INTRODUCTION

Tellurite–molybdate glasses prepared from precipitates obtained by adding aqueous ammonia to hydrochloric acid solutions of tellurium(IV) and molybdenum(VI) compounds offer low optical absorption in the visible and near-IR spectral regions [1–3] and are thus promising materials for fiber-optic applications. Glass transition temperatures determined by differential scanning calorimetry (DSC) for samples of various compositions were reported to be close to those of glasses prepared by melting oxide mixtures [4].

One possible reason for additional optical losses in glass is the formation of crystalline inclusions as a consequence of nonoptimal melt cooling and glass heat treatment schedules. Glass crystallization kinetics in the system in question has not yet been studied.

Thermal analysis techniques are being used increasingly in studies of glass crystallization [5, 6]. The reason for this is that these techniques provide clear, informative data on the crystallization behavior of glasses in the form of corresponding peaks, ensure high-speed measurements, and employ advanced, readily available DSC instruments. Unfortunately, existing techniques for mathematical processing of crystallization peaks [7, 8] as a rule do not fully take into account that DSC measurements are made under nonisothermal conditions. An even more serious drawback of these techniques is that the dependence of model exponents on the heating rate is not substantiated physically.

The objectives of this work were to choose and improve a procedure for DSC data processing using test data on the crystallization kinetics of glassy GeS₂ and to find kinetic characteristics of crystallization by processing DSC data for a series of (TeO₂)₁₋ₓ(MoO₃)ₓ glasses and determine the degree of crystallization as a function of temperature and time with the aim of minimizing the crystallization effect in optical applications of tellurite–molybdate glasses.

MATHEMATICAL MODEL FOR PROCESSING DSC PEAKS OF CRYSTALLIZATION

The enthalpy increment ΔH for the crystallization of glass A, represented by the quasi-chemical reaction A → *A, is determined [9] by a molar coordinate ξ and the enthalpy of the crystallization reaction ΔH:

\[ \Delta H = \xi \Delta H = \alpha n_0 \Delta H = \alpha n_0 (\Delta H/M). \]  (1)

The second and third expressions in (1) include the degree of crystallization, \( \alpha = \xi/n_0 \), as the fraction of the number of moles, ξ, relative to the initial amount, \( n_0 = m_0/M \), of the starting (mother) phase (where \( m_0 \) and \( M \) are, respectively, the initial and molar masses of the crystallizing substance).
Dividing Eq. (1) by \( m_0 \), we obtain a relation between the enthalpies under consideration and, accordingly, between the corresponding heats in specific quantities, that is, per unit mass:

\[
\frac{\Delta H}{m_0} = \alpha \frac{\Delta H}{M}, \quad Q_m = \alpha Q_{mM}. \tag{1’}
\]

The second equation in (1’) relates the specific heat flux, \( Q_m = -\Delta H/m_0 \) to the specific heat of the reaction: \( Q_{mM} = -\Delta H/M \).

Within certain limits, a signal proportional to the specific heat flux, \( \dot{Q}_m = dQ_m/dt \), in heat-flow DSC instruments is commonly believed to be independent of the mass of the sample [10]:

\[
S_{DSC} = C\dot{Q}_m = C\alpha Q_{mM} = C_N \alpha, \tag{2}
\]

where the flux \( \dot{Q}_m = \alpha Q_{mM} \) is obtained by differentiating the second equation in (1’) with respect to time. Thus, at constant \( C \) and \( Q_{mM} \), the shape of the crystallization peak is determined by the crystallization rate \( \dot{\alpha} = d\alpha/dt \), and its area is determined by the integral of relation (2), which is \( C\alpha Q_{mM} \). Clearly, the area of the entire peak after the crystallization of the sample \( (\alpha = 1) \) is \( Q_{mM} \).

Such reasoning is applicable as well to melting peaks, which are used to calibrate instruments. Therefore, the magnitude and dimensions of the instrumental or normalization constant \( C_N = C\alpha Q_{mM} \) for a calibrated instrument \((C = 1) \) correspond to those of the specific heat of the process, \( Q_{mM} \) \((J/g) \), ensuring the dimensions of the DSC signal \((J/(g \text{ s})) \) as a specific heat flux or specific power.

When the dimensions of the \( S_{DSC} \) signal of an uncalibrated instrument are \( \mu\text{V/mg} \), the dimensions of the normalization constant are \([C_N] = [S_{DSC}/\dot{\alpha}] = \mu\text{V/s/mg} \).

The Johnson–Mehl–Avrami (JMA) model, which is most frequently used to determine the crystallization rate \( \dot{\alpha} \), is a considerable simplification of the Kolmogorov–Johnson–Mehl theory. In this three-parameter model, the degree of crystallization as a function of temperature and time has the form

\[
\alpha(t, T) = 0.01 + \exp(-\tau^n), \tag{3}
\]

where \( \tau = kt \); \( k = Aexp(-E_a/(RT)) \) is the crystallization rate constant in Arrhenius representation; \( A \) is the pre-exponential factor; \( E_a \) is the activation energy; and \( n \) is the JMA exponent, which qualitatively corresponds to the size parameter in the Kolmogorov–Johnson–Mehl theory. To the integral form of the JMA model (3) corresponds its differential form:

\[
\dot{\alpha} = \frac{d\alpha}{dt} = k\alpha^p(\alpha); \quad \alpha^p(\alpha) = n(1 - \alpha)\left[-\ln(1 - \alpha)\right]^{1-1/n}. \tag{4}
\]

Note that the derivative of \( \alpha \) with respect to dimensionless time \( \tau \) is denoted in the literature by \( \dot{\alpha}^p(\alpha) = f(\alpha) \).

Another simplified, semiempirical form of the Kolmogorov–Johnson–Mehl theory was proposed by Erofeev [11]. The differential equation representing this semiempirical model has the form

\[
\dot{\alpha} = k_{\text{eff}} \alpha^p(1 - \alpha)^b. \tag{5}
\]

As shown by Sestaik and Berggren [12] and then by Malek et al. [7], the semiempirical model has an advantage over the JMA model in processing DSC peaks due to crystallization. At the same time, the lack of an analytical solution to the differential equation for the semiempirical model or its integral form \( \alpha(t, T) \) complicates numerical processing of experimental data, makes it difficult to fully take into account that DSC measurements are made under nonisothermal conditions, and markedly limits the model’s predictive power, which is quantified by a parametrically defined, explicit function: \( \alpha(t, T) \). Another important drawback to the semiempirical model is that its meaning is hidden in the empirical exponents \( a \) and \( b \) and that the rate constant \( k_{\text{eff}} \) has an effective character. These factors make it difficult to identify details of the crystallization mechanism in terms of the Kolmogorov–Johnson–Mehl concepts.

A modified semiempirical (MSE) model we propose here is free of the above drawbacks. Its integral form is represented by

\[
\alpha(t, T) = \frac{1}{(1 + 1/\tau^n)^p}. \tag{6}
\]

Comparison of formulas (3) and (6) suggests a procedure—common to the JMA and MSE models—for determining the temperature–time dependence \( \alpha(t, T) \) only through the \( \tau = kt \) product.

Differentiating relation (6) yields an appropriate differential form of the MSE model:

\[
\dot{\alpha} = \alpha^p(\alpha) = k\alpha^{1-p}(1 - \alpha)^b. \tag{7}
\]

Comparison of formulas (4) and (7) indicates that the \( np \) product in the MSE model plays the role of the crystallization parameter \( n \), which is important for the JMA model and effectively determines the crystallization mechanism. Finally, comparison of formulas (5) and (7) indicates that the MSE model discloses not only the meaning of the exponents \( a \) and \( b \) in the semiempirical model but also that of the effective rate constant \( k_{\text{eff}} \).

Equation (4) for the JMA model and Eq. (7) for the MSE model correspond to isothermal kinetics because, when differentiating, the temperature-dependent rate constant \( k \) was taken to be time-independent. However, when thermal analysis is carried