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THERMO-OPTICAL STUDY OF $NaPO_3$ CRYSTALLIZATION

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The optical transmittance records taken on the small polished plates of $NaPO_3$ glass at different linear heating rates, previously kinetically analyzed to derive the activation energy of the glass crystallization applying the Kissinger equation, are presently analyzed according to the modified Johnson–Mehl–Avrami kinetic model. A decrease in the relative transmitted light intensity is taken, as previously, as an inverse measure of the volume fraction of crystallized $NaPO_3$. The activation energy of 131±11 kJ mol^{-1}, derived under these circumstances, is in good agreement with the results published in literature (138 kJ mol^{-1}), derived from the isothermal heating-quenching and XRD measurements.

Keywords: *activation energy, $NaPO_3$, crystallization, optical transmittance, thermo-optical*

Introduction

The present method of thermo-optical investigation [1] has features of thermal analysis at which the transmitted light intensity is evaluated as a physical parameter of the sample. In general, the method yields records of cumulative nature, where the corresponding thermal processes are manifested by smooth sigmoidals, similarly as in TG or dilatometric measurements.

The method has been found useful for many practical applications at which thermal changes of plate-like, or thick films samples occur inside of their transparency – opaqueness limits. The measurements therefore cover a variety of investigations, mostly of a kind at which the originally transparent glass or sol–gel thick film matrix is loosing transparency because of the crystallization, recrystallization, melting and the phase change phenomena. The samples at the end of heating, at different thermal modes, either retain their transparency, regain it after an intermediate loss [11], show different degrees of translucency, or are fully opaque. Up to now, only the qualitative side of the measured optical transmittance dependences was concerned [1].

In the previous work [2], however, the first preliminary attempt has been made to kinetically analyze the recorded curves, specifically the ones obtained during the crystallization of $NaPO_3$ glass. The records have been taken at different linear heating rates. The activation energy of $NaPO_3$ crystallization was derived on the most simple assumption that the relative transmitted light intensity corresponding to the recorded descending sigmoidals was inversely proportional to the volume fraction of crystalline $NaPO_3$, e.g. of the degree of conversion of the precipitating phase. This assumption was substantiated by previous results [3–5] at which crystallization of polymers was investigated in situ, using the depolarized transmitted light. It was also substantiated by the usual ex situ experiments followed by the optical transmittance examination experiments, during crystallization of the lithium disilicate glass [6].

The activation energy we derived using Kissinger equation (183 kJ mol^{-1}) [2], was in good agreement with the values of 175 and 186 kJ mol^{-1} obtained from DTA records, using Kissinger [7] or Ozawa models, respectively [8]. This value was, however, not consistent with the values of 138 and 135 kJ mol^{-1} obtained from isothermal crystallization of $NaPO_3$ samples, followed by their XRD phase analysis [9]. In our application of the Kissinger model, the temperatures corresponding to the maximum rates of crystallization have been determined as inflex points of the sigmoidals obtained by the non-linear regression of the measured optical transmittance data [2].

In this work we extended therefore the kinetic evaluation of the measured records of the non-isothermal data, attempting to fit them with Johnson–Mehl–Avrami (JMA) model. Our approach to the non-isothermal data evaluation according to the JMA model seems to be much more straightforward than e.g. the one published in [10].

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Table 1 Values of the *A, E, n,* $T_{0,\beta}$ parameters for individual heating rates

β/K min^{-1}	$10^{-5}A$/s^{-1}	$10^{-3}E$/J mol^{-1}	n	$T_{0,\beta}$/K	R^2
1.25	3.0±4.4	129.3±9.3	1.82±0.10	598.2±0.8	0.9993
2.50	1.4±2.6	131.6±10.8	2.04±0.15	603.1±1.6	0.9994
4.17	3.4±8.4	131.1±14.9	1.98±0.16	611.7±1.9	0.9991
10.0	17.8±98.8	131.7±36.4	1.92±0.36	630.0±4.1	0.9991
20.0	12.1±60.4	129.6±30.7	2.00±0.29	634.7±4.6	0.9997

Experimental

The $NaPO_3$ glass was prepared from reagent grade $NaH_2PO_4{\cdot}H_2O$, heated in a Pt-crucible at 800°C for 2 h. The glass melt was cooled by casting on a steel plate. The bulk glass was cut and polished to 5x5 mm plates of the 0.50±0.02 mm thickness. The glass plates were colorless, optically clear samples. The optical transmittance measurements were accomplished at heating rates of 1.25, 2.5, 4.17, 10 and 20 K min^{-1}, using an instrument described elsewhere [1, 11–13]. The 'white' light emitting diode (LED) was used as a light source. In the measurements, the sample is placed in a vertical electric tubular furnace. The light incites the sample plate perpendicularly. The transmitted light intensity is measured by a Si photo-diode. The Pt/Rh thermocouple (type S) was in-situ calibrated *vs.* melting point of $NaPO_3$ (627°C) [14] and *vs.* α/β quartz transition (573°C), using β-quartz single crystal plate. Transmitted light intensities were measured in 5 s intervals. The furnace temperature control and data processing is accomplished by Windows compatible software.

Results and discussion

A typical pattern of the optical transmittance record of $NaPO_3$ glass samples is shown in Fig. 1. The optical transmittance is measured in an arbitrary scale, set initially to approx. 1000 light intensity units by the receiving camera aperture, remaining then the same for all experiments. Attenuation of the transmitted light intensity is predominantly brought about by the light scattering (multiple light reflection) on the precipitating and growing $NaPO_3$ crystals. Small light attenuation, on comparable terms for all samples, is caused by the specular reflection on outer sample surfaces, by scattering on the surface and volume imperfections. The crystallized sample is believed to be free of pores.

The optical transmittance (*OT*) of samples in the course of heating (as seen from Fig. 1) remains on a high level (as an in-line transmittance) until the start of the crystallization, which is manifested by a sigmoidal *OT* decrease.

A nature of the slight transmittance increase in *OT* in the pre-crystallization period needs further study. Previously, it was ascribed to thermal healing of the surface defects [15], a process believed to occur slightly above the T_g temperature. Simulations to thermally planarize (heal) the rough glass surface have shown, however, that the thermal elimination of scratches would occur at temperatures appreciably higher than T_g temperature [16].

The light intensity data corresponding to the sigmoidal decrease of the optical transmittance were normalized to values within <0, 1> intervals and then converted to the ascending sigmoidals form of the

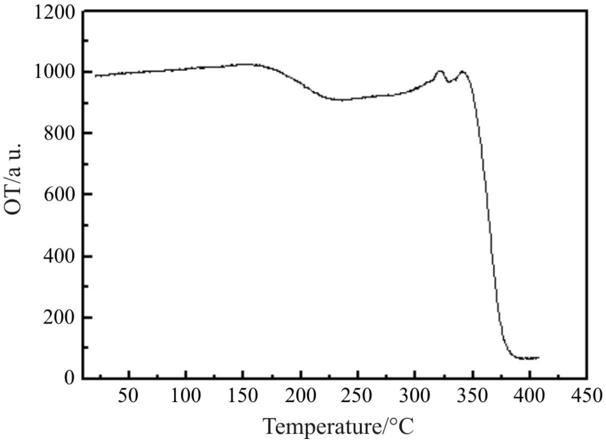

Fig. 1 Optical transmittance (*OT*) record of $NaPO_3$ glass plate sample at heating rate 4.17 K min^{-1}

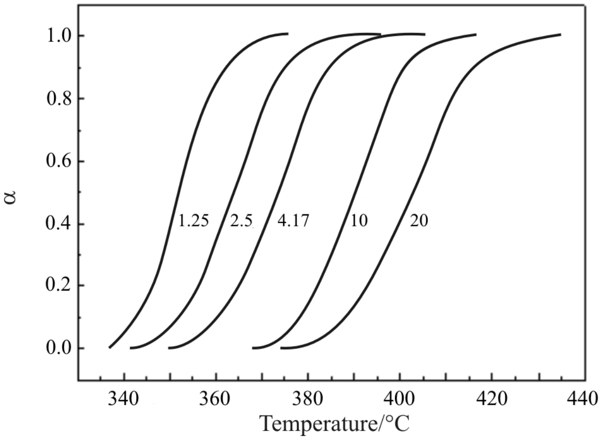

Fig. 2 Conversion α *vs.* temperature at specified heating rates (K min^{-1})

conversion degree α dependencies on temperature (Fig. 2) using the formula:

$$\alpha = \frac{OT_{\max} - OT_t}{OT_{\max} - OT_{\min}} \tag{1}$$

where $OT_{\max}$ and $OT_{\min}$ are measured intensities at maximum and minimum points of sigmoidals and OT_t is the intensity recorded at actual temperature.

Kinetic analysis of experimental data

The data within the range of conversion $\alpha \in <0.02, 0.98>$ were fitted for each heating rate β by the Johnson–Mehl–Avrami Eq. (2)

$$\alpha = 1 - \exp(-k\tau^n) \tag{2}$$

where τ is time of the crystallization, k is temperature dependent parameter (rate constant), n is parameter independent of temperature (shape factor). In this case, temperature dependence of the parameter k is supposed to obey the Arrhenius-like relationship

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{3}$$

where A, E/R are temperature independent parameters, and temperature T is linearly dependent on time of the reaction τ :

$$T = \beta\tau + T_{0,\beta} \tag{4}$$

where β is the heating rate and $T_{0,\beta}$ is the temperature at which the reaction starts (dependent on heating rate). Equation (3) then gets the form

$$\alpha = 1 - \exp\left\{-\left[A\exp\left(-\frac{E}{RT}\right)\right]\left(\frac{T - T_{0,\beta}}{\beta}\right)^n\right\} \tag{5}$$

For each set of experimental data $\alpha = f(T)$, four parameters ($A, E, n, T_{0,\beta}$) have been thus obtained, which are listed in Table 1. An example of the goodness of fitting is shown in Fig. 3.

As is seen from the results listed in Table 1, the parameter E, considered the apparent activation energy, is found to be 131 kJ mol^{-1} and the exponent n is approximately 2. The values of the parameter $T_{0,\beta}$ are dependent on the heating rate β, the function $T_{0,\beta} = f(\beta)$ is an ascending one.

The present thermo-optical study represents actually a kinetic evaluation of the obtained thermoanalytical curves, accompanying $NaPO_3$ crystallization. It does not concern mechanisms responsible for the transmitted intensity light attenuation, i.e. the light scattering phenomena. The previous result showed the surface nucleation of the $NaPO_3$ crystals [2]. Further experiments will be accomplished in order to analyze the influence of the sample plate thickness on optical transmittance curves and to relate the size and crystals morphology, as well as the thickness of the crystallized layer to light transmittance by means of freezing the crystallization at certain temperatures with subsequent inspection of samples, microstructure.

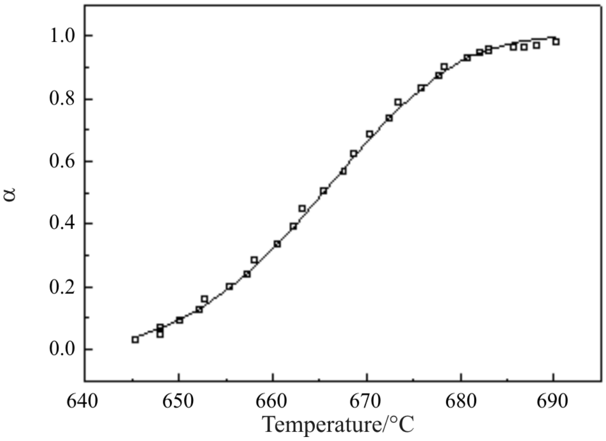

Fig. 3 Fitting of the ascending sigmoidal representing the primary data set by the kinetic Eq. (5), heating rate=20 K min^{-1}; □ – exp. data; — – Eq. (5) fit

Conclusions

The non-isothermal optical transmittance measurements performed and their kinetic analysis using modified JMA equation has yielded the apparent activation energy of $NaPO_3$ crystallization in good agreement with the value derived from isothermal measurements using Avrami equation. Two conclusions can be drawn from this fact. Firstly, the measured transmitted light intensities can be taken, as in the present simplistic approach, to be reciprocally proportional to the degree of conversion α. Secondly, the non-isothermal kinetic data can be evaluated in a proposed procedure on a basis of the JMA model, with a proper substitution for its temperature dependent parameters. The hint still remains that the activation energies are fairly well comparable as far as equal kinetic models are used for their determination.

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References

1 J. Majling, Solid State Phenomena, 90–91 (2003) 75.
2 S. C. Mojumdar, M. Drábik, V. Kovár and J. Majling, Proc. 30th NATAS Conf., pp. 239–244, Pittsburg, USA 2002.

3 A. J. Kovacs and S. Y. Hobbs, J. Appl. Polym. Sci., 16 (1972) 301.
4 J. H. Magill, Polymer, 2 (1961) 221.
5 E. M. Barrall, J. F. Johnson and R. S. Porter, Appl. Polym. Symp., 8 (1969) 191.
6 J. Voldán, Kinetics of the Glass Crystallization, IP 3/1972, Research Institute of Glass, Hradec Králové.
7. A. Abdel-Kader and I. Salesh, Thermochim. Acta, 181 (1991) 203.
8 A. Ghule, R. Murugan and H. Chang, Inorg. Chem., 40 (2001) 5917.
9 J. Rocherullé, F. Trochet and R. Marchand, Key Eng. Mater., 206–213 (2002) 2045.
10 A. L. Campos, N. T. Silva, F. C. L. Melo, M. A. S. Oliveira and G. P. Thim, J. Non-Cryst. Solids, 304 (2002) 19.
11 J. Majling, V. Kremničan, L. Pach and J. Chocholoušek, High Temperatures-High Pressures, 33 (2001) 43.
12 L. Pach, L'. Bača and J. Majling, Chem. Papers, 54 (2000) 265.
13 J. Majling, P. Šimon and V. Khunová, J. Therm. Anal. Cal., 67 (2002) 201.
14 J. Majling and J. Chocholoušek, Ceramics-Silikáty, 43 (1999) 78.
15 P. Lichvár, D. Galusek, M. Liška and J. Majling, Ceramics-Silikáty, 46 (2002) 74.
16 M. Chromčíková, M. Liška and M. Martišková, J. Therm. Anal. Cal., 76 (2004) 107.

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