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Kinetics of the LiPO$_3$ glass devitrification studied by differential thermal analysis

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Crystallization affects material stiffness and generally enhances mechanical characteristics. Also, the kinetics are critical in determining those glass compositions that can be converted into practical fine grained glass ceramics. Differential thermal analysis (DTA) is the usual and convenient means to perform studies of this first order phase transformation. Up to today, investigation in this area concerns essentially silicate or aluminosilicate glass compositions. Consequently, the aim of this work is to determine, from non-isothermal studies, the devitrification kinetic parameters of a phosphate model glass. We have chosen the lithium metaphosphate composition which exhibits a simple crystalline phase with a monoclinic symmetry (fiche JCPDS-ICDD 70-0274) and can be vitrified by a common melting and quenching method. Moreover this glass is less sensitive to moisture than the sodium metaphosphate one.

The Avrami's law applies well to isothermal devitrification studies of glasses [1]. This law may be written as:

$$x = 1 - \exp(-kt)^{\mathrm{n}} \tag{1}$$

where x is the volume fraction crystallized after time t, n is the Avrami's exponent and k is defined as the apparent reaction rate, which is usually assigned an Arrhenius temperature dependence:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{2}$$

where E is the activation energy describing the overall crystallization process. After rearrangement of Equation 1, one obtains:

$$\ln[-\ln(1-x)] = n \ln k + n \ln t \tag{3}$$

Relation (3) gives directly the values of n by plotting $\ln[-\ln(1-x)]$ versus $\ln t$. It should be noted that Equation 1 strictly applies to isothermal studies. However, it is commonly used to describe non-isothermal crystallization for which experimental studies are easier to conduct. Several different treatments have been summarized by Yinnon and Uhlmann [1]. All these methods are based on Equations 1 and 2 and assume a constant heating rate Q in all DTA or DSC experiments.

In this study, the method proposed by Ozawza [1] has been used to determine the order of the crystallization reaction. On this basis, plotting $\ln[-\ln(1-x)]$ versus $\ln Q$ at a fixed temperature, yields to the n value, the relation being written as:

$$\frac{d[\ln[-\ln(1-x)]]}{d[\ln Q]} = n \tag{4}$$

For the determination of the apparent activation energy for crystallization E, the variety of analytical treatments shows the complexity of the physical problem. So we have used common methods in analyzing our crystallization data. The first one was developed by Kissinger [1] and relates the linear dependence between $\ln(T_\mathrm{p}^2/Q)$ and $1/T_\mathrm{p}$:

$$\frac{d\left[\ln\left(T_\mathrm{p}^2/Q\right)\right]}{d[1/T_\mathrm{p}]} = \frac{E}{R} \tag{5}$$

where T_p is the crystallization peak temperature at the heating rate Q. With a different approach, Ozawa [1] observed that the plot of $\ln Q$ versus $1/T_\mathrm{p}$ was a straight line with a slope of E/R (6). Furthermore, Yinnon and Uhlmann [1] suggested a method leading to E by plotting $\ln(T_\mathrm{p}/Q)$ versus $1/T_\mathrm{p}$ (7):

$$\frac{d[\ln Q]}{d[1/T_\mathrm{p}]} = -\frac{E}{R} \tag{6}$$

$$\frac{d[\ln(T_\mathrm{p}/Q)]}{d[1/T_\mathrm{p}]} = \frac{E}{R} \tag{7}$$

The lithium metaphosphate glass was prepared by the conventional melt-quenched method. Commercial reagents of ammonium phosphate ($NH_4H_2PO_4$) and lithium carbonate (Li_2CO_3) were mixed in appropriate proportions and melted in air at 700 °C in a graphite crucible. The melt was then poured into a stainless steel mold and pressed between two stainless steel plates. Table I summarize some physical data of this glass measured on bulk samples. To determine the Young's modulus, we have used the Grindosonic® system, a non-destructive technique developed by Jos Lemmens Ltd. (NL). The experiment consist to excite an object with a precise geometry (a disc in this study), by means of an external mechanical impulse, then to analyze the self temporary frequency of the object during the relaxation. This excitation is done to obtain the desired vibration modes (i.e., flexion and torsion). So

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TABLE I Physical characteristics of the glass

T_g (°C)	T_p (°C)	T_l (°C)	ρ (g·cm^{-3})	Hv (MPa)	α (°C^{-1})	E (GPa)	ν
327	442	653	2.461	220	182.10^{-7}	46.3	0.28

Glass transition temperature (at 10 °C/min)—Crystallization peak temperature (at 10 °C/min)—Lquidus temperature—Experimental density—Vickers microhardness—Thermal expansion coefficient—Young modulus—Poisson's ratio.

the detector (microphone or piezoelectric) needs to be placed with attention to select and isolate the interesting frequencies. The analytic treatment is possible with the EMODV9.10 software. This program allows the calculation of the Young's modulus and the Poisson's ratio from the physical characteristics (dimension and weight) and the self frequency vibrations of the object. Non-isothermal studies were carried out with a TA Instruments-SDT 2960. The overall accuracy of the instrument is expected to be better than 1 °C. The glass samples were contained in a Pt pan, and an empty Pt pan was used as the standard. Measurements were performed in air using a constant sample weight of 30 mg. Heating rates in the range from 5 to 15 °C/min were employed. The crystalline phase obtained during the heat treatments was identified by X-ray powder diffraction. Data were collected with a Philips diffractometer (Cu K_{α_1,α_2}) using a Bragg-Brentano geometry.

Ray *et al.* [2] have developed a DTA method, saving time, not much consumer of product and allowing reliable information about nucleation to be obtained. In this DSC method, the maximum height of the crystallization peak $(\delta T)_p$), which is a function of the total number of nuclei, is plotted as a function of different variables including the sample particle size, the nucleation temperature and time. To determine the dominant crystallization mechanism, the quenched glass was ground and screened to nine different particle size ranges, <20, 20–38, 38–63, 63–100, 100–200, 200–315, 315–500, >500 μm and bulk. The effect of particle size on DSC crystallization peak is shown in Fig. 1. According to the shape of the curve, the surface crystallization is the dominant mechanism. The time and temperature nucleation rate curves (see Fig. 2) have been determined from DTA scans performed with the 315–500 μm particle size range, because it acts as a bulk sample. As a result, the optimum conditions are 320 °C and 1 h.

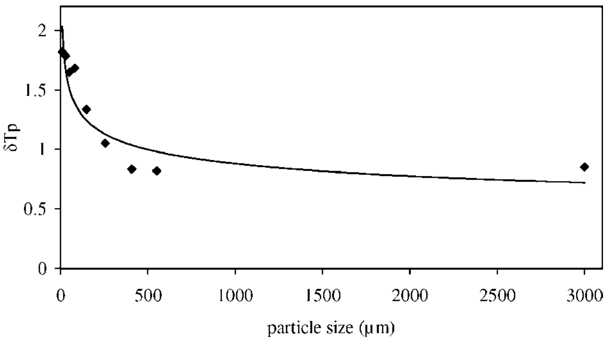

Figure 1 DTA crystallization peak height as a function of the sample particle size (heating rate 10 °C/min).

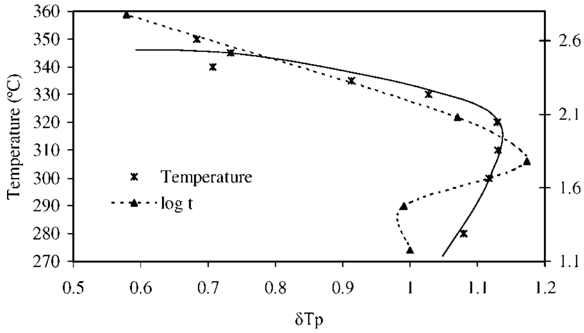

Figure 2 Temperature and time nucleation rate curves.

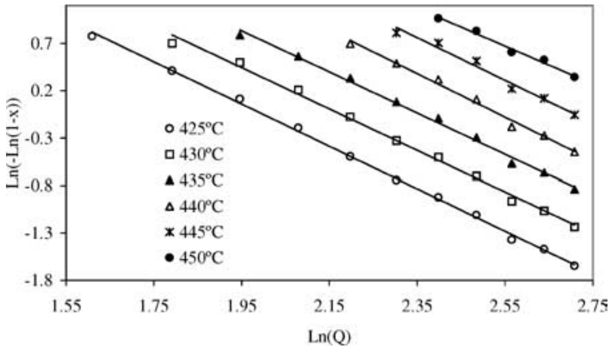

Figure 3 Determination of the Avrami exponent.

The Avrami exponent was obtained by plotting $\ln[-\ln(1-x)]$ versus $\ln Q$ (see Fig. 3) at different temperatures. The slopes of the straight lines lead to an average n value of 2.2 ± 0.1. Such a value, close to 2, indicates that glass crystallization has a bidimensional growth controlled by the progression of the crystal-glass interface with a zero nucleation rate in the temperature range explored. In comparison, the value of the Avrami exponent for the sodium metaphosphate glass [3] is 1.6 ± 0.1 and surface crystallization is also the dominant mechanism. The difference between the values of the Avrami exponent can be attributed to the difficulty to achieve the nucleation sites saturation before growth. In agreement with the relation (5), (6) and (7), the plots of $\ln(T_p^2/Q)$, $\ln Q$ and $\ln(T_p/Q)$ versus $1/T_p$, give straight lines (see Fig. 4). The slope of the different straight lines allow the determination of the E values, which are in the range 125 to 137 kJ/mol. Table II summarizes these different values with their

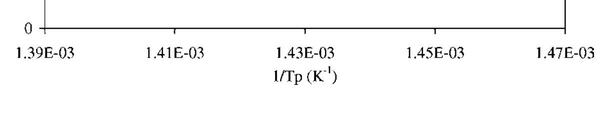

Figure 4 Determination of the apparent activation energy for crystallization.

TABLE II Non-isothermal determination of the apparent crystallization activation energy

$f(1/T_p)$	$E \pm \Delta$ (kJ/mol)
Ln (T_p^2/Q)	127 ± 8
Ln (T_p/Q)	125 ± 8
Ln (Q)	137 ± 8

corresponding maximum deviation. The values of the apparent activation energy are in good agreement and 130 ± 8 kJ/mol can be considered as representative. Furthermore, the value of the crystallization activation energy for the sodium metaphosphate glass [3], which is equal to 55 kJ/mol, is 2.5 times lower. Many reasons can explain such a difference, however the main one is the macroscopic phase segregation observed, at relatively low temperatures, for the sodium metaphosphate composition. Several isothermal thermogravimetric analysis, conducted at temperatures just above T_g have shed light on the phosphorus oxide weight loss and the simultaneous occurance of a new crystalline phase identified as $Na_5P_3O_{10}$ [3].

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