



Structural interpretation of the enthalpy relaxation kinetics of $(\text{GeTe}_4)_y(\text{GaTe}_3)_{1-y}$ far-infrared glasses



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ABSTRACT

Differential scanning calorimetry was used to study enthalpy relaxation kinetics of the $(\text{GeTe}_4)_y(\text{GaTe}_3)_{1-y}$ infrared chalcogenide glasses for the compositional range $y = 0.4 - 1.0$. The relaxation behavior was described in terms of the Tool-Narayanaswamy-Moynihan (TNM) model. Direct curve-fitting procedure was used to determine the values of TNM parameters; these results were successfully correlated with data provided by the non-fitting methodology based on the evaluation from constant-ratio (CR) cycles. The addition of GaTe_3 into the GeTe_4 matrix led to a moderate decrease of activation energy of the relaxation process and to a large increase of the relaxation linearity – the structural relaxation became driven solely by temperature. Interpretation of the compositional evolution of the TNM parameters was used to verify structural information provided by Raman spectroscopy and molecular dynamics simulations: the initial GaTe_3 addition causes dilution of the GeTe_4 tetrahedral network, which carries the main portion of the relaxation motions; further increase of GaTe_3 content then leads to an increase of connectivity outside the GeTe_4 sub-networks due to the threefold coordinated Ga atoms bonding with the lone-pair electrons of Te dimers and short chains.

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1. Introduction

The Ge-Ga-Te chalcogenide glasses belong to the most promising materials regarding the far-infrared optics applications. [1–4] The applications of interest involve construction of e.g. self-aligning CO_2 detectors/traps fighting global warming or IR optics telescopes detecting biological life markers on exoplanets. [3,5] Due to the fully telluride matrix, these glasses exhibit one of the highest transmittances in the far-IR region (above $\sim 18 \mu\text{m}$) [6,7], the addition of gallium then increases the resistance of these glasses against crystallization. Despite the importance of the Ge-Ga-Te system, thermal behavior of these glasses was never studied in detail – only the values of characteristic temperatures corresponding to glass transition (T_g) and crystallization (T_c) were reported. [2,8].

In the present article the glass transition kinetics and structural relaxation mechanics will be described for the $(\text{GeTe}_4)_y(\text{GaTe}_3)_{1-y}$ chalcogenide pseudo-binary line. Since the relaxation processes are responsible for the long-term changes of the structure-related properties (optical, mechanical and electrical) of the glass, their knowledge is crucial for successful processing, production and the practical application of all optical elements made of (infrared) glasses. Full glass-forming range along the above-mentioned line will be investigated – the region of

interest (from the pure GeTe_4 to approx. 65 at.% of GaTe_3) will be covered by seven selected compositions.

The relaxation behavior will be described in terms of one of the best contemporary structural relaxation models, the Tool-Narayanaswamy-Moynihan (TNM) model [9–11]:

$$\Phi(t) = \exp \left[- \left(\int_0^t \frac{dt}{\tau(T, T_f)} \right)^\beta \right] \quad (1)$$

$$\tau(T, T_f) = A_{TNM} \cdot \exp \left[x \frac{\Delta h^*}{RT} + (1-x) \frac{\Delta h^*}{RT_f} \right] \quad (2)$$

where $\Phi(t)$ is the relaxation function of the given property, t is time, τ is the relaxation time, β is the non-exponentiality parameter ($0 < \beta \leq 1$), A is the pre-exponential factor, x is the non-linearity parameter ($0 < x \leq 1$), Δh^* is the apparent activation energy of the structural relaxation, R is the universal gas constant, T is temperature and T_f is the fictive temperature, which is defined as the temperature of the undercooled liquid with the same structure as that of the relaxing glass. Extensive testing of the TNM formalism has confirmed that it very well describes all the main structural relaxation features – hysteresis, non-linearity, non-exponentiality, thermorheological complexity. Despite certain shortcomings [see e.g. 12] of the TNM model, none of the contemporary rival models can overcome these shortcomings and, at the same time,

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provide a comparably accurate direct description of the volume and heat capacity relaxation data.

2. Experimental

Pure elements (5 N, Sigma Aldrich) were used to prepare the following $(\text{GeTe}_4)_y(\text{GaTe}_3)_{1-y}$ compositions, where $y = 0.40, 0.50, 0.60, 0.67, 0.75, 0.86$ and 1 . The melt-quenching was performed by first annealing the batched fused-silica ampoule for 24 h at 950°C and then quenching it in water. The amorphous character of the prepared glasses was confirmed by X-ray diffraction technique (Bruker AXS diffractometer D8 Advance equipped with a horizontal goniometer and scintillation counter utilizing $\text{CuK}\alpha$ radiation). Structural information was obtained by the Nicolet DXR Raman spectrometer (Thermo Fisher Scientific) utilizing 780 nm excitation laser (10 mW, 200 scans \rightarrow 10 s each) with laser spot size equal to $3.1\ \mu\text{m}$. Compositional homogeneity of the glasses was confirmed by measurements of the glass transition effect for samples taken randomly from the as-prepared glassy ingot taken out of the ampoule – both position and height of the relaxation peak matched perfectly; no shoulders or double-peak effects occurred. In addition, neither the infrared micrographs nor the XRD amorphous halos (see Supplemental material) indicate any signs of phase separation or compositional in homogeneity.

The relaxation behavior was studied by means of differential scanning calorimetry (DSC), using the conventional Q2000 DSC (TA Instruments) equipped with cooling accessory, autoloid, autosampler, and T-zero Technology. Dry nitrogen at a rate of $50\ \text{cm}^3\ \text{min}^{-1}$ was used as the purge gas. The calorimeter was calibrated by means of melting temperatures of In, Zn, and H_2O . All the prepared $(\text{GeTe}_4)_y(\text{GaTe}_3)_{1-y}$ glasses were ground to powders using an agate mortar and the $125\text{--}180\ \mu\text{m}$ particle size fraction was separated by sieving (this particle size fraction was found to be least influenceable by experimental conditions and thermal gradients effects [13,14]); standard low-mass aluminum DSC pans and careful spreading of the powders

on the pan bottom were used to further minimize the thermal gradients effects. Masses of the powdered samples varied between 8 and 10 mg.

Two cyclic temperature programs were used to study the relaxation behavior: constant ratio (CR) cycles [15] and constant heating rate (CHR) cycles [16]. In both these thermal histories the sample is repeatedly cooled and heated through T_g at various rates. During the CR cycles the ratio between the cooling rate and the consequently applied heating rate q^+/q^- remains constant, while in case of the CHR cycles the cooling rates vary and all the heating rates remain same – schematic representation of both thermal histories and corresponding typical DSC responses is shown in Fig. 1. The applied cooling rates were $0.5, 1, 2, 3, 5, 7, 10, 15, 20$ and $30^\circ\text{C}\ \text{min}^{-1}$. The heating rates were set followingly: for the CR cycles the ratio $q^+/q^- = 3$ was used (standard choice is usually 1), the heating rate used for CHR cycles was $30^\circ\text{C}\ \text{min}^{-1}$ (usually $10^\circ\text{C}\ \text{min}^{-1}$ is applied). This choice was very beneficial with respect to the present materials, as will be explained in the next section. All cycles within a given set were performed using the same sample, which was not removed from the measuring DSC cell for the entire duration of the given set of measurements; each set of cycles was repeated using a fresh sample in order to verify the reproducibility of the measurements.

3. Results

3.1. Enthalpy relaxation data

In Fig. 2 the glass transition temperatures determined at two selected heating rates (1.5 and $15^\circ\text{C}\ \text{min}^{-1}$) are shown in dependence on the molar ratio of GeTe_4 (y) along the $(\text{GeTe}_4)_y(\text{GaTe}_3)_{1-y}$ pseudo-binary line. Although such data can be under certain circumstances used to estimate the relative proportions between the glass transition activation energies (such estimates are often performed by means of the Kissinger-type methods [17]), it has been shown recently [18,19] that such estimates are in most cases inaccurate and the absolute values of activation energies Δh^* cannot be determined in this way. The accuracy

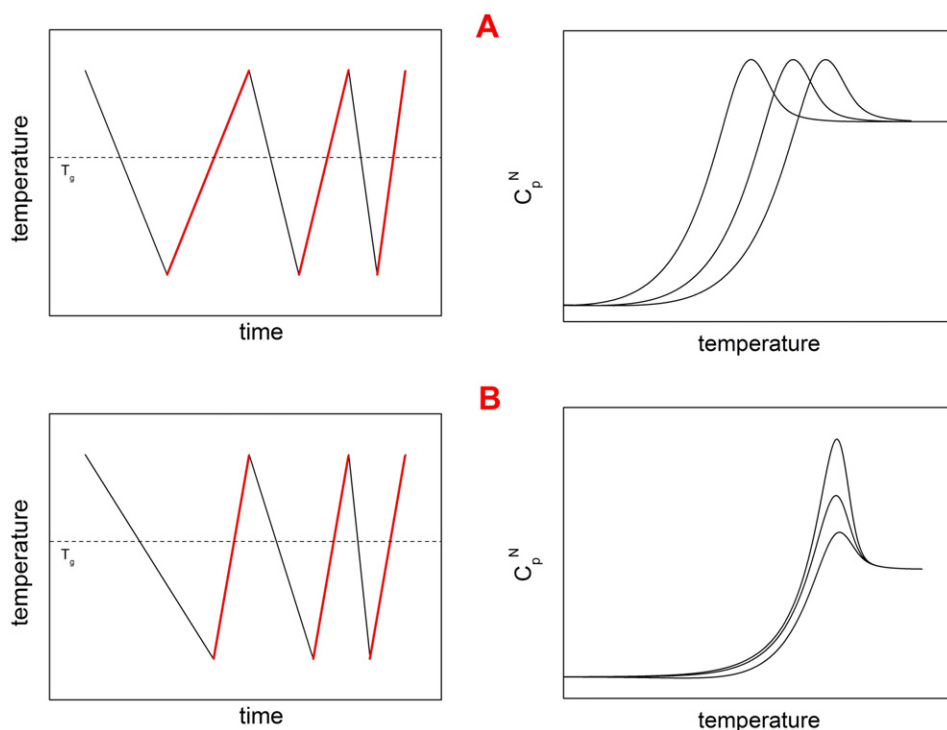


Fig. 1. Left column depicts schematic representations of the temperature histories corresponding to the constant ratio A) and constant heating rate B) cycles. The right column depicts the DSC curves corresponding to the respective heating scans (red lines in the left column graphs).

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