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# THERMAL PROPERTIES AND STABILITY OF LITHIUM TITANO-PHOSPHATE GLASSES

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DTA was used to study thermal properties and thermal stability of $(50–x)Li_2O–xTiO_2–50P_2O_5$ ($x$=0–10 mol%) and $45Li_2O–yTiO_2–(55–y)P_2O_5$ ($y$=5–20 mol%) glasses. The addition of $TiO_2$ to lithium phosphate glasses results in a non-linear increase of glass transition temperature. All prepared glasses crystallize under heating within the temperature range of 400–540°C. The lowest tendency towards crystallization have the glasses with $x$=7.5 and $y$=10 mol% $TiO_2$. X-ray diffraction analysis showed that major compounds formed by annealing of the glasses were $LiPO_3$, $Li_4P_2O_7$, $TiP_2O_7$ and NASICON-type $LiTi_2(PO_4)_3$. DTA results also indicated that the maximum of nucleation rate for $45Li_2O–5TiO_2–50P_2O_5$ glass is close to the glass transition temperature.

***Keywords:*** *phosphate glasses, thermal properties, thermal stability, titanium oxide*

## Introduction

The additions of $TiO_2$ into oxide glass-forming systems, usually contribute to the stabilization of their structure [1–3] and to the improvement of their properties [4, 5], e.g. chemical durability, mechanical properties, electrical conductivity, etc. From the glasses with a higher $TiO_2$ content glass-ceramic materials can be prepared by controlled crystallization. In some cases these glassy-crystalline materials show better properties than their parent glasses [6]. For the preparation of glass-ceramic materials the knowledge of thermal behaviour of parent glasses and the mechanism of crystallization is very useful. Beside basic thermal parameters as glass transition temperature, dilatation softening temperature, thermal expansion coefficient, crystallization temperature etc. it is also useful to know nucleation rate under controlled heat treatment.

The aim of this work is the investigation of thermal properties and crystallization processes in $TiO_2$-doped lithium phosphate glasses. Glasses and glass-ceramics based on lithium titanium phosphate can find interesting applications, e.g. as solid electrolytes in high energy density batteries due to their high $Li^+$ ionic mobility and their high stability. Ceramics conductors with the NASICON (Na Super Ionic CONductor) type structure [7] belong even to most promising oxide based $Li^+$ conductor group studied in recent years [8, 9].

## Experimental

Lithium titanophosphate glasses with composition $(50–x)Li_2O–xTiO_2–50P_2O_5$ (series A) and $45Li_2O–yTiO_2–(55–y)P_2O_5$ (B) were prepared in the batches of 20 g using analytical-grade $Li_2CO_3$, $TiO_2$ (anatase) and $H_3PO_4$. Starting mixture was heated slowly up to 1320°C in a platinum crucible with a lid and after 15 min at the maximum temperature the obtained melt was cooled slowly in a graphite mould or quenched between two copper blocks (glasses with $x$=7.5; 10 mol% $TiO_2$ for series A and with $y$=15; 20 mol% $TiO_2$ for series B). The obtained glasses were annealed for 15 min at the temperature 5°C below their glass transition temperature, $T_g$. The presence of glassy state was checked by X-ray diffraction.

Thermal behaviour of glasses was studied with the DTA 404 PC (Netzsch) operating in the DSC mode at the heating rate of 10°C $min^{-1}$. Measurements were carried out with 50 mg powder samples with a mean diameter 8–10 μm in corundum crucibles under inert atmosphere of $N_2$. From DSC curves the values of the glass transition temperature, $T_g$, (as the midpoint of the change in heat capacity, $c_p$, in the glass transition region), the values of crystallization temperature, $T_c$, (the onset of the first crystallization peak) and the values of melting temperature, $T_m$, (onset of the first melting peak) were determined.

For the evaluation of the mechanism of crystallization glasses were milled and screened to four fractions with the average particle sizes of 130, 300, 600 and 900 μm. From DSC curves of these

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fractions obtained at the heating rate of 10°C $\min^{-1}$ the peak crystallization temperature $T_p$, its maximum height, $(\delta T)_p$, and the width at the half-peak maximum, $(\Delta T)_p$, were determined.

For the evaluation of the nucleation rate 50 mg of the glass with the average particle size of 300 μm was first heated in DTA equipment from room temperature to a nucleation temperature, $T_N$, between transition temperature, $T_g$, and crystallization temperature, $T_c$ (onset of the first crystallization peak) and then nucleated at $T_N$ for 30 min. After subsequent cooling to 100°C the sample was heated again to the temperature above crystallization peaks at a rate of 10°C $\min^{-1}$. This process was applied for several nucleation temperatures $T_N$. At the temperature corresponding to a maximum nucleation, determined in the previous step from the plot of crystallization peak height, $(\delta T)_p$ *vs.* $T_N$, the glass was then heat-treated for 1–300 min.

Crystalline samples were prepared using isothermal heating of powdered glasses in temperature range of 460–580°C (series A) and 550°C (series B) in a graphite mould for 2 h under inert atmosphere of $N_2$. Crystalline phases were identified by X-ray powder diffraction analysis with Bruker D8 Advance diffractometer.

## Results and discussion

Two compositional series of lithium titanophosphate glasses (A) $(50-x)Li_2O-xTiO_2-50P_2O_5$ with $x$=0; 2.5, 5, 7.5 and 10 mol% $TiO_2$) and (B) $45Li_2O-yTiO_2-(55-y)P_2O_5$ ($y$=5, 10, 15 and 20 mol% $TiO_2$) were synthesized and studied. The obtained compositional range corresponds to glass forming regions in $Li_2O-TiO_2-P_2O_5$ system described by Kishioka *et al.* [10]. Colour of the glasses slowly changed from clear ($x$=0) to brownish ($x$=2.5; 5 and $y$=5; 10 mol% $TiO_2$) and violet for $x$>5 and $y$>10 mol% with increasing $TiO_2$ content in the both series of glasses.

DSC curves obtained for the glass series (A) and (B) are shown in Figs 1 and 2. The values of glass transition temperature, $T_g$, crystallization temperature, $T_c$, melting temperature, $T_m$, and the values of the change in heat capacity, $\Delta C_p$, in the glass transition region determined form DSC curves are given in Table 1. As can be seen in this table, $T_g$ values in the glass series (A) increase with increasing $TiO_2$ content from 335°C for the $50Li_2O-50P_2O_5$ glass up to 383°C for the glass composition $40Li_2O-10TiO_2-50P_2O_5$. Similar increasing was observed in the glasses of the compositional series $45Li_2O-yTiO_2-(55-y)P_2O_5$ (B), where $T_g$ increases from 357°C ($y$=5) up to 460°C for the glass with $y$=20 mol% $TiO_2$. An increase of $T_g$ values can be ascribed to an increasing number of Ti–O–P bonds formed with increasing $TiO_2$ content and therefore to the strengthening of glass network by $TiO_x$ structural units [1]. The value of $\Delta C_p$ (Table 1) in compositional series (A) first decreases steeply from 15 J $\mathrm{mol^{-1}\ K^{-1}}$ (for $50Li_2O-50P_2O_5$ glass) to 7.7 J $\mathrm{mol^{-1}\ K^{-1}}$ for $47.5Li_2O-2.5TiO_2-50P_2O_5$ glass, but with additional replacement of $Li_2O$ by $TiO_2$ the $\Delta C_p$ values are practically constant. On the other hand, an increase in the $TiO_2$ content for $45Li_2O-yTiO_2-(55-y)P_2O_5$ glasses leads to a gradual increase of $\Delta C_p$ values within the range of 7.1–14.5 J mol $K^{-1}$. The observed $\Delta C_p$ changes could indicate that the fragility of the $(50-x)Li_2O-xTiO_2-50P_2O_5$ (A) glasses decreases with replacement of $Li_2O$ by $TiO_2$ while the

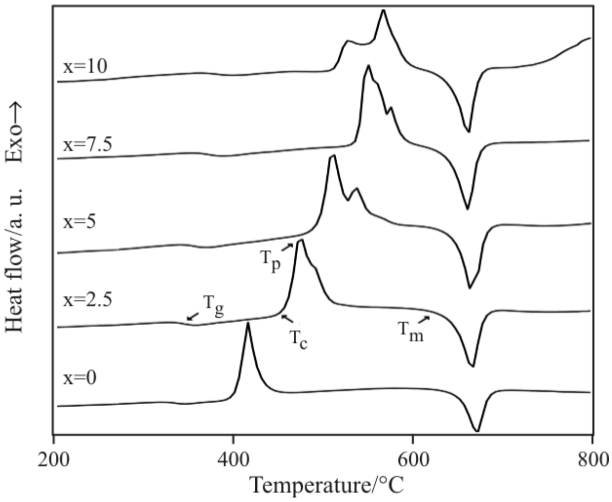

**Fig. 1** DSC curves of the glass series $(50-x)Li_2O-xTiO_2-50P_2O_5$

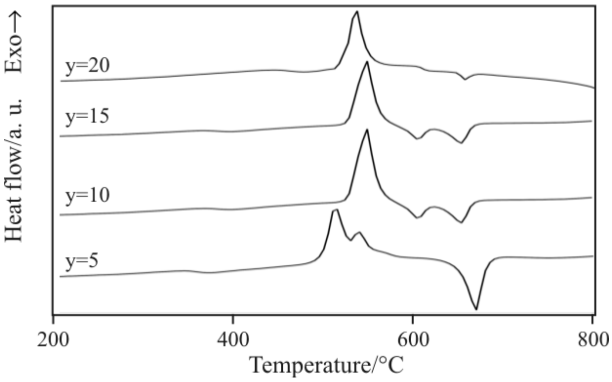

**Fig. 2** DSC curves of the glass series $45Li_2O-yTiO_2-(55-y)P_2O_5$

**Table 1** Glass transition temperature, $T_g$, the change in heat capacity at the glass transition region, $\Delta C_p$, crystallization temperature, $T_c$, melting temperature, $T_m$, and criterions of glass stability, $\Delta T$ and $K_{gl}$, of $Li_2O$–$TiO_2$–$P_2O_5$ glasses

| $LiO_2$/ mol% | $TiO_2$/ mol% | $P_2O_5$/ mol% | $T_g$±2/ °C | $\Delta C_p$±0.5/ J mol$^{-1}$ K$^{-1}$ | $T_c$±2/ °C | $T_m$±2/ °C | $T_g/T_m$ | $\Delta T$/°C | $K_{gl}$ |
|---|---|---|---|---|---|---|---|---|---|
| 50 | 0 | 50 | 335 | 15.0 | 403 | 649 | 0.52 | 68 | 0.28 |
| 47.5 | 2.5 | 50 | 347 | 7.7 | 461 | 645 | 0.54 | 114 | 0.62 |
| 45 | 5 | 50 | 357 | 7.1 | 497 | 649 | 0.55 | 140 | 0.92 |
| 42.5 | 7.5 | 50 | 372 | 7.3 | 539 | 643 | 0.58 | 167 | 1.61 |
| 40 | 10 | 50 | 383 | 7.2 | 513 | 645 | 0.59 | 130 | 0.99 |
| 45 | 5 | 50 | 357 | 7.1 | 497 | 649 | 0.55 | 140 | 0.92 |
| 45 | 10 | 45 | 380 | 8.5 | 524 | 592 | 0.64 | 144 | 2.12 |
| 45 | 15 | 40 | 418 | 11.7 | 521 | 599 | 0.70 | 103 | 1.32 |
| 45 | 20 | 35 | 460 | 14.5 | 524 | 603 | 0.76 | 64 | 0.81 |

replacement of $P_2O_5$ by $TiO_2$ in the compositional series (B) leads to an increase of the fragility of the glasses [11]. The heat capacity changes were found independent of the heating rate.

DSC curves (Figs 1 and 2) show also that all glasses crystallize on heating in the temperature range of 403–539°C, some of them in 2 crystallization steps. The first crystallization temperature, $T_c$, in the glasses of the $45Li_2O$–$y$$TiO_2$–$(55–y)P_2O_5$ (B) series increases with increasing $TiO_2$ content up to $x$=10 mol% $TiO_2$ and then remains nearly unchanged (Table 1), whereas in the metaphosphate glass series $(50–x)Li_2O$–$x$$TiO_2$–$50P_2O_5$ (A) $T_c$ reveals a maximum in the glass with $x$=7.5 mol% $TiO_2$. XRD patterns of the crystallized samples are shown in Figs 3 and 4. In the parent glass of the series (A) with composition $50Li_2$–$50P_2O_5$ we found that the crystallization peak corresponds to the formation of lithium metaphosphate $LiPO_3$. With increasing addition of $TiO_2$, this compound is gradually replaced by titanium pyrophosphate $TiP_2O_7$. X-ray diffraction patterns of the series $45Li_2O$–$y$$TiO_2$–$(55–y)P_2O_5$ (B) (Fig. 4) show that by heating the starting glass composition $45Li_2O$–$5TiO_2$–$50P_2O_5$ crystalline $LiPO_3$ and $TiP_2O_7$ phases are formed. With increasing $TiO_2$ content, these compounds are gradually replaced by lithium pyrophosphate $Li_4P_2O_7$ and by NASICON-type lithium titanophosphate compound $LiTi_2(PO_4)_3$ (Fig. 4).

For the evaluation of the thermal stability of glasses, $\Delta T=T_c–T_g$ and Hruby criterion $K_{gl}=(T_c–T_g)/(T_m–T_c)$ [12] were applied. Higher values of these criterions usually correspond to a higher thermal stability and glass-forming tendency. The obtained values of the $\Delta T$ and $K_{gl}$ for the studied glasses in compositional series (A) and (B) are given in Table 1. We can see that the values of both criterions for the glasses in metaphosphate compositional series $(50–x)Li_2O$–$x$$TiO_2$–$50P_2O_5$ (A) reveal a maximum at the glass containing 7.5 mol% $TiO_2$. It means that this glass has the highest thermal stability and the lowest tendency towards crystallization. On the other hand the lowest thermal stability and therefore the highest tendency towards crystallization in compositional series (A) were found for the parent $50Li_2O$–$50P_2O_5$ metaphosphate glass. In the series $45Li_2O$–$y$$TiO_2$–$(55–y)P_2O_5$ (B) the highest thermal stability was found for the glass containing 10 mol% $TiO_2$ (Table 1).

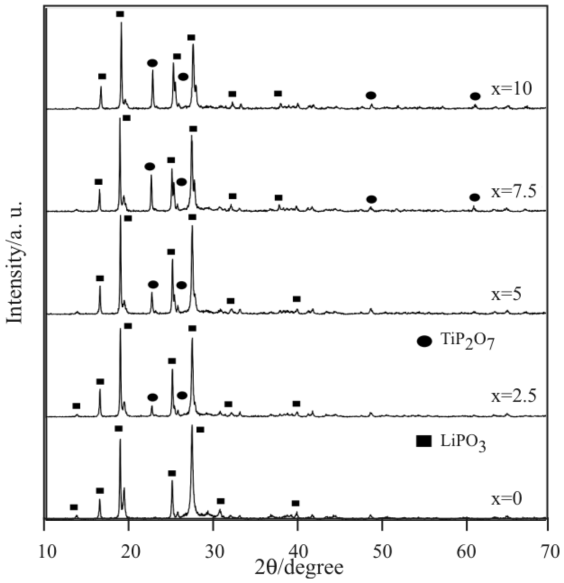

**Fig. 3** X-ray diffraction patterns of the crystallized samples of the series $(50–x)Li_2O$–$x$$TiO_2$–$50P_2O_5$

In order to control the shape and dimension of resulting crystalline phases and subsequently their properties, it is important to know the crystallization mechanism. The mechanism of crystallization (surface or volume) was evaluated from the changes in the shape and position of the crystallization peak on DSC curves in dependence on the particle size

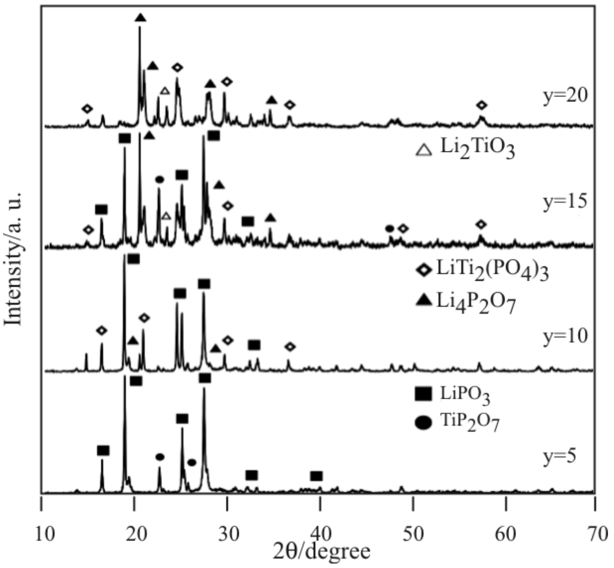

**Fig. 4** X-ray diffraction patterns of the crystallized samples of the series $45Li_2O–yTiO_2–(55–y)P_2O_5$

(130, 300, 600 and 900 μm) of the studied glasses [13]. From the crystallization peaks on DSC curves the values of the peak temperature, $T_p$, its maximum height, $(\delta T)_p$, and the width at the half-peak maximum, $(\Delta T)_p$, were determined. The ratio of the volume to the total effective surface area of all glass particles increases with an increasing particle size for a given amount of sample. Thus the parameters $(\delta T)_p$ and $T_p^2/(\Delta T)_p$ should increase with an increasing particle size when the internal crystallization predominates, while for the dominant surface crystallization the reverse effect should be observed [13]. This analysis was carried out only for the samples with the composition of $50Li_2O–50P_2O_5$, $45Li_2O–5TiO_2–50P_2O_5$ and $45Li_2O–15TiO_2–40P_2O_5$. The estimated parameter of $[(\delta T)_p]^R$ reduced to the sample with the lowest particle size of 130 μm (the values of $(\delta T)_p$ were divided by the values obtained with the smallest particle size), are plotted as a function of particle size in Fig. 5. As can be seen from this figure, the values of $[(\delta T)_p]^R$ parameter continuously decrease with increasing particle size only for the sample containing 15 mol% of $TiO_2$, i.e. in this sample the surface nucleation is the prevailing process. For both other samples the values of $[(\delta T)_p]^R$ parameter initially decrease with increasing particle size and then increase (Fig. 5). These results suggest that the glasses nucleate predominantly by surface crystallization mechanism when the particle size is <600 μm (for $x=$ 5 mol% $TiO_2$) or <300 μm (for $x=0$ mol% $TiO_2$), respectively, but for the higher particle sizes internal crystallization becomes the dominant crystallization mechanism. Similar conclusions can be done also from the changes of $[T_p^2/(\Delta T)_p]^R$ reduced parameter as a function of particle size. From the changes in both $[(\delta T)_p]^R$ and $[T_p^2/(\Delta T)_p]^R$ parameters with particle size of analyzed glasses is also evident that with increasing $TiO_2$ content the contribution of the surface crystallization mechanism increases. This conclusion is in a good agreement with observed changes in $T_g/T_m$ values as a function of $TiO_2$ content (Table 1). According to [14] when $T_g/T_m>0.6$, only surface crystallization is observed in laboratory time scales, while internal crystallization is easily observed in glasses where $T_g/T_m<0.6$.

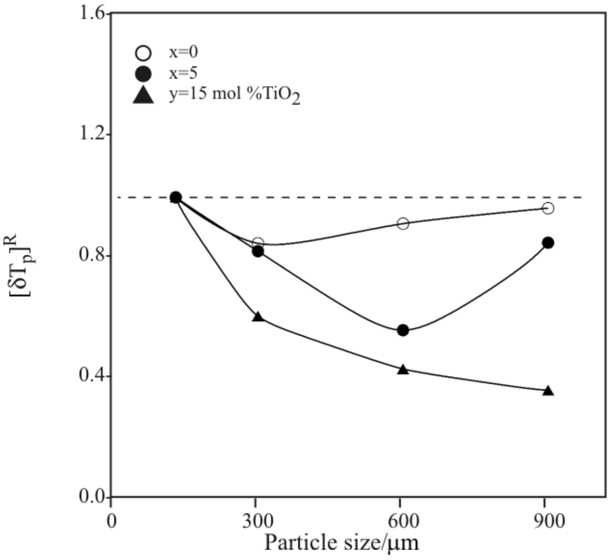

**Fig. 5** Reduced values of peak height, $[(\delta T)_p]^R$ as a function of particle size for the $(50–x)Li_2O–xTiO_2–50P_2O_5$ ($x=0$; 5 mol% $TiO_2$) and $45Li_2O–yTiO_2–(55–y)P_2O_5$ ($y=15$ mol% $TiO_2$) glasses. The lines are only a guide to eye

Besides the knowledge of crystallization mechanism in some cases it is also useful to know the nucleation rate. We studied the nucleation rate by the method described in paper [15] for the glass with composition of $45Li_2O–5TiO_2–50P_2O_5$. The method consists in heating the glass at different constant temperatures for a fixed time in DSC equipment before being crystallized at a fixed heating rate. A plot of the maximum DSC peak height, $\delta T_p$, as a function of the nucleation temperature, produced a nucleation-rate-like curve that, determined the temperature range for nucleation and the temperature of the maximum nucleation rate [15]. DSC curves that were obtained after heat treatments of the glass sample at various nucleation temperatures, $T_N$, (from 360 to 510°C) for 30 min are shown in Fig. 6. X-ray diffraction analysis revealed that first crystallization

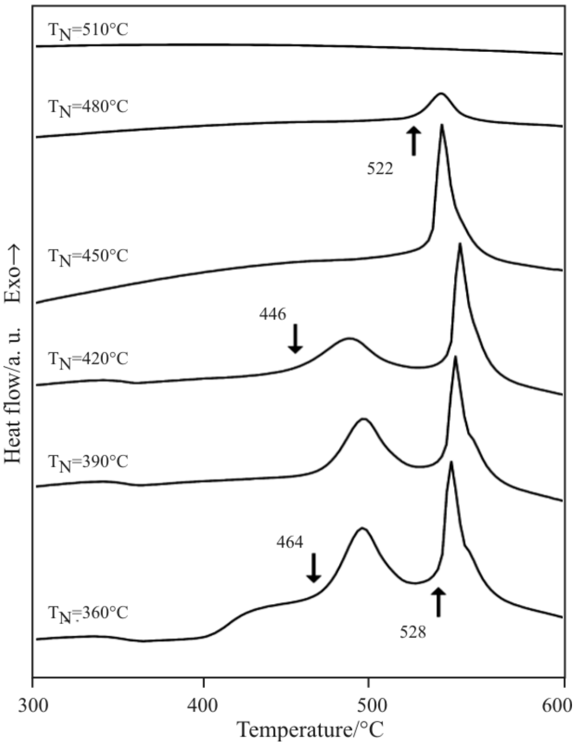

**Fig. 6** DSC curves for the $45Li_2O–5TiO_2–50P_2O_5$ glass nucleated at various nucleation temperatures, $T_N$, for 30 min

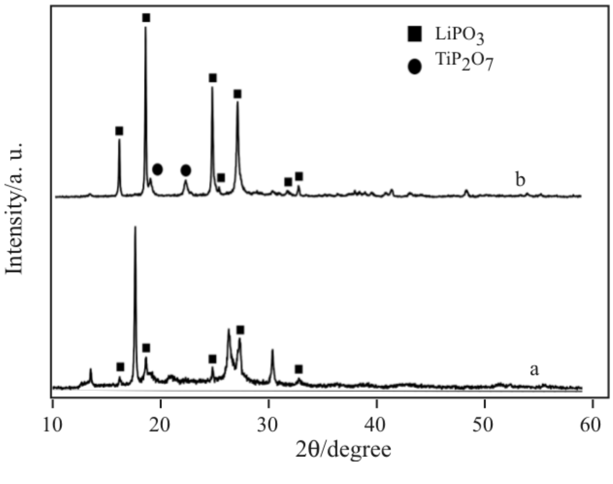

**Fig. 7** X-ray diffraction patterns of the $45Li_2O–5TiO_2–50P_2O_5$ glass nucleated at $T_N$=360°C for 5 min and then heated up to a – 540 and b – 580°C in the DSC equipment

peak is associated particularly with the formation of an unknown, probably lithium titanophosphate crystalline phase, which is at higher temperature transformed to $LiPO_3$ and $TiP_2O_7$ compounds (Fig. 7). As we can see in Fig. 8, with increasing nucleation temperature, $T_N$, both first and then second crystallization peaks gradually disappear. Figure 8 shows that the peak height of the first crystallization peak, $\delta T_{p1}$, gradually decreases with increasing nucleation temperature within the temperature region of $T_N$ from 360 to 420°C and for the nucleation temperature above 420°C the first crystallization peak practically disappears. This suggests that the highest amount of nuclei of unknown crystalline phase is formed at the temperature slightly above its $T_g$ (357°C). With increasing nucleation temperature the nucleation rate decreases and above 420°C is too small to produce any additional nuclei. For the second crystallization peak associated with the formation of $LiPO_3$ and $TiP_2O_7$, the nucleation rate (peak height $\delta T_{p2}$) has a maximum at 450°C (Fig. 8) and for the sample nucleated at 510°C, the second glass transition temperature practically disappear. Figure 9 shows the changes of the maximum of crystallization peak temperature, $T_p$, with nucleation time for the $45Li_2O–5TiO_2–50P_2O_5$ glass nucleated at 360°C (nearby above $T_g$). From this figure it is evident that

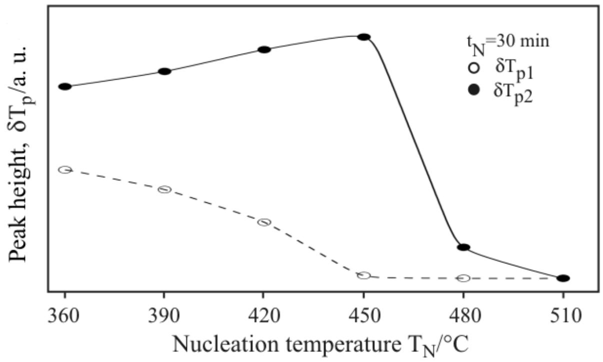

**Fig. 8** The height, $(\delta T)_p$, of the ○ – first and • – second DSC crystallization peaks for the $45Li_2O–5TiO_2–50P_2O_5$ glass as a function of nucleation temperature, $T_N$. The lines are only a guide to eye

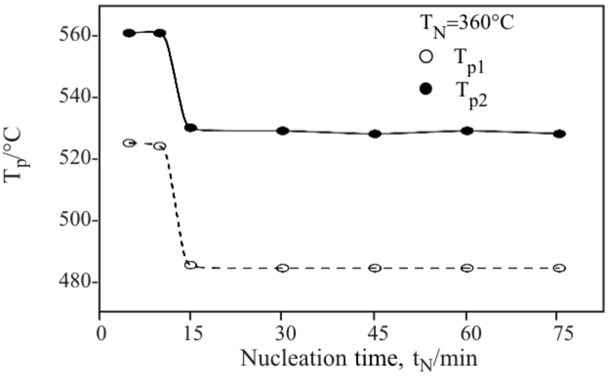

**Fig. 9** Crystallization peak temperature, $T_p$, of the ○ – first and • – second DSC peaks for the $45Li_2O–5TiO_2–50P_2O_5$ glass as a function of nucleation time, $t_N$. The lines are only a guide to eye

the peak temperature, $T_p$, of both crystallization peaks ($T_{p1}$ and $T_{p2}$) steeply decreases with increasing nucleation time from 10 to 15 min and then it is nearly constant. This indicates that the glass is saturated with nuclei of all crystalline phases within a relatively short time (up to 15 min) at 360°C.

## Conclusions

Study of lithium titanophosphate glasses revealed that both replacement of $Li_2O$ by $TiO_2$ or $P_2O_5$ by $TiO_2$ lead to changes in thermal properties of these glasses. The incorporation of $TiO_2$ into the structural network of the glasses is reflected by increasing values of the glass transition temperature, which shows on the strenghtening of chemical bonds in the structural network. The doping of lithium phosphate glasses by $TiO_2$ resulted also in the changes of their thermal stability, crystallization temperature and the crystallization mechanism. Study of nucleation rate shows that it is possible to control nucleation and crystallization process of the studied glasses using DSC technique.

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