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Crystallization kinetics of Al_2O_3–Yb_2O_3 glasses

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Abstract Crystallization kinetics of Al_2O_3–Yb_2O_3 glass microspheres with two different compositions was studied by DTA. Heating rates ranging from 3 to 15 °C min^{-1} were used for DTA measurement. The DTA curves obtained were transformed into the dependence of conversion, α, on temperature. The model $f(\alpha) = \alpha^n(1 - \alpha)^m$, i.e., the model of Sestak and Berggren, was found suitable for the description of crystallization kinetics. The best fit of experimental data was obtained if the full set of measured conversion degrees was used for calculation of kinetic parameters. In this manner, the following results were obtained: $A = 6.10 \times 10^{20}$ min^{-1}, $E = 4.68 \times 10^5$ J mol^{-1}, $n = 0.634$, $m = 1.037$ for 30 wt% Al_2O_3–70 wt% Yb_2O_3 glass, and $A = 6.98 \times 10^{25}$ min^{-1}, $E = 5.97 \times 10^5$ J mol^{-1}, $n = 0.562$, $m = 0.975$ for 45 wt% Al_2O_3–55 wt% Yb_2O_3 glass.

Keywords Aluminate glass · Crystallization kinetics · Regression analysis · DTA

Introduction

Aluminate glasses with high alumina content are considered as potential candidates for various applications, such as infrared transparent windows or host for rare earth elements in materials used for solid state lasers. The synthesis of aluminate glasses requires high melting temperatures and high cooling rates due their enormous tendency to crystallize [1]. Aluminate glasses can be prepared by spray flame synthesis in the form of microspheres [2]. The requirement of high cooling rates is fulfilled by this type of glass preparation. The crucial factor of preparation of these progressive materials in glassy form is the crystallization kinetics [3–8].

The crystallization kinetics of two binary glasses with the composition: 30 wt% Al_2O_3–70 wt% Yb_2O_3 (A30Yb 70), and 45 wt% Al_2O_3–55 wt% Yb_2O_3 (A45Yb55) was studied by DTA in this study.

Experimental

The DTA measurements were performed by the digitized Derivatograph OD102 (MOM Budapest) in temperature range of (30–1000) °C. Sample mass of 153 mg was chosen for experiments performed at the heating rate $\beta = (3,$ 5, 7, 9, 11, 13, and 15) °C min^{-1}, thus the temperature, T; time, t, course was described by $T(t) = T_0 + \beta t$. The measurements started at the temperature $T_0 = 30$ °C. The measurements were carried out in a static air atmosphere. The α-Al_2O_3 was used as a reference material.

After obtaining $\alpha(t)$ and $d\alpha(t)/dt$, resp. $\alpha(T)$ and $d\alpha(T)/dT$ from DTA curve as proportional to the area under the DTA curve after subtracting the baseline, the following basic crystallization kinetic equations were considered [9–14]:

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$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) = A\exp(-E/RT)f(\alpha) \tag{1}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\exp[-E/RT(t)]f\{\alpha[T(t)]\} \tag{2}$$

where $\alpha(t)$ is the conversion degree, $\mathrm{d}\alpha(t)/\mathrm{d}t$ represents the crystallization rate (directly proportional to the measured DTA signal), R is the molar gas constant, k is the formal rate constant expressed by the Arrhenian form using the preexponential factor A and the formal activation energy of crystallization E.

Three particular forms of $f(\alpha)$ were considered:

$$f(\alpha) = \alpha^n - \text{model 1} \tag{3}$$

$$f(\alpha) = (1-\alpha)^m - \text{model 2} \tag{4}$$

$$f(\alpha) = \alpha^n(1-\alpha)^m - \text{model 3} \tag{5}$$

where n and m are formal reaction orders. The most general model 3 represents the model of Sestak and Berggren (S–B).

The kinetic triplet (A, E, and n, m) was obtained by two-step process of regression analysis. As the first, the Eq. 2 was linearized:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln A - \ln\beta - \frac{E}{RT(t)} + n\ln(\alpha) + m\ln(1-\alpha) \tag{6}$$

and using the following substitutions:

$$p_{i,j}^{\exp} = \ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{i,j}^{\exp} + \ln\beta_i \tag{7}$$

$$x_{i,j} = \ln(\alpha_{i,j}) \tag{8}$$

$$y_{i,j} = \ln(1-\alpha_{i,j}) \tag{9}$$

$$z_{i,j} = -\frac{1}{RT(t_{i,j})} \tag{10}$$

$$T(t_{i,j}) = T_0 + \beta_i t_{i,j} \tag{11}$$

the system of linear equations was obtained:

$$p_{i,j} = A' + nx_{i,j} + my_{i,j} + Ez_{i,j},\ i = 1, 2\ldots N;\quad j = 1, 2\ldots M_i \tag{12}$$

where $A' = \ln A$, N is the number of DTA curves, and M_i stands for the number of points of the ith DTA curve. The linear least squares problem was solved by minimizing the following sum of squares of deviations:

$$U(A', m, n, E) = \sum_{i=1}^{N}\sum_{j=1}^{M_i}\left[p_{i,j}^{\exp} - p_{i,j}^{\mathrm{clc}}\right]^2 = \min \tag{13}$$

where $p_{i,j}^{\mathrm{clc}}$ is given by Eq. 12.

As a next step, the non-linear least squares problem:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = A\exp[-E/RT(t)]f\{\alpha[T(t)]\} \tag{14}$$

$$q_{i,j}^{\exp} = \beta\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{i,j}^{\exp} \tag{15}$$

$$\alpha_{i,j} = \alpha^{\exp}[T(t_{i,j})] \tag{16}$$

was solved by minimizing the following sum of squares of deviations:

$$V(A, m, n, E) = \sum_{i=1}^{N}\sum_{j=1}^{M_i}\left\{q_{i,j}^{\exp} - A\exp[-E/RT(t_{i,j})]f(\alpha_{i,j})\right\}^2 = \min \tag{17}$$

The results of multilinear regression Eq. 13 were used as the starting values of optimized parameters. MATLAB® software was used for calculations.

Results and discussion

Figure 1 shows DTA curves of both examined glasses measured at various heating rates.

In the first step, the kinetic parameters (A, E, n, and m) were calculated by nonlinear regression analysis Eq. 17 by using the results of linearized model Eq. 12 as starting parameters. The statistical regression characteristics (sum of squares of deviations—ssd, and correlation coefficient—r) were calculated too. Obtained results are summarized in Table 1.

From the comparison of obtained results for considered models, it can be seen that the S–B model (i.e., model 3) is the best model for both glasses. In the next step, the dependence of regression results on the range of conversion of experimental data considered in the regression was studied. Only for the S–B model was considered in this study. Test results are summarized in Tables 2 and 3 for A30Yb70 and A45Yb55 glass, respectively. On the basis of reported statistical characteristics, it can be deduced that there is no strong difference between the results obtained for data from different ranges of conversion degree.

However, the situation is different from the point view of values of obtained regression estimates of kinetic parameters. These can be divided into two groups according to considered ranges of conversion experimental data. The first group includes the intervals which contain low and/or middle values of conversion. The second group includes the intervals which contain higher values of conversion, but does not contain initial values of conversion. In the first group, the values of kinetic parameters are mutually comparable and we can consider them as plausible. In contrary, the values of kinetic parameters are markedly lower in the second group.

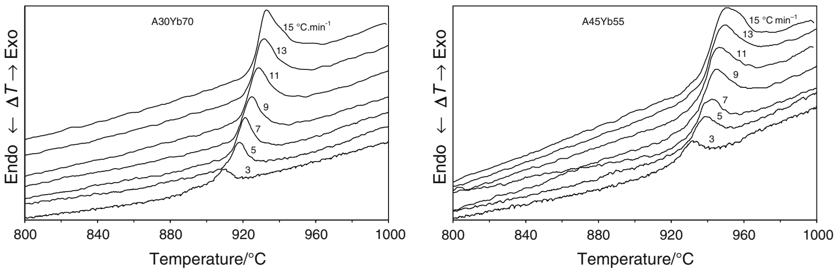

Fig. 1 DTA curves of glasses A30Yb70 and A45Yb 55 at various heating rates

Table 1 The kinetic parameters and statistical regression characteristics (sum of squares of deviations—ssd, correlation coefficient—*r*) obtained by nonlinear regression analysis

Glass	Model Eqs. 3–5	A/min^{-1}	E/J mol^{-1}	n	m	ssd	r
A30Yb70	1	3.83×10^{16}	3.87×10^{5}	−0.147	–	29.65	0.526
	2	1.22×10^{18}	5.12×10^{5}	–	0.339	16.10	0.801
	3	6.10×10^{20}	4.68×10^{5}	0.634	1.037	2.64	0.967
A45Yb55	1	5.13×10^{18}	4.45×10^{5}	−0.161	–	17.28	0.517
	2	1.36×10^{24}	6.94×10^{5}	–	0.371	8.26	0.845
	3	6.98×10^{25}	5.97×10^{5}	0.562	0.975	1.41	0.970

Table 2 The kinetic parameters of S–B model obtained by nonlinear regression using experimental data from limited conversion range for sample A30Yb70

Range of α	A/min^{-1}	E/J mol^{-1}	n	m	ssd	r
0.05–0.35	5.49×10^{28}	6.49×10^{5}	0.690	1.270	0.31	0.990
0.35–0.65	3.35×10^{21}	4.84×10^{5}	0.663	1.158	1.01	0.956
0.65–0.95	2.50×10^{14}	3.29×10^{5}	−0.192	0.672	0.38	0.973
0.05–0.65	8.38×10^{24}	5.61×10^{5}	0.710	1.259	1.85	0.969
0.35–0.95	4.05×10^{17}	3.98×10^{5}	0.399	0.868	1.50	0.971
0.05–0.95	6.10×10^{20}	4.68×10^{5}	0.634	1.037	2.64	0.967

Table 3 The kinetic parameters of SB model obtained by nonlinear regression using experimental data from limited conversion range for sample A45Yb55

Range of α	A/min^{-1}	E/J mol^{-1}	n	m	ssd	r
0.05–0.35	7.09×10^{32}	7.54×10^{5}	0.801	1.745	0.18	0.989
0.35–0.65	6.81×10^{27}	6.42×10^{5}	0.552	1.111	0.33	0.975
0.65–0.95	4.60×10^{20}	4.81×10^{5}	0.171	0.715	0.45	0.955
0.05–0.65	9.86×10^{29}	6.90×10^{5}	0.704	1.336	0.57	0.984
0.35–0.95	4.49×10^{23}	5.49×10^{5}	0.274	0.787	0.91	0.970
0.05–0.95	6.98×10^{25}	5.97×10^{5}	0.562	0.975	1.41	0.970

Figures 2 and 3 show the comparison of experimental and calculated values of crystallization rate for various heating rates for conversion ranges $\langle 0.05;0.95 \rangle$ and $\langle 0.65;0.95 \rangle$. It can be seen that the calculated data fit the experimental values with quite sufficient accuracy for both considered ranges.

However, the most representative evaluation of quality of kinetic parameters for various ranges of conversion value was carried out by comparison of experimental conversion curves $\alpha^{\mathrm{exp}}(T)$ with the $\alpha^{\mathrm{clc}}(T)$ values calculated by numerical integration of $\mathrm{d}\alpha^{\mathrm{clc}}(T)/\mathrm{d}T$ values within the conversion range $\alpha \subset \langle 0.05;0.95 \rangle$. Values of $\mathrm{d}\alpha^{\mathrm{clc}}(T)/\mathrm{d}T$ were calculated on the basis of particular set kinetic parameters obtained by nonlinear regression for various ranges of value of conversion. The results of the above comparison are shown in Figs. 4 and 5 for conversion

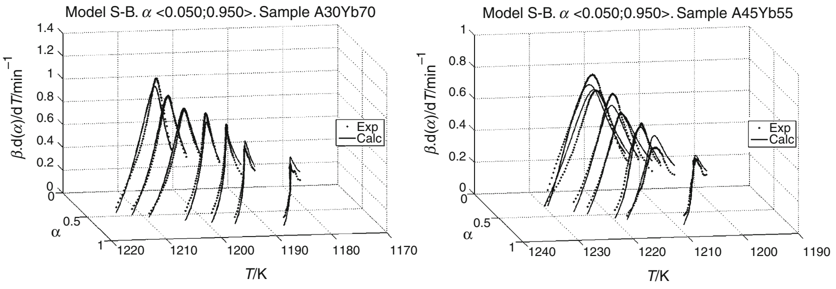

Fig. 2 Comparison of experimental (exp) and calculated values (calc) of crystallization rate for conversion range of ⟨0.05;0.95⟩ for various heating rates

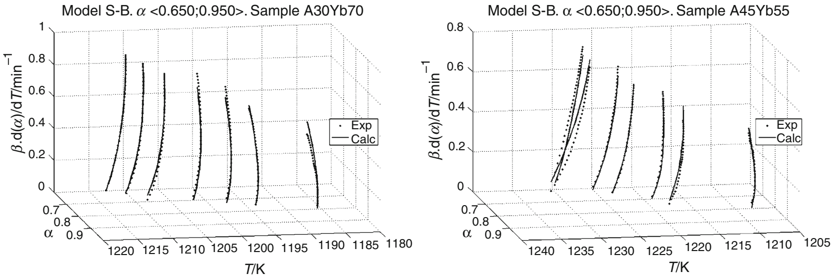

Fig. 3 Comparison of experimental (exp) and calculated values (calc) of crystallization rate for conversion range of ⟨0.65;0.95⟩ for various heating rates

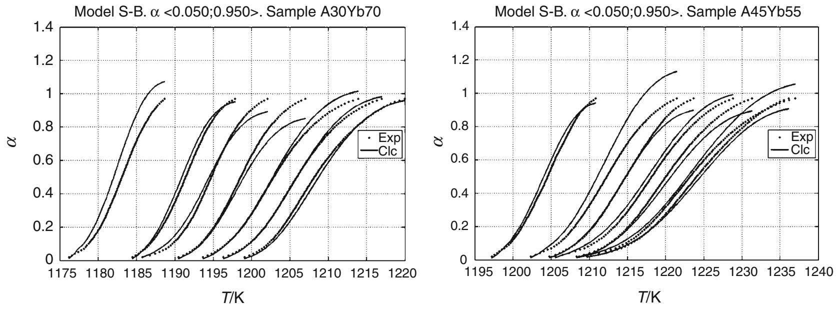

Fig. 4 Experimental (exp) and calculated (clc) values of conversion versus temperature. Curves were calculated on the basis of kinetic parameters obtained by regression analysis of experimental data from the conversion range ⟨0.05;0.95⟩

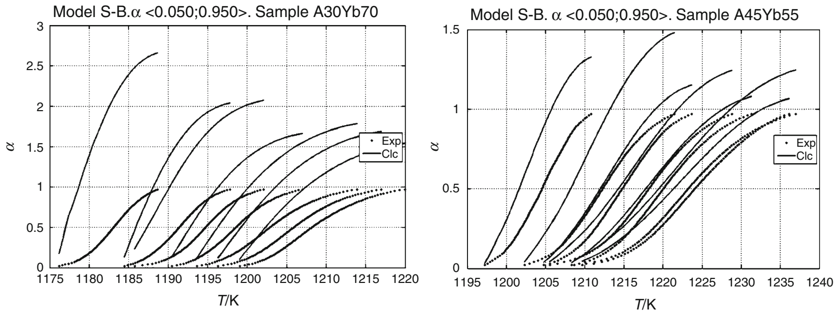

Fig. 5 Experimental (exp) and calculated (clc) values of conversion versus temperature. Curves were calculated on the basis of kinetic parameters obtained by regression analysis of experimental data from the conversion range ⟨0.65;0.95⟩

intervals ⟨0.05;0.95⟩ and ⟨0.65;0.95⟩. The strong difference can be seen between approximation quality when the full interval of conversion degrees is considered as input regression data on one side and for the case when only a limited range of experimental data is taken into account (i.e., data for $\alpha \subset \langle 0.65;0.95\rangle$). The similar situation is found for other limited conversion ranges. This unambiguously shows that the experimental data from the full conversion range have to be used in regression treatment for evaluation of crystallization kinetic parameters.

Conclusions

Crystallization kinetics of two Al_2O_3–Yb_2O_3 glass microspheres of composition: 30 wt% Al_2O_3–70 wt% Yb_2O_3 (A30Yb70), and 45 wt% Al_2O_3–55 wt% Yb_2O_3 (A45Yb 55) was studied by DTA analysis by the method of nonlinear regression analysis. The linearized form of kinetic equation was used for obtaining the starting values of regression parameters for iterative process of nonlinear regression analysis. The model $f(\alpha) = \alpha^n(1 - \alpha)^m$, i.e., the model of Sestak and Berggren, was found as the appropriate for quantitative description of studied crystallization kinetics. It was found that the compulsory prerequisite for obtaining the reliable estimates of kinetic data is using of the experimental data from the full range of conversion degree in nonlinear regression treatment. The following kinetic parameters were obtained by this method: $A = 6.10 \times 10^{20}$ min^{-1}, $E = 4.68 \times 10^5$ J mol^{-1}, $n = 0.634$, $m = 1.037$ for A30Yb70 glass, and $A = 6.98 \times 10^{25}$ min^{-1}, $E = 5.97 \times 10^5$ J mol^{-1}, $n = 0.562$, $m = 0.975$ for A45Yb55 glass.

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