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$NaPO_3$ GLASS SURFACE CRYSTALLIZATION STUDIES BY THE LIGHT TRANSMITTANCE THERMAL ANALYSIS

S. C. Mojumdar[1], M. Drabik[2], J. Chocholoušek[3], V. Kovár[3] and J. Majling[3]*

[1]Institute for Research in Construction, National Research Council of Canada, M-20, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada
[2]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska Cesta 9, SK-842 36 Bratislava, Slovakia
[3]Department of Ceramics, Glass and Cement, Slovak University of Technology, Radlinskeho-9, SK-81237 Bratislava, Slovakia

Light transmittance was measured during heating of thin $NaPO_3$ glass plates at different heating rates. According to the results, the crystallization of orthorhombic textured $NaPO_3$ glass proceeds from sample surfaces into their interior due to the foregoing surface nucleation. The glass surface crystallization process resulted in the sigmoidal decrease of the optical transmittance. Elaborated data lead to the activation energy of glass surface crystallization of the value of 182.8 kJ mol^{-1}.

Keywords: *DTA, light transmittance thermal analysis, SEM, X-ray diffraction*

Introduction

Glasses are very important and magnificent materials. Therefore, many authors have investigated various glasses and also examined their thermal, structural, biological and electrical properties [1–6]. We focused our attention in this work especially on $NaPO_3$ glass. The literature reports a few of results on the activation energy of $NaPO_3$ crystallization. The activation energy obtained from DTA non-isothermal measurements on nucleated $NaPO_3$ glass yielded value of 55 kJ mol^{-1} [7]. When the measurements were performed using isothermal experiments of X-ray phase analysis, the activation energy was found to be 138 kJ mol^{-1}, considering 021 diffraction and 135 kJ mol^{-1}, considering 111 diffraction of $NaPO_3$ [7]. Other values of the activation energy issue from the DTA dehydration study of $NaH_2PO_4{\cdot}2H_2O$ [8]. Those based on a peak at 345°C, associated with $NaPO_3$ crystallization, resulted in a value of 175.69 kJ mol^{-1}, using Kissinger method and in a value of 185.98 kJ mol^{-1}, using Ozawa method of evaluation. This peak was found to be present also at 344°C at DTA measurement and at 334°C at DSC measurement [9].

In this contribution the activation energy of $NaPO_3$ glass surface crystallization has been derived from in situ measurements of the optical transmittance of the polished thin glass plates. The method itself has been found previously quite versatile in use and applicable to fairly high temperatures [10, 11]. Recently it has been referred to as 'The Light Transmittance Thermal Analysis' [3]. The decrease of the optical transmittance as a measure of a degree of crystallization has been already tested by heating-quenching-examining experiments performed on the opal glass [12].

Experimental

Sample preparation

The $NaPO_3$ glass was prepared from reagent grade $NaH_2PO_4{\cdot}H_2O$, heated at 800°C for 2 h. The glass melt was cooled casting it on a steel plate. The sample plates with 5·5 mm square size and 0.5 mm thickness were prepared by cutting and polishing procedures. The glass plates were highly transparent, clear with mirror like polish.

Measurements

Optical transmittance measurements were accomplished using an instrument described elsewhere [3, 10, 11]. The 'white' light emitting diode (LED) was used as a light source. The light incites the sample plate perpendicularly. The transmitted light intensity is evaluated by Si-photo diode. The Pt/Rh thermocouple (type S) was in-situ calibrated *vs*. melting point of $NaPO_3$ (627°C) [13] and *vs*. α/β quartz transition (573°C), using β-quartz single crystal plate. Electric furnace temperature control and data processing is accomplished by windows compatible software. DTA measurements were performed on a TA SDT 2960 instrument by using platinum crucible (sample mass

* Author for correspondence: subhas.mojumdar@nrc-cnrc.gc.ca

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

10–20 mg, heating rate 10°C min^{-1}, in flowing air). X-Ray patterns were taken on STOE Theta/Theta Diffractometer. SEM micrographs were taken on Tesla B-300 instrument.

Results and discussion

Optical transmittance thermal analysis

The typical pattern of the optical transmittance record is given in Fig. 1. The transmittance is on a high level until the crystallization starts at temperature about 345°C. Figure 2 exhibits decrease of transmittance of individual samples on a relative scale. The curves´ course fit *vs*. decreasing sigmoidal dependence yielded in each case the R-value >0.999, and resulted in inflexion point temperatures given in Table 1.

The activaction energy was calculated from the data of Table 1. Kissinger equation in the form

$$\ln(\beta/T_m^2) = -E/(R\,T_m)+C$$

was used for this purpose. A plot of $\ln(\beta/T_m^2)$ *vs*. $1/T_m$ gives straight line with the slope of $(-E/R)$ as seen in Fig. 3. The derived activation energy has a value of 182.8 kJ mol^{-1}.

Table 1 Heating rates and inflexion point temperatures of samples 1–5

Sample/plate	β-Heating rate /°C min^{-1}	T_m –inflextion temperature/°C
1	1.25	352.01
2	2.5	364.13
3	3.75	373.27
4	10	389.83
5	20	402.19

SEM analysis

As further observed, the crystals nucleate and start to grow from the surface. This is illustrated in Fig. 4 showing a part of the cross section of the plate 5. The surface crystallization process was interrupted in this case by quenching the plate in time when its transmittance reached the half of its initial value. Figure 4

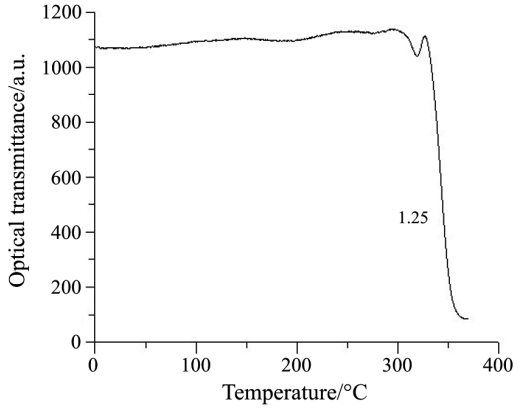

Fig. 1 Optical transmittance record of the sample heated at a rate of 1.25°C min^{-1}

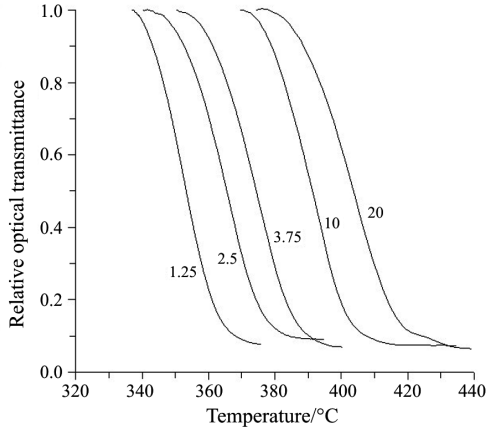

Fig. 2 Optical transmittance curves at temperatures associated with crystallization process (heating rates in °C min^{-1})

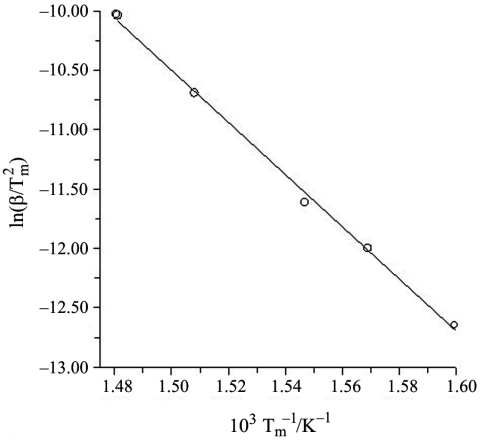

Fig. 3 Arrhenius plot to derive the activation energy

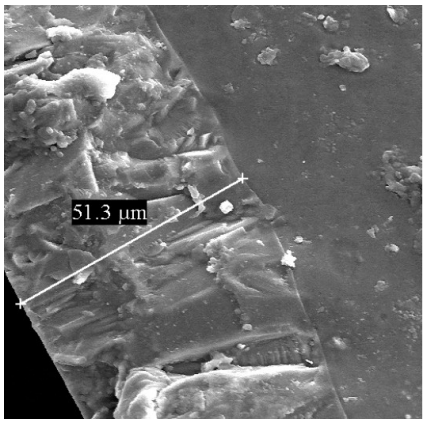

Fig. 4 SEM picture of the adhering crystallized layer and the glassy inside part (dark side of the picture) of the cross sectional fracture surface of the plate No.5

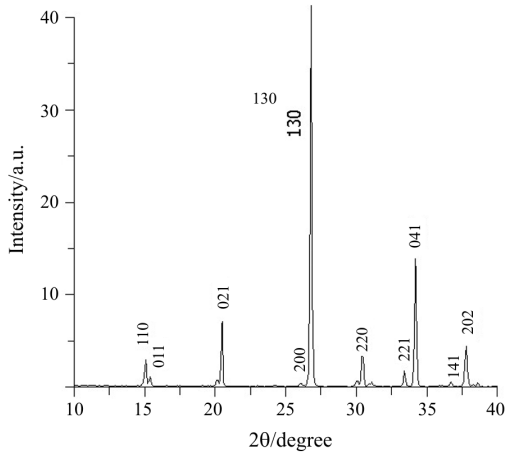

Fig. 5 X-ray pattern of crystallized $NaPO_3$ glass

shows that only a small volume of the sample is crystallized in this time. The percentage of the crystallized sample volume, with respect to Fig. 4, can be expressed as (2·51.3/500)·100, i.e. approx. 20% (500 is the glass plate thickness).

X-ray diffraction analysis

The determined value of the activation energy is close to the values given in [8]. $NaPO_3$ glass crystallizes in its orthorhombic phase (PDF card No. 11-0648). The X-ray pattern was taken from the plate surface (Fig. 5). Its peak intensities differ strongly from the referenced PDF card. Dominating the 130 diffraction, while the strongest diffraction according to the PDF card, (220) is nearly extinct. This shows that the crystals keep some preferential orientation during their growth.

Conclusions

The experiments performed proved that $NaPO_3$ glass crystallization kinetics could be well mapped by the optical transmittance thermal analysis. Where necessary, the samples can be quenched for the further investigation from such temperatures, which are in distinct correspondence to the desired levels of the optical transmittance. Moreover, the results confirmed surface nucleation of $NaPO_3$ glass perpetuating in the oriented crystal growth.

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