Kinetic processes in Se-Te glassy system

Jiří Málek, Roman Svoboda, Jaroslav Barták
Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic, jiri.malek@upce.cz

ABSTRACT

Selenium-tellurium glasses were studied by means of differential scanning calorimetry. Thorough kinetic analysis of the structural relaxation and crystallization phenomena showed its importance and potential for further development and search for new application possibilities of these materials.

Key words: Se-Te glasses, structural relaxation, crystallization

1. INTRODUCTION

Continually increasing interest in chalcogenide glasses results from their unique physical properties, as e.g. great distinction of amorphous and crystalline states by means of their reflectivity or electrical conductivity, 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 \[1\] (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.

It is obvious that quality of the prepared glasses (or their thin layers) and their stability are the key factors for utilization in the hi-tech applications. In this regard two physical processes occurring in glassy material have to be considered – structural relaxation and crystallization. Considering the structural relaxation, the applicability of chalcogenide glasses may be influenced by the changes in important physical properties accompanying the structural changes in consequence of the relaxation processes. In a similar way also the crystallization process can be limiting for the applicability of a newly developed glass. Crystallization has to be either avoided in order to obtain perfect and stable glass with finest optical or electrical properties or, on the contrary, controlled crystallization process in glassy matrix is in fact the fundamental basis of the technology – this is the case of data-storage media. Nevertheless, in either case it would appear to be extremely important to know precise mechanisms of nucleation and crystallization processes.

However, current approach to the development of new modern PCM 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.

2. EXPERIMENTS

Glasses of chosen compositions (Se\(_{90}\)Te\(_{10}\), Se\(_{80}\)Te\(_{20}\), Se\(_{70}\)Te\(_{30}\)) were prepared from pure elements (5N, Sigma Aldrich) by the classical melt-quenching technique – annealing at 450 °C for 24 hours, quenching in water. The amorphous nature of each glass was checked by X-ray diffraction, homogeneity of the glasses was verified from the position of the relaxation peak at \(T_g\).

Enthalpy relaxation and crystallization of the prepared glasses was studied using a conventional DSC 822\(^\circ\) (Mettler, Toledo) equipped with cooling accessory. Dry nitrogen was used as the purge gas at a rate of 20 cm\(^3\)/min. The calorimeter was calibrated through the use of melting temperatures of In, Zn and Ga. Baseline was checked daily. Each prepared glass was ground to powder with particle size in the range 50 – 180 µm. Thin layer of the powder was spread on the bottom of aluminum pan to improve thermal contact. Masses of the samples varied between 9 – 10 mg. Measurements were performed in the 20 – 180°C temperature range.

3. RESULTS AND DISCUSSION

The experimental data were described in terms of nowadays most popular kinetic models for the respective processes – phenomenological Tool-Narayanaswamy-Moynihan model (parameters: apparent activation energy \(\Delta h^*\), non-linearity parameter \(x\), non-exponentiality parameter \(\beta\), pre-exponential factor \(A_{TNM}\)) for structural relaxation and the nucleation-growth Johnson-Mehl-Avrami model (activation energy \(E\), kinetic parameter \(m\),...
pre-exponential factor $A_{\text{TEA}}$ in the case of crystallization behavior. Curve-fitting was applied in order to evaluate the relaxation model parameters for all studied glasses, the results were further confirmed by several non-fitting methods (evaluation from classic and intrinsic cycles, peakshift method). In the case of crystallization data the activation energy was determined according to Kissinger equation; estimation of the most appropriate kinetic model and its parameters was done based on Málek’s characteristic functions $y(\alpha)$ and $z(\alpha)$. More about all these methods as well as about specific procedures associated with the particular evaluations can be found in our previous works and references mentioned there – [2,3] for structural relaxation and [4] for crystallization.

Obtained parameters are for the two studied kinetic processes and three Se-Te chalcogenide glasses listed in the Table. It was found that, under an assumption of carefully performed experiments and evaluations, consistent sets of model parameters capable of precise describing of every possible applied thermal history can be obtained for both studied phenomena, structural relaxation and crystallization. Moreover, it was proven that the determined model parameters provide a reasonable description also outside the tested intervals of experimental conditions, thus granting possibility of highly reliable predictions.

Nevertheless, kinetic analysis is not just a tool for description and consequent predictions of the material’s behavior. In our study it was found that detailed interpretation of the obtained model parameters and other observed characteristics can lead also to structure-related information, making the differential scanning calorimetry even more useful and universal technique.

In particular, based on a premise that with addition of tellurium into a glassy selenium matrix the intra-chain forces decrease while interchain forces increase, decreasing apparent activation energy $\Delta h^*$ with increasing Te content thus implies that primary processes involved in structural relaxation of the polymeric Se matrix are based on local destruction and re-formation of interatomic bonds rather than large changes in chain conformations with only insignificant fraction of breaking bonds (which would, on the contrary, result in an increase of $\Delta h^*$ due to the need for interruption of larger number of stronger van der Waals inter-chain bonds). The increase in parameter $\beta$, associated with narrowing of the relaxation times distribution can be then explained in terms of gradual initial (with respect to the increasing Te content) saturation of a number of weaker bonds engaged in the relaxation process. A lower value of activation enthalpy per relaxing cluster due to the increased number of weaker Te-Se bonds may also imply a decreased degree of cooperativity (high $\beta$) and lower number of chain segments involved in the relaxation process. The crystallization kinetic parameter $m_{\text{JMA}}$ is related to the type and nature of involved processes. Therefore, such information can be derived from its value, e.g. prioritization of internal bulk crystallization over the surface mechanism or decrease in dimensionality of the surface growth with increasing Te content.

### Table: Structural relaxation and Crystallization Parameters

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\Delta h^*/R$ kK</th>
<th>$\ln A_{\text{TEA}}$ s</th>
<th>$x$</th>
<th>$\beta$</th>
<th>$E_{\text{Kissinger}}$ kJ mol$^{-1}$</th>
<th>$m_{\text{JMA}}$ s$^{-1}$</th>
<th>$A_{\text{TEA}}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$<em>{70}$Te$</em>{30}$</td>
<td>38 ± 1</td>
<td>-113 ± 2</td>
<td>0.50 ± 0.04</td>
<td>0.83 ± 0.03</td>
<td>95 ± 4</td>
<td>1.3 ± 2.5</td>
<td>4.2 ± 7.10$^4$</td>
</tr>
<tr>
<td>Se$<em>{65}$Te$</em>{35}$</td>
<td>36 ± 1</td>
<td>-106 ± 3</td>
<td>0.45 ± 0.05</td>
<td>0.81 ± 0.05</td>
<td>120 ± 3</td>
<td>1.2 ± 1.3</td>
<td>2.1 ± 0.2 · 10$^4$</td>
</tr>
<tr>
<td>Se$<em>{60}$Te$</em>{40}$</td>
<td>34.5 ± 1</td>
<td>-100 ± 3</td>
<td>0.43 ± 0.03</td>
<td>0.73 ± 0.02</td>
<td>148 ± 4</td>
<td>1</td>
<td>4.8 ± 0.6 · 10$^3$</td>
</tr>
</tbody>
</table>

4. CONCLUSION

Purpose of this contribution was to demonstrate the extent of information accessible by the kinetic analysis of structural relaxation and crystallization processes by using experimental data provided by the differential scanning calorimetry and to suggest its importance and merit for the development of new high-tech PCM materials. Set of Se-Te chalcogenide glasses was chosen as model materials. It was shown that thorough kinetic analysis of the both most important phenomena associated with the usage and development of PCM materials can give not only precise description of measured data but also reliable predictions of material behavior as well as additional information about nature of involved molecular processes and mechanisms.

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REFERENCES

Biographies

Jiří Málek received his Ph.D. degree from Inst. Chem. Technology, Pardubice in 1986. In 2000 he was awarded D.Sc. degree from the Institute of Chemical Technology in Prague. He spent two years as a visiting researcher at the NIMS, Tsukuba, Japan, two years at University of Seville, Spain and one year at the Polytechnic University of Catalunya in Barcelona, Spain. He is currently professor in Physical Chemistry at University of Pardubice. His research interests cover kinetics of nucleation-growth processes, structural relaxation and viscoelastic behavior of non-crystalline materials and highly supercooled glass-forming liquids, with more than 110 papers published. He is a fellow of Engineering Academy of the Czech Republic, member of the scientific board of the Czech Science Foundation and member of the Council of International Confederation for Thermal Analysis and Calorimetry.