of oxygen (Fig. 3b) obtained from X-ray measurements (black square).

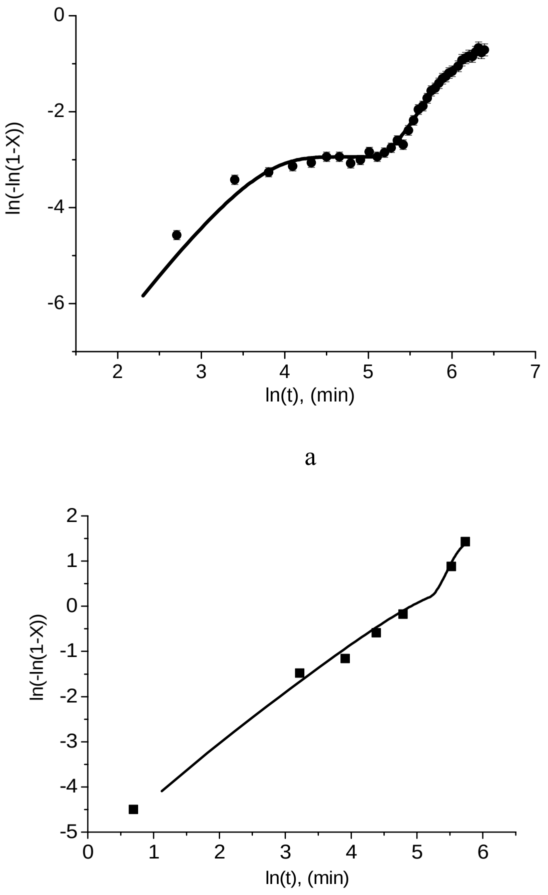


a

b

Fig. 3. Evolution of the crystalline volume fraction x, during isothermal annealing in (a) $Ge_2Sb_2Te_5$ film and (b) in $Ge_1Sb_2Te_4$ film with 12 at % of oxygen. Black square – results of calculation from X-ray measurements, continue lines- results fitting using analytical model.

Fig. 4 shows the ln[-ln(1-x)] versus ln(t) plot (black circles – experimental results, continuous line – results from fitting) which demonstrates a large deviation from linearity, as expected according to the classical JMAK model.



a

b

Fig. 4. Dependencies of ln(-ln(1-x)) on lnt obtained from X-ray diffraction measurements (black square) in (a) $Ge_2Sb_2Te_5$ film, (b) in $Ge_1Sb_2Te_4$ film with 12 at % of oxygen and from fitting using analytical model (continue lines).

4. Analytical model

An analytical model based upon the combination of JMAK-type equations is proposed in this article to represent and analyze the experimental data showing the formation of metastable, stable, or two competitive stable phases.

The first stable or metastable volume fraction can be represented by a KJMA-type equation:

$$\alpha_1(t) = \alpha_{\max}(1-\exp(-K_1(t-t_1)^{n1})) \text{ for } t \geq t_1$$

and

$$\alpha_1(t) = 0 \text{ for } t < t_1 \qquad (1)$$

where α_1 represent the transformed fractions of the first stable or metastable phase, α_{max} the maximum transformed fraction of the first stable or metastable phase, with t_1 as the incubation time and K_1 the crystallization rate constant and n_1 the Avrami exponent.

In the case when the metastable phase appears first, we assume that the metastable phase grows up to a certain fraction (due to external parameters such as temperature, variations in concentration, etc.), and then stops growing when the stable phase, which has nucleated into it, overpasses the metastable grain boundaries. The second stage consists of nucleation and growth of the stable phase into the metastable one, until the limit of the grains is reached. Without such assumption it is impossible to obtain the same transformation dependence as observed experimentally [8]. The kinetic behavior of the stable-in-metastable transformed fraction can be represented by a classical KJMA formula:

$$\alpha_{sm}(t) = \alpha_{\max}(1-\exp(-K_{sm}(t-t_{sm})^{n_{sm}})) \text{ for } t \geq t_{sm}$$

and

$$\alpha_{sm}(t) = 0 \text{ for } t < t_{sm} \qquad (2)$$

where α_{sm} represent the transformed fractions of the stable in metastable phase, t_{sm} is the incubation time, K_{sm}- is the crystallization rate constant, and n_{sm} - is the Avrami exponent.

The third and last stage, deals with the classical growth and eventual nucleation of the stable phase α_2 within the amorphous one.

$$\alpha_2(t) = (1-\alpha_{\max})(1-\exp(-K_2(t-t_2)^{n2})) \text{ for } t \geq t_2$$

and

$$\alpha_2(t) = 0 \text{ for } t < t_2 \qquad (3)$$

where α_2 is the fraction of stable phase in amorphous (from 0 to 1-α_{max}), K_{sa} and n_{sa} are the KJMA parameters and t_2- represents the incubation time.

The total volume fraction equals the sum of those for the metastable, the stable in amorphous, and the stable in metastable:

$$\alpha_{total}(t) = \alpha_1(t) + \alpha_{sm}(t) + \alpha_2(t) \qquad (4)$$

In the case of formation of two stable phases, the analytical model is based upon the linear combination of the two JMAK equations (1) and (2), to represent and analyze the experimental data and to show the formation of two competitive stable phases with volume fractions α_1 and α_2. The total fraction of transformed material is given by the equation:

$$\alpha_{total}(t) = \alpha_1(t) + \alpha_2(t) \qquad (5)$$

5. Discussion

In order to verify the validity of the proposed model for representing the experimental plots, a computer program was developed. Fig. 3 and 4 show results of fitting experimental data using the proposed model (solid lines). In the case of $Ge_2Sb_2Te_5$ films, curve 1 on Fig. 3a represents the volume fraction of the metastable $Ge_1Sb_4Te_7$ phase, whereas curve 2 shows the stable crystalline $Ge_2Sb_2Te_5$ phase. In the case of $Ge_1Sb_2Te_4$ with 12 atomic % (Fig.3b), curve 3 represents the total volume fraction of crystalline phases, curve 4 the volume fraction of the first crystalline phase, and curve 5 the volume fraction of the second one. As one can see, the proposed analytical model allows us to simulate similar transformation curves as those obtained from the experiments in different materials. It should be noted that the model is capable of predicting the non-linear dependencies on the JMAK plot (Fig. 4). The non-linear dependencies on the JMAK plot appeared because the different phases that can be observed in such type of crystallization processes do not appear at the same time. In the case of $Ge_2Sb_2Te_5$, the metastable phase starts to nuclei and grows at the beginning of the crystallization process and stops when a maximum metastable phase is reached. Then, the stable phase stars to grow on a metastable phase and on the remaining amorphous material. In the case of $Ge_1Sb_2Te_4$ films doped by 12 atomic % of oxygen, the first $Ge_1Sb_2Te_4$ stable phase begins to nucleate and grows during the crystallization process and stops when it reaches a maximum volume fraction value and, subsequently, the second stable phase (crystalline Sb_2Te_3) begins to grow.

6. Conclusions

Results from this investigation, using X-ray measurements, have shown that in $Ge_2Sb_2Te_5$ thin films a metastable phase first appears, with the crystalline $Ge_1Sb_4Te_7$ composition. In $Ge_1Sb_2Te_4$ doped with oxygen, two stable crystalline phases are formed, but do not appear at the same time: the first $Ge_1Sb_2Te_4$ stable phase begins to nucleate and grows during the crystallization process and stops when it reaches a maximum volume fraction value. Subsequently, the second stable phase (crystalline Sb_2Te_3) begins to grow.

In this work, we have presented an analytical model capable of representing the experimental data in materials with the formation of a two crystalline phases from the same parent amorphous phase. The proposed model also allows representing the non-linear dependencies on the JMAK plot because the different phases that can be observed in such type of crystallization processes do not appear at the same time.

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