

Crystallization behavior of Ge₁₇Sb₂₃Se₆₀ thin films

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ABSTRACT

Crystallization behavior in Ge₁₇Sb₂₃Se₆₀ thin films was studied by means of differential scanning calorimetry. Detailed information about the occurring crystallization mechanisms was obtained based on the shapes of characteristic kinetic functions and dependence of activation energy on α . Strengths and advantages of the DSC technique used in combination with nowadays kinetic analysis are discussed for the case of PCM thin films.

Key words: crystallization, Ge-Sb-Se, thin film, DSC

1. Introduction

Continually increasing interest in chalcogenide glasses results from their unique physical properties, namely low and often also close temperatures of glass transition and crystallization, large variety in crystallization tendency strongly depending on actual compositions, great distinction of amorphous and crystalline state by means of their reflectivity or electrical conductivity, numerous photoconductive effects or high transmittance in near, middle and far infrared region. Most important applications of chalcogenide glasses then involve large capacity data-storage media (i.e. non-volatile PCRAMs where data are written via electric pulses or optically recorded CDs, DVDs and BlueRay Discs), sophisticated devices and elements for infrared optics and optoelectronics (fibers, planar guides, lenses) or various electronic thresholds and memory switches.

However, current approach to the development of new modern materials for the hi-tech applications is rather empirical and exact kinetics of the occurring basal processes is rarely known. In our opinion, it is the deeper understanding of important (and application-relevant) processes proceeding in these materials that will be essential for their further development and search for new application possibilities.

Current work demonstrates the extent of information accessible by the nowadays kinetic analysis of data provided by the differential scanning calorimetry and suggests its importance and merit for the development of new high-tech materials. The Ge₁₇Sb₂₃Se₆₀ glass from the Ge-Sb-Se family (selenium analog of the famous GST glasses) was chosen as a model material.

2. Experimental

Polycrystalline bulk sample was prepared from a mix of pure elements (5N) sealed in a fused silica ampoule, which was annealed in a rocking furnace (950 °C, 24h) and let cool on air afterwards. Thin films were then deposited by flash evaporation, when finely powdered bulk material was slowly and uniformly poured into heated molybdenum boat and immediately evaporated. Deposition proceeded in a vacuum chamber (background pressure $2 \cdot 10^{-4}$ Pa); cleaned microscope glass slides were used as substrate; thickness of the films was approximately 700 nm. Exact composition of the films (Ge₁₇Sb₂₃Se₆₀) was verified using an electron microscope JEOL JSM-5500LV with energy-dispersive X-ray (EDX) microanalyser (IXRF Systems, detector GRESHAM Sirius 10).

Crystallization behavior was studied using the heat-flow differential scanning calorimeter DSC Q2000 (TA Instruments) equipped with autosampler, RCS90 cooling accessory and T-zero technology. The instrument was calibrated using In, Zn and H₂O; dry N₂ was used as purge gas at flow of 50 cm³·min⁻¹. Fresh zeroline calibration was performed before the measurements. The deposited chalcogenide thin film was scratched off the substrate and sealed into standard Al pans – average sample mass was approx. 2 mg. Regarding the temperature program, each sample was first equilibrated at 150 °C for 3 min. and then it was heated at a defined heating rate to 400 °C; following heating rates were applied: 0.5, 1, 2, 3, 5, 7, 10, 20, 30, 50 and 100 °C·min⁻¹. Each measurement was reproduced in order to

reveal any experimental errors. Spline-type baseline was used to imitate and subtract the thermokinetic background so that the pure peak signal corresponding solely to the crystallization process is obtained. Linear acquisition of experimental data points was applied.

3. Results and discussion

In the first step of the kinetic analysis the activation energy of the crystallization process E needs to be determined. Two methodologies – those by Kissinger [1] and Friedman [2] – were employed for this task within the framework of the present contribution. According to Kissinger the activation energy is determined from the dependence of temperature corresponding to the maximum of the crystallization peak T_p on heating rate q^+ - see Fig. 1. Very good linearity of the dependence suggests uniformity of the dominant crystallization mechanism as well as absence of data-distortive effects (thermal gradients, underlying secondary processes etc.). The important assumption for application of the Kissinger equation is constant value of degree of conversion at the maximum of the peak. In case of the isoconversional Friedman method the activation energy is determined in dependence of degree of conversion α – see Fig. 2. This may be advantageous in case of independent partially overlapping processes, where this method provides gradually changing dependence of E on α , as the degree of overlay changes from the first process towards the second one (with the limiting values of E corresponding to those for the particular processes). On the other hand, as this methodology utilizes artificially determined value of α , it is a lot more susceptible to various negative influences compared to the Kissinger method. This can be seen in Fig. 2, where values of E for very high and very low α significantly differ from the average correct value. This is a consequence of the crystallization peak tails being very easily influenced by all types of data-distortive effects and it is also why E is in case of a single process usually averaged only in the 0.3 – 0.7 interval of α . As can be seen, in this interval both methodologies provide similar results.

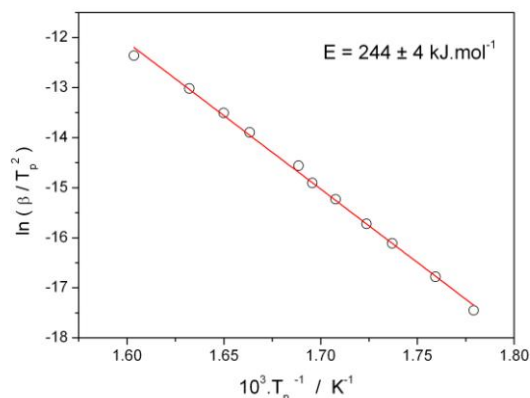


Fig. 1: Kissinger plot

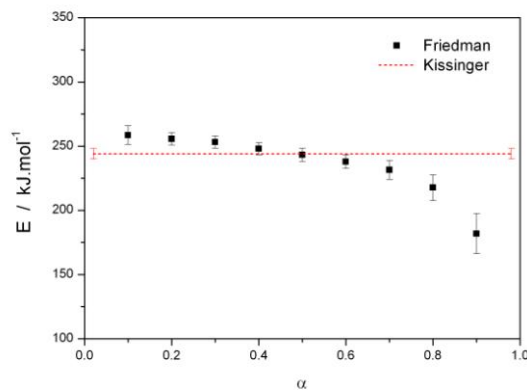


Fig. 2: Dependence of activation energy on α

In the second step of kinetic analysis the reaction mechanism is usually determined. For this task the so-called characteristic kinetic functions $z(\alpha)$ and $y(\alpha)$ [3] may be effectively used. These functions are based on simple transformation of the raw heat-flow data provided by DSC; the transformed data are for better comparison normalized and plotted against α . Originally, only the maxima of these functions were utilized, however, recently it was shown [4,5] that the overall shape of these functions also contains important kinetic information – the procedure of “advanced interpretation of characteristic kinetic functions” was developed.

Kinetic functions $z(\alpha)$ and $y(\alpha)$ are for the $\text{Ge}_{17}\text{Sb}_{23}\text{Se}_{60}$ thin films measured at different heating rates shown in Fig. 3. Shapes of the $z(\alpha)$ functions are consistent, which suggests single crystallization mechanism. Furthermore, the maxima of the $z(\alpha)$ function relatively well correspond to value of $\alpha = 0.632$, which is a fingerprint for the nucleation-growth Johnson-Mehl-Avrami model. Slight evolution of the shape with increasing q^+ is then caused by more pronounced manifestation of the crystallization peak tail, which probably corresponds to slower final transformation of the remaining amorphous matrix deformed/stressed by the preceding rapid crystal growth. Compared to the previously studied $\text{Ge}_2\text{Sb}_2\text{Se}_5$ powder and bulk samples [5] a markedly better correspondence to the ideal JMA behavior was obtained for the present material. This is quite surprising because decreasing particle size usually results

in autocatalytic process of crystallization originating from the strains, stresses and heterogeneities introduced into the sample by grinding/milling. Although similar mechanism is expected to proceed also in case of thin films, almost ideal JMA behavior usually occurring for bulk samples (where crystallization proceeds classically from randomly dispersed nuclei) was observed. Possible explanations may involve e.g. homogeneity and compactness of the deposited thin layer, slightly higher Se content (which may support its inherent JMA-like crystallization) or absence of the prenucleation period.

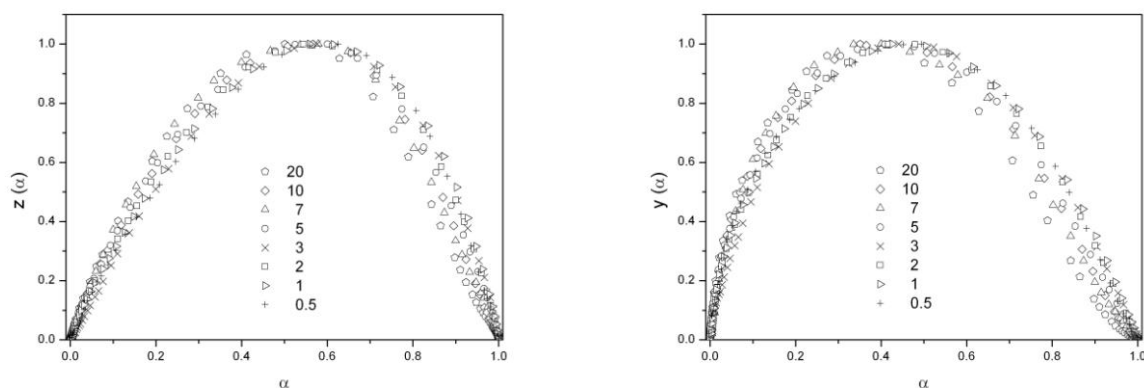


Fig. 3: Characteristic kinetic functions $z(\alpha)$ and $y(\alpha)$

4. Conclusions

As was shown, careful kinetic analysis of DSC crystallization data may even in case of thin films provide large amount of information on proceeding transformation mechanisms - thus offering cheap and fast way of gaining knowledge of nature of manifesting microstructural processes. The critical aspects for DSC measurements of thin films are: reproducibility of “sample” preparation and employment of modern DSC instrument with good zeroline flatness and high sensitivity (one standard microscopy glass slide with 700 nm thick layer then may suffice to prepare 3 high-quality DSC samples). Nevertheless, despite the amount of provided kinetic information, the DSC technique always performs better when coupled with supplemental TA techniques as e.g. optical microscopy or electrical conductivity measurements.

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Biographies

Jaroslav Barták received the MS diploma in Physical Chemistry at the University of Pardubice in 2009 and currently is a 4th year Ph.D. student at the Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Czech Republic. He is working in group of prof. Málek whose research interests cover kinetics of nucleation-growth processes, structural relaxation and viscoelastic behavior of noncrystalline materials and highly supercooled glass-forming liquids. Jaroslav Barták’s thesis is focused on studying of crystallization kinetics in chalcogenide glasses and thin films using different experimental techniques (DSC, TMA, optical and electron microscopy, XRD, electrical measurements).