MINING AND METALLURGY INSTITUTE BOR

and

TEHNICAL FACULTY BOR, UNIVERSITY OF BELGRADE

IOC 2018

International October Conference

50th International October Conference
on Mining and Metallurgy

PROCEEDINGS

Editors:

Ana Kostov
Milenko Ljubojev

30th September – 3rd October 2018

Hotel "Jezero" Bor Lake, Serbia

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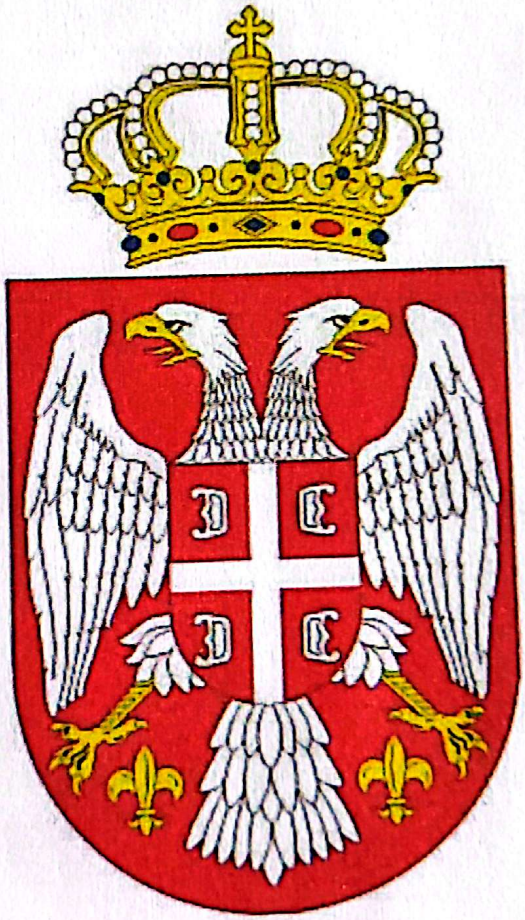

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NON-ISOTHERMAL ANALYSIS OF NUCLEATION THE Li_2O-GeO_2-Al_2O_3-P_2O_5 GLASS

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Abstract

Nucleation of the powder glass from the system Li_2O-Al_2O_3-GeO_2-P_2O_5 was studied. The investigations were performed under the non-isothermal conditions using the DTA method. The field of nucleation is determined. It was observed that there is a possibility of simultaneous nucleation and crystal growth in glass. Dependence $(T_p^{-1})^{max}$ of T_n is linear for the studied glass system.

***Keywords**: germanium phosphate glass, nucleation, crystallization*

1 INTRODUCTION

The Li_2O–Al_2O_3–GeO_2–P_2O_5 glassy system is one of the most promising materials for application in the high energy density batteries and other electrochemical devices [1]. These materials can be obtained by the classical powder sintering route, sol–gel method and common glass–ceramic processes [2]. The studies of crystallization of $6.4Li_2O{\cdot}8.6Al_2O_3{\cdot}42GeO_2{\cdot}43P_2O_5$ (wt%) glasses have showed that one of the dominant crystal phase, precipitated in a glass matrix, is the NASICON - type $LiGe_2(PO_4)_3$ crystals. The $LiGe_2(PO_4)_3$ NASICON-type crystallizes in the 3D network structure (rhombohedral crystal system, space group R3c) which has channels for the Li ions migration. In this crystal, there are two types of polyhedrons: GeO_6 octahedra and PO_4 tetrahedr, attached by their corners to form the $[Ge(PO_4)]^-$ framework with 3D interconnected channels and interstitial cavities. The Li^+ ions migrate in channels of this framework [3]. A partial substitution of the Ge^{4+} ions by the trivalent cations, such as the Al^{3+} ions increases the unit cell dimensions. A residual negative charge is neutralized by the additional Li^+ ions that occupy the interstitial cavities. A change in the unit cell dimensions and Li ion concentration in the crystal leads to an increase of ionic conductivity [4–7]. A high Li^+-ion conductivity (~10^3 S cm^{-1} at room temperature) has recently been reported in the NASICON-type structure [8,9]. It is important to know the nucleation and crystallization behavior of the parent lithium phosphate glass in order to define the technological parameters for fabrication of these structured materials. The aim of the present study is an investigation of nucleation the germanium phosphate glass under the non-isothermal conditions.

2 EXPERIMENTAL

The glass was prepared by melting a homogeneous mixture of reagent-grade Li_2CO_3, Al_2O_3, GeO_2 and $(NH)_2HPO_4$ in a covered platinum crucible. The melting was performed in an electric furnace BLF 17/3 at T=1400°C during t=0.5 h. The melt was

cast and cooled between two steel plates. The chemical analysis was carried out using a spectrophotometer AAS PERKIN ELMER Analyst 300.

To examine temperature of glass nucleation, the non-isothermal crystallization was studied using a DTA-Netzsch STA 409 EP instrument with Al_2O_3 powder as a reference material. The powder sample (100 mg) was prepared by crushing and grinding the bulk glass in an agate mortar and sieving thus prepared specimen up to the appropriate grain size of 0.5 - 0.65 mm. The glass was heated from 20 to 1000°C at a heating rate of 10°C min^{-1}. Previously, the DTA analysis samples were heated to the nucleation temperature during different periods of time, t_n= 15, 30, 60, 180 and 300 minutes. Nucleation temperatures were T=500-620°C, with 10 °C step.

3 RESULTS AND DISCUSSION

The glass samples were transparent, without visible residual gas bubbles. The results of the chemical analysis have showed that a glass composition of $6.4Li_2O{\cdot}8.6Al_2O_3{\cdot}42GeO_2{\cdot}43P_2O_5$ (wt%) was obtained. Figure presents the 1 DTA diagrams of glass samples that were thermally treated before the non-isothermal crystallization for different periods of time at different nucleation temperatures.

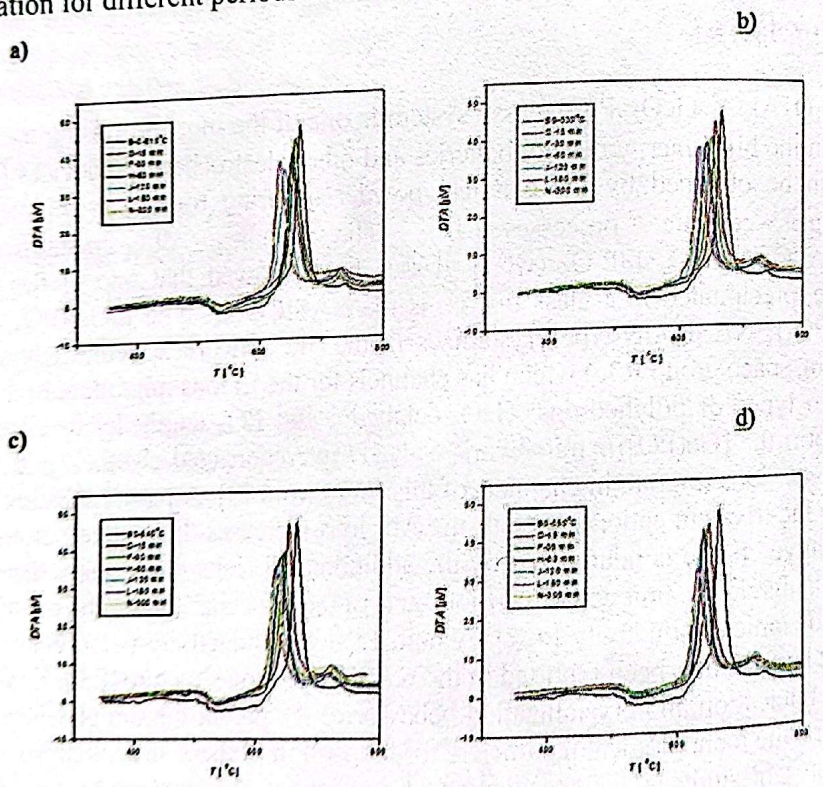

Figure 1 *Crystallization peaks temperatures for different times of thermal treatment T_n=510 °C, b) T_n=530 °C, c) T_n=540 °C, d) T_n=550 °C*

Figure 2 presents a dependence $(\delta T)_p$ of T_n for different periods of time of the thermal treatment, where $(\delta T)_p$ are the height values of crystallization peak of the previously heat-treated samples, and T_n is nucleation temperature.

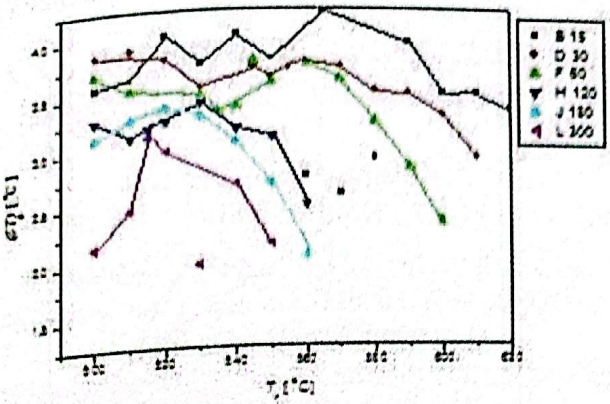

Figure 2 *$(\delta T)_p$ vs. T_n for different thermal treatment times*

A shape of curve in Figure 2 indicates that there is possibility of simultaneous nucleation and crystal growth in the studied glass, or that there is a time-dependent nucleation. This conclusion supports a different shape of curves, showed in Figure 3.

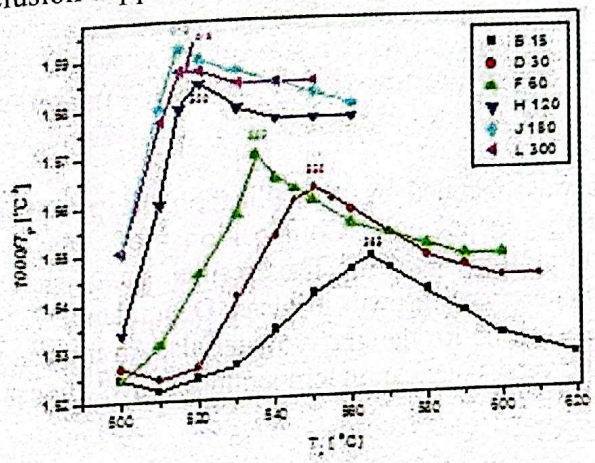

Figure 3 T_p^{-1} vs. T_n different thermal treatment times

Figure 3 presents a dependence T_p^{-1} of T_n for different periods of time of the thermal treatment. It can be observed that T_p^{-1} increases reaching the maximum value, then drops making a "bell" shaped curve that is characteristic for the glassy materials.

Table 1 presents the maximum values of T_p^{-1} and $(\delta T)_p$ for the LAGP glass at nucleation temperature T_n^{max} as a function f(T,t).

Table 1 *Maximum temperatures of nucleation as a function of thermal treatment*

f(T,t)	T_p^{-1}	$(\delta T)_p$
180	1.5923	3.375
300	1.5873	3.127
120	1.5848	3.416
60	1.5618	3.777
30	1.5625	3.804
15	1.5480	4.199

It can be observed from Table 1 that with an increase of temperature, there is a decrease of crystallization peak temperatures. With an increase of thermal treatment time, the temperature between the peaks increases and height of crystallization peak drops.

Plot $(T_p^{-1})^{max}$ vs T_n is shown in Figure 4. A linear dependence $(T_p^{-1})^{max}$ of T_n for this glass system can be observed.

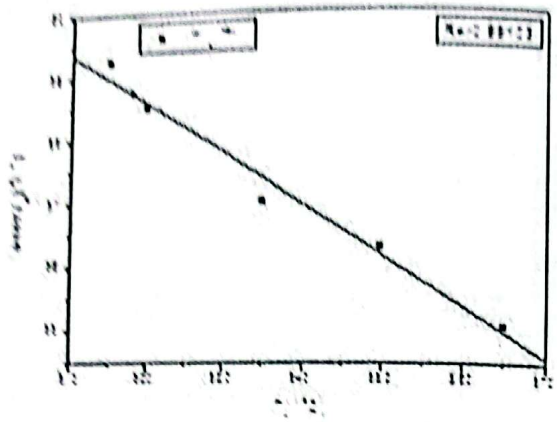

Figure 4 *$(T_p^{-1})^{max}$ vs T_n for different thermal treatment times*

It is obtained from Figure 4 that a dependence $(T_p^{-1})^{max}$ of T_n can be presented as an equation:

$$Y=2.00324+(-8.0311\cdot10^{-4}\cdot X) \quad (1)$$

4 CONCLUSION

The glass-ceramic was obtained by crystallization the parent glass prepared by the standard melt-quenching technique. Composition of the parent glass was $6.4Li_2O{\cdot}8.6Al_2O_3{\cdot}42GeO_2{\cdot}43P_2O_5$ (wt%). The results have showed a possibility of simultaneous nucleation and crystal growth in glass. Dependence T_p^{-1} of T_n shows a "bell" shaped curve that is characteristic for the glassy materials. An inverse function of maximum crystallization temperature versus nucleation temperature shows alinear dependence.

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REFERENCES

[1] N. Anantharamulu, K.K. Rao, G. Rambabu, B.V. Kumar, V. Radha, M. Vithal, J. Mater. Sci., 46 (2011) 2821-2837.
[2] J. W. Fergus, J. Power Sources, 195 (2010) 4554-4569.
[3] Y. Sun, Nano Energy 2 (2013) 801.
[4] P. Maldonado-Manso, E.R. Losilla, M. Martinez-Lara, M. Aranda, S. Bruque, F. Mouahid, M. Zahir, Chem. Mater. 15 (2003) 1879.
[5] A.I. Svitanko, S.A. Novikova, D.V. Safronov, A.B. Yaroslavtsev, Neorganicheskie Mater. 47 (2011) 1521.
[6] J. Fu, J. Mater. Sci. 33 (1998) 1549.
[7] B.V.R. Chowdari, G.V. Subba Rao, G.Y.H. Lee, Solid State Ionics 136 (2000) 1067.
[8] M.A. Subramaman, R. Subramanlan, A. Clearfield, Solid State Ionics, 18/19 (1986) 562 569.
[9] H. Aono, E. Sugimoto, Y Sadaoka, N. Imanaka, G. Adachi, J. Electrochem. Soc., 136 (1989) 590-591.