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# Thermal stability of $Li_2O$–$SiO_2$–$TiO_2$ gels evaluated by the induction period of crystallization

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**Abstract** To evaluate the thermal stability of materials, various criteria have been used. Not only the simple parameters, as characteristic temperatures, but also the combined criteria $E/RT_p$, $k_f(T)$ and criterion based on the length of induction period of crystallization have been taken into account. Four gels with the composition $Li_2O$–$2SiO_2$–$nTiO_2$ ($n = 0.00$, 0.03, 0.062, and 0.1) were prepared and the validity of the criteria was tested by applying them to these gels. The results indicate that thermal stability of the studied gels decrease with amount of $TiO_2$.

**Keywords** DTA · Crystallization · Thermal stability · Induction period and gels

## Introduction

Many authors studied the evaluation of thermal stability of materials (especially glasses) employing the characteristic temperatures of DTA or DSC curves [1–5], crystallization activation energy [6–9] or crystallization rate constants [10, 11]. Unfortunately, these stability criteria are not fixed physical parameters, since they mostly depend on the heating rate and temperature [12]. A review of thermal stability criteria can be found in Ref. [13].

Processes occurring in the condensed phase often exhibit an induction period. During the induction period, the technique used registers no signal so that the sample seemingly remains unchanged. As a matter of fact, the induction period is a preparatory stage where the species and intermediates necessary for the occurrence of the main stage of the process are formed. Formation of these intermediates could be detected by another technique [14]. The end of induction period is determined as a sudden increase in the rate of the process under study, i.e., it is determined as the onset time for isothermal measurements or the onset temperature for measurement with linear heating. At the end of induction period, also a sudden change in material characteristics mostly takes place so that the length of induction period is often considered a relative measure of material stability [14]. If it is assumed that the crystallization obeys the Arrhenius kinetics, for a given constant temperature the length of induction period can be expressed by an Arrhenius-like relationship [14–18]:

$$t_i = A\exp\left[{}^{B}\!/_{T}\right] \tag{1}$$

where $t_i$ is the length of induction period, $A$ and $B$ are constants, and $T$ is the absolute temperature. In the case the measurements are carried out at linear increase of temperature, the parameters $A$ and $B$ occurring in Eq. 1 can be obtained from Eq. 2:

$$\beta = \int_0^{T_x} \frac{\mathrm{d}T}{A\exp\left[{}^{B}\!/_{T}\right]} \tag{2}$$

where $T_x$ is the onset temperature of the crystallization peak.

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## Experimental

### Preparation of gels

For silica acid sols′ preparation the solution of sodium silicate prepared for 2 h in boiling flask by 120 °C by the reaction of $SiO_2$ with the solution of NaOH; ratio of $Na_2O:SiO_2$ was 1:2. For the preparation of silica acid sol, this solution was about 9 wt% of $SiO_2$.

Pure silica acid sol was prepared by ion exchange by an acid ionexchanger Amberlite use. After the transition of solution through the ionexchanger layer substitution of sodium ions by hydrogen ions was reached. To silica acid sol was added LiCl and $TiOSO_4$. $TiOSO_4$ was prepared by the reaction of $TiO_2$ and $H_2SO_4$.

Prepared samples were dried in the drier by the temperature of 120 °C for the duration of 4 h. Gels prepared this way were dried and burned, respectively, from laboratory temperature to 200 °C (heating rate 1 °C/min) and from 200 to 900 °C (heating rate 5 °C/min), for 2 h. Thereafter, samples were burned in a platinum crucible at 1400 °C for 2 h.

### Measurements

The thermal stabilities were studied by a computerized Derivatograph OD 102 (MOM, Hungary). The measurements of DTA curves were carried out in air. Sample masses of about 20–22 mg and rates of temperature increase of 5, 10, 15, 20 and 25 °C/min were used. Calibration of the temperature change of the enthalpy axes was made with pure $SiO_2$ ($T_{\alpha \to \beta} = 821.15$ K, $\Delta H = 20.19$ J/mol).

## Results and discussion

Typical DTA curves of $Li_2O$–$2SiO_2$–$nTiO_2$ gels at the heating rate 10 °C/min are shown in Fig. 1. As shown in Fig. 1, when the crystallization proceeds, an exothermic peak is observed since the crystallization is accompanied by a rapid heat evolution. The composition of gels and the characteristic temperatures, i.e., the onset temperatures, inflection point temperature and the maximum peak temperatures are summarized in Table 1. All these temperatures decrease with increasing the content of $TiO_2$. The characteristic temperatures increase with increasing the heating rate. Besides the single parameters ($T_x$, $T_f$, and $T_p$) combined criteria also exist. Branda et al. [9] suggested that the ratio of $E/RT$ could be used to evaluate the thermal stability of materials (especially glasses). Higher value of $E/RT$ imply greater devitrification tendency. Cheng [12] proposed $k_f$ criterion as follows:

$$k_f(T) = A\exp\left[(-E/RT)\left(T_p - T_f\right)/T_f\right] \tag{3}$$

According to Cheng, not only the kinetic parameters of crystallization of gels, but also thermodynamic factor $T_p - T_f/T_f$ have been taken account in the $k_f(T)$ criterion. A higher value of $k_f(T)$ means a poorer stability. These combined criteria are summarized in Table 2.

The length of induction period is calculated by Eq. 1. The range of temperatures for the calculation of the lengths of induction period of crystallization was chosen from interval where the onset temperatures of crystallization have been observed. Hence, it can be expected that the values of calculated induction periods are quite realistic since no extrapolation outside the temperature region of the measurement has been carried out. The temperature dependence of the lengths of isothermal induction period for individual gels is shown in Fig. 2. The agreement between experimental and calculated values of onset temperatures for various heating rates is shown in Fig. 3. The resulting values of $A$ and $B$ are listed in Table 3. It can be seen from Table 3 that the adjustable parameter $B$ is approximately constant for the gel samples under study. The difference in the stabilities can be accounted for by the difference in the values of the parameter $A$. Since the onset temperature is determined as a point of the steep increase of the DTA record due to crystallization, the induction period of crystallization corresponds to the moment where the crystallization nuclei have already been formed and the intense growth of crystals starts.

It can be seen that the stability of the gels against crystallization is in the temperature region 750–850 K is in the order a < d < c < b, i.e., the thermal stability of gels against crystallization with $TiO_2$ decreases. Equation 2 enables to calculate the length of induction period for any temperature regime and, thus, to evaluate the order of thermal stabilities for that regime. The order of stabilities

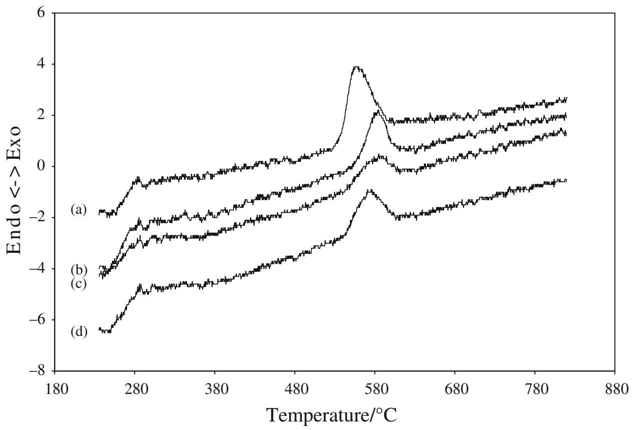

**Fig. 1** DTA records of $Li_2O$–$2SiO_2$ (*a*) $Li_2O$–$2SiO_2$–$0.03TiO_2$, (*b*) $Li_2O$–$2SiO_2$–$0.062TiO_2$, (*c*) $Li_2O$–$2SiO_2$–$0.1TiO_2$, and (*d*) gels samples at the heating rate of 10 °C/min

**Table 1** Onset $T_x$, temperature of inflexion point $T_f$, and peak temperature $T_p$ for the gels under study

| | Gel | $\beta$/K/min | | | | |
|---|---|---|---|---|---|---|
| | | 5 | 10 | 15 | 20 | 25 |
| $T_x$/K | a | 804.2 | 808.4 | 817.9 | 821.5 | 824.3 |
| | b | 826.6 | 827.4 | 836.4 | 841.7 | 852.3 |
| | c | 818.6 | 823.8 | 824.5 | 826.7 | 834.6 |
| | d | 813.5 | 821.1 | 822.6 | 826.5 | 838.8 |
| $T_f$/K | a | 814.0 | 819.4 | 827.9 | 833.7 | 842.4 |
| | b | 840.5 | 849.3 | 856.3 | 861.2 | 871.6 |
| | c | 840.1 | 843.3 | 847.6 | 851.6 | 855.3 |
| | d | 833.6 | 837.2 | 843.2 | 845.2 | 851.6 |
| $T_p$/K | a | 821.4 | 833.0 | 842.2 | 857.4 | 863.2 |
| | b | 847.9 | 856.0 | 867.8 | 870.5 | 882.0 |
| | c | 851.1 | 856.0 | 862.4 | 873.3 | 878.6 |
| | d | 844.4 | 848.2 | 859.4 | 864.8 | 871.4 |

**Table 2** Kinetic parameters of the gels under study: (a) $Li_2O$–$2SiO_2$, (b) $Li_2O$–$2SiO_2$–$0.03TiO_2$, (c) $Li_2O$–$2SiO_2$–$0.062TiO_2$, and (d) $Li_2O$–$2SiO_2$–$0.1TiO_2$

| Gel | $E(T_p)/RT_p$ | | | | | $k_f(T_f)$/s$^{-1}$ | $k_f(T_p)$/s$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | $\beta$/°C/min | | | | | | |
| | 5 | 10 | 15 | 20 | 25 | | |
| a | 22.2 | 22.3 | 22.5 | 22.7 | 22.9 | 6.3E+18 | 1.0E+14 |
| b | 27.9 | 28.2 | 28.4 | 28.6 | 28.9 | 4.5E+18 | 3.8E+16 |
| c | 31.4 | 31.5 | 31.7 | 31.8 | 32.0 | 1.7E−26 | 1.0E+19 |
| d | 31.7 | 31.9 | 32.1 | 32.2 | 32.4 | 2.4E+31 | 2.9E+19 |

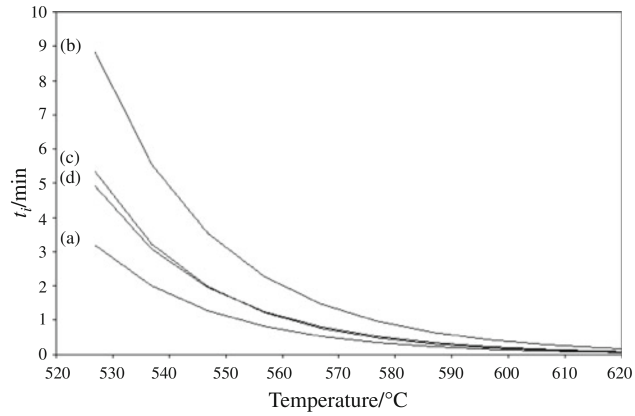

**Fig. 2** Induction period of crystallization for individual gels samples calculated by Eq. 1

evaluated by the new criterion is in agreement with the order based on the characteristic temperatures (Table 1) and combined criteria (Table 2).

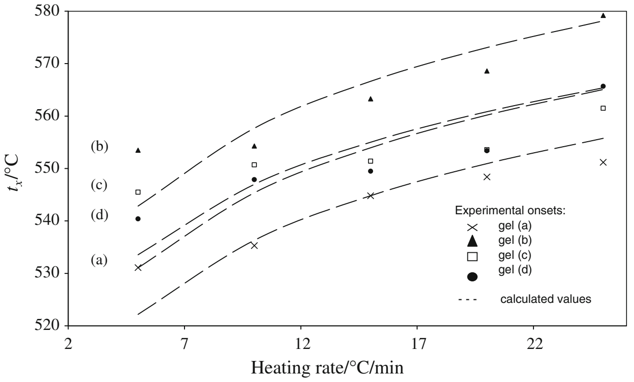

**Fig. 3** Experimental and calculated values of onset temperatures of gel crystallization for various heating rates

**Table 3** Parameters *A* and *B* describing the length of induction period using Eq. 2 for the gels

| Sample | A × $10^{16}$/min | B × $10^{-3}$/K |
|---|---|---|
| (a) $Li_2O$–$2SiO_2$ | 1.65 | 30.00 |
| (b) $Li_2O$–$2SiO_2$–$0.03TiO_2$ | 4.41 | 30.03 |
| (c) $Li_2O$–$2SiO_2$–$0.062TiO_2$ | 0.11 | 32.56 |
| (d) $Li_2O$–$2SiO_2$–$0.1TiO_2$ | 1.77 | 30.29 |

## Conclusions

The length of isothermal induction period of crystallization is suggested as a new criterion to evaluate the thermal stability of gels. The lengths of induction periods are calculated using Eq. 2, where the parameters *A* and *B* are obtained from the treatment of the dependence of onset temperature of the crystallization peak on the heating rate in the nonisothermal DTA measurements. For a set of gels the order of stabilities obtained by the new method coincides with the order determined by stability criteria based on the characteristic temperatures and combined criteria.

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