



Thermal behavior of $\text{Ge}_{20}\text{Se}_y\text{Te}_{80-y}$ infrared glasses (for y up to 8 at.%)



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ARTICLE INFO

Article history:

Received 28 December 2015

Received in revised form

14 April 2016

Accepted 18 April 2016

Available online 20 April 2016

Keywords:

Ge-Se-Te infrared glasses

Thermal behavior

Glass transition

Crystallization kinetics

Glass stability

ABSTRACT

The Te-rich $\text{Ge}_{20}\text{Se}_y\text{Te}_{80-y}$ infrared chalcogenide glasses (for y up to 8 at.%) were studied by means of DSC, XRD, Raman spectroscopy and infrared microscopy. Thorough non-isothermal thermo-kinetic characterization of the glass transition, crystallization and melting phenomena was performed in dependence on the particle size. The Tool–Narayanaswamy–Moynihan model was successfully used to describe the structural relaxation processes; the compositional evolution of the relaxation parameters was then explained in terms of the structural changes and movements of the characteristic structural units detected by Raman spectroscopy. The nucleation-growth Johnson-Mehl-Avrami model and empirical Autocatalytic model were used to describe the complex kinetics of the DSC crystallization data. Based on the XRD and microscopic analyses the following crystallization mechanisms were revealed: initial nucleation-growth precipitation of hexagonal Te (surface-located) followed by a bulk-located autocatalytic growth of rhombohedral GeTe; in case of higher Se contents an additional formation of the Ge-Te-Se crystalline phase occurred at high temperatures. Higher glass-stability determined for increasing Se content can be associated with the partial inhibition of the crystallization processes, the initial Te precipitation remains, however, further unaffected once Se content reaches ~4 at.%. © 2016 Elsevier B.V. All rights reserved.

1. Introduction

High transmittance in the (far) infrared region of spectrum belongs to the most important qualities of chalcogenide glasses due to its utilization in numerous hi-tech applications like e.g. construction of IR optics elements, sensors or switches. [1–5]. Large portion of the nowadays research interest regarding these materials aims at finding an ideal compromise between the transmittance in the far IR region and glass thermal stability (which would allow for proper processing of the raw glassy material – molding, fiber-drawing etc.). Since high IR transmittance is characteristic for thermally unstable fully telluride chalcogenides, various dopants (Se, I, Ga ...) are tested in order to improve the thermal stability of these materials. [6,7].

It was established some time ago that the Te-rich pseudo-binary $\text{GeTe}_4\text{-GeSe}_4$ line shows great promise regarding the far-IR optics applications. [8,9]. It was found that the pure $\text{Ge}_{20}\text{Te}_{80}$, which exhibits transmission up to ~22 μm , can be prepared in bulk glass but its glass stability is not sufficient to endure the fiber-drawing process. Therefore, low amounts of Se were added into the glassy

matrix to stabilize the glass whereas the width of the transmission window would still not be influenced – optimum compromise regarding the Se content was searched. [8,9]. However, systematic research of thermal properties of these compositions is still not available in literature – only values of characteristic temperatures associated with glass transition (T_g), cold crystallization (T_c) and melting (T_m) are reported in several articles [10–13]. In the present study the thermal behavior of $\text{Ge}_{20}\text{Se}_y\text{Te}_{80-y}$ infrared glasses (for y up to 8 at.%) will be examined. Aside from the basic thermal characterization given by the calculation of the glass stability (GS) and glass-forming ability (GFA) criteria, the compositional evolution of the glass transition and cold crystallization kinetics will be also presented. It will be shown that simple determination of the T_g , T_c and T_m values is not sufficient to evaluate the glass stability and thermal behavior. The present data will be consequently used to discuss the real-life applicability of the $\text{Ge}_{20}\text{Se}_y\text{Te}_{80-y}$ glasses.

2. Experimental

The $\text{Ge}_{20}\text{Se}_y\text{Te}_{80-y}$ glassy ingots, where $y = 0, 2, 4, 6$ and 8 , were prepared by melt-quenching technique. Adequate amounts of pure elements (5 N, Sigma Aldrich) were inserted into a fused silica ampoule; the ampoules were degassed, sealed and placed in a rocking furnace. The following synthesis was applied: heating up to

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950 °C, annealing for 24 h, slow cooling to 650 °C, annealing for 6 h and quenching in cold water. The prepared glass ingots were crushed and sieved; the following particle size fractions were prepared: 0–20, 20–50, 50–125, 125–180, 180–250, 250–300, 300–500 µm and bulk (pieces of approx. 1 mm size). The structural relaxation and crystallization behavior of the $\text{Ge}_{20}\text{Se}_y\text{Te}_{80-y}$ glasses was hence studied in dependence on particle size.

Heat-flow differential scanning calorimeter Q2000 (TA Instruments) equipped with an autosampler, RCS90 cooling accessory, and T-zero technology was used to perform the DSC measurements. The instrument was calibrated using In, Zn, and H_2O ; dry N_2 was used as purge gas at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The baseline was checked daily. A thin layer of the powder was always spread on the bottom of the low-mass aluminum pans to improve the thermal contact and at the same time to minimize the variety of heat transfer processes. The sample masses were approximately 10 mg.

The crystallization measurements were performed as simple heating scans realized at a set of various heating rates: 0.5, 1, 2, 3, 5, 7, 10, 15, 20, and 30 °C min^{-1} (applied for each particle size fraction of each studied material). As-prepared materials were measured. To study the glass transition kinetics the constant heating rate (CHR) cycles [14,15] were applied in accordance with the state-of-art methodological guide [16] for evaluation of glass transition kinetics. During this type of temperature program the sample is repeatedly cooled through T_g at various cooling rates, while the consequent heating scans through T_g are always performed at the same rate (30 °C min^{-1} in the present work). The used cooling rates were: 0.5, 1, 2, 3, 5, 7 and 10 °C min^{-1} . Each set of cyclic experiments was performed using the same sample to maximize baseline repeatability within each set of cycles. Reproducibility of all types of performed DSC measurements was confirmed.

Confirmation of the amorphous nature of the glass as well as identification of the crystalline phases in case of DSC-crystallized samples was performed by X-ray diffraction (Bruker AXS diffractometer D8 Advance equipped with a horizontal goniometer and scintillation counter utilizing CuK_α radiation) – the diffraction patterns of the as-prepared amorphous materials are shown in Supplemental material; diffraction patterns of the crystallized glasses will be shown in Section 3.1. The Raman data were collected using a Senterra Raman microscope (Bruker; 785 nm laser). Infrared microscope Olympus BX51 equipped with XM10 camera used in the reflection mode was used to identify the particular types of formed crystallites.

3. Results and discussion

This section will be divided into three sub-sections. In the first sub-section the basic information on thermal behavior will be provided – the full-scale DSC data (ranging from glass transition to melting) will be introduced. The section will be focused on the basic description of the thermal effects observed on DSC curves; most importantly the XRD technique will be used to identify the crystalline phases formed during the observed crystallization effects. At the end of the first sub-section the T_g , T_c and T_m values will be used to determine the glass stability and glass-forming ability of the studied systems. The second sub-section will be devoted to the detailed description of the glass transition kinetics; based on the structural information provided by Raman spectra the DSC relaxation data will be interpreted. The third sub-section will deal in detail with the crystallization kinetics and complexity of the observed crystallization effects.

3.1. Basic thermal and structural characterization

Basic thermal behavior of the prepared chalcogenide glasses is demonstrated in Fig. 1a, where the raw DSC curves obtained for the 125–180 µm particle size fractions and heating rate 10 °C min^{-1} are displayed. The other graphs in Fig. 1 then show zoomed-in particular regions of interest. As can be seen in Fig. 1b, the glass transition effect is rather indistinctive and becomes more stretched and smeary with increasing Se content. This indicates weak structural dependence of the relaxation motions, which become more variable in their nature with Se addition. Even though as-prepared materials were measured, there is no apparent relaxation peak (overshoot) effect. In addition, the very position of the glass transition shifts only very slightly with increasing Te content. All these features will be addressed later in the section 3.2 dealing with the glass transition kinetics.

In Fig. 1c the evolution of the crystallization effect with rising Se content is displayed. It is clear that the complex peak observed in case of the pure $\text{Ge}_{20}\text{Te}_{80}$ matrix (0% Se) becomes progressively separated as Se content increases. Addition of Se also inhibits the overall crystallization process, shifting the crystallization effects to higher temperatures. Moreover, a third crystallization peak occurs and increases in magnitude with addition of Se. In the following paragraphs the assignment of particular crystallographic data will be done; detailed kinetic behavior as well as the reason for progressive separation of the particular crystallization peaks will be discussed later in Section 3.3. In order to identify the crystallization products, XRD technique was used – Fig. 2 shows the diffraction patterns of the 125–180 µm powders crystallized in DSC; heating rate 10 °C min^{-1} was used to heat the sample from room temperature above the last crystallization effect, where 10 min isotherm was applied. In addition to the two well resolved crystalline phases, hexagonal tellurium (P3121, $a = 4.4572$, $b = 4.4572$, $c = 5.9290$, where “a”, “b” and “c” stand for the lattice parameters) and rhombohedral GeTe (R3m, $a = 8.3280$, $b = 8.3280$, $c = 10.690$), a third unidentified phase occurs with increasing Se content (marked by red arrows in the respective graphs). Considering possible combinations of the involved elements and data from the corresponding phase-diagrams [17,18], the unidentified phase most probably contains all the three elements and does not represent any of the Se ↔ Te substituted already present phases – Te(Se) and GeTe(Se).

To further investigate the crystallization products, series of DSC experiments performed at different conditions (heating rate, particle size, composition, temperature and duration of final annealing) were performed and the crystalline products were submitted to XRD analysis. While in most cases the typical crystalline phases (Te, GeTe, and unidentified third phase) occurred, under certain conditions approaching the equilibrium conditions (very slow heating rate, large bulk-to-surface ratio) new phase has appeared – see Fig. 3a where monoclinic GeSe_2 phase (P21/c, $a = 7.016$, $b = 16.796$, $c = 11.831$, $\alpha = 90^\circ$, $\beta = 90.65^\circ$, $\gamma = 90^\circ$) was identified for the crystallized $\text{Ge}_{20}\text{Se}_2\text{Te}_{78}$ composition, replacing the rhombohedral GeTe. This implies that under the equilibrium-like conditions the energy surplus is not large enough to overcome the kinetic barriers associated with the growth of the GeTe phase and the “next-in-line” crystalline phase forms instead. The poor overall crystallinity indicated by the diffraction pattern in Fig. 3a also suggests that the crystallization of Te and GeTe phases is interconnected and that the GeTe phase is responsible for the continuation of the crystallization process (note that the poor overall crystallinity is in agreement with the significantly low amount of the potential GeSe_2 phase being present in the original $\text{Ge}_{20}\text{Se}_2\text{Te}_{78}$ glassy matrix).

Lastly, a series of DSC crystallization experiments was

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