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Original Scientific paper

DEVELOPMENT OF $LiGe_2(PO_4)_3$ CRYSTALLINE PHASE IN GLASS SUBJECTED TO NON ISOTHERMAL TREATMENT

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Abstract: The nucleation behavior of germanium phosphate glass under non isothermal conditions was examined using differential thermal analysis (DTA). The study focused on how both the duration and temperature of pre DTA heat treatment affect the characteristic DTA peak temperature (Tp). A complex relationship between these parameters was observed. At constant temperatures, extending the annealing time during the pre DTA treatment led to a reduction in the Tp value. Furthermore, the effect of pre DTA treatment temperature on DTA parameters revealed that, for annealing times longer than tind, the inverse dependence of Tp on T mirrored nfluence of temperature on nucleation rate (I), particularly in cases where the nucleation and crystallization regions partially overlapped. Differential thermal analysis (DTA), which we used in the manuscript, is one of the most reliable methods for monitoring phase transformations in glass systems. This method enables accurate detection of energy changes during heating. The application of this technique in non-isothermal conditions provides key data on the thermal stability of the samples and the kinetic parameters governing the crystallization process. Special importance is attached to the study of nucleation, which, as the initial phase of crystal growth, directly determines the final morphology and properties of the resulting glass-ceramic

Keywords: germanium phosphate glass, nucleation, non-isothermal conditions

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1 INTRODUCTION

NASICON (Na Super Ionic Conductor) type materials have been widely investigated due to their high ionic conductivity. In their crystalline form, these compounds follow the general formula $AB_2(PO_4)_3$, where A represents an alkali ion. The B site is typically occupied by a metal with a valency of four or higher, though trivalent elements can also substitute. Crystalline NASICON materials exhibit a rhombohedral $R\bar{3}c$ structure, characterized by (BO_6) octahedra connected through corner-sharing with (PO_4) tetrahedra. Their framework is notably “open,” allowing alkali ions to migrate with reduced activation barriers, which makes them promising candidates for fast ion conductors (Rao, Sobha and Kumar, 2001; Anantharamulu et al., 2011).

Most syntheses of these materials rely on the traditional powder sintering technique, and many different compositions have been described. Alternatively, NASICON ceramics can be successfully prepared through glass ceramic processing (Cruz, Ferreira, and Rodrigues, 2009; Fu, 1998). Compared to sintered samples, glass ceramics offer significant advantages, as they can be easily shaped into desired dimensions and exhibit dense microstructures. Successful execution of this process depends on detailed knowledge of the crystallization characteristics of the glass precursor. Precisely defining the temperature ranges where phase transformations occur allows for the avoidance of undesirable secondary phases that could impair the electrical properties of the final product. Furthermore, controlling nucleation within the glass matrix directly influences microstructural homogeneity, which is vital for achieving high mechanical strength and stability under real operating conditions. Therefore, a detailed kinetic analysis of the process represents not only a theoretical challenge but also a practical necessity for the technological development of these materials.

NASICON materials have gained significant interest in the past few years as solid electrolytes for future lithium battery technologies, where ensuring safety and stability is essential. Because they unite excellent ionic conductivity with chemical stability, they are considered potential replacements for liquid electrolytes. Beyond ionic conductivity alone, it is essential to understand how the sample's thermal history influences grain-boundary formation, as these can act as significant barriers to ion transport. Optimizing these parameters through controlled glass crystallization offers a pathway toward developing materials that are not only high-performing but also economically viable for large-scale industrial production. Previous studies have shown that doping with elements such as Al, Ti, or Zr can further enhance conductivity and improve structural stability, but challenges remain in controlling nucleation and crystallization processes (Fokin et al., 2006; Wakasugi, Kadoguchi and Ota, 2001). Moreover, the compatibility of NASICON phases with metallic lithium is a crucial factor for their practical application in solid state batteries.

Germanophosphate glasses represent an attractive starting point for NASICON type glass ceramics because they combine high ionic conductivity with the ability to be processed into various shapes. However, the parent glass is unstable in contact with molten lithium, which limits its direct application. Crystallization into $LiGe_2(PO_4)_3$ phases significantly improves chemical stability and compatibility with lithium anodes, while maintaining high lithium ion conductivity, often reaching values around 4×10^{-4} S/cm at room temperature (Matijašević et al., 2022). Furthermore, the incorporation of Al_2O_3 into the glass composition can lead to partial substitution of Ge^{4+} by Al^{3+}, compensated by Li^+ ions, resulting in the modified structure $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ and enhanced thermal stability (Đorđević et al., 2025).

In this study, emphasis is placed on the nucleation of the $LiGe_2(PO_4)_3$ phase in germanophosphate glass under non isothermal conditions. By investigating the influence of annealing time and temperature on nucleation behavior, the work aims to clarify the crystallization mechanism and its impact on ionic transport. The results are expected to contribute to a deeper understanding of NASICON type glass ceramics and their potential role as reliable solid electrolytes in advanced energy storage systems.

Reagent-grade Li_2CO_3, Al_2O_3, GeO_2, and $(NH_4)_2HPO_4$ were used as the initial raw materials. Following careful homogenization, the mixture was slowly heated to 300 °C to remove volatile species and subsequently melted at 1400 °C for half an hour in a platinum crucible. The resulting melt was poured onto a steel plate and allowed to cool in air. The obtained glass samples were transparent and free from visible gas inclusions. Chemical composition analysis was carried out using a spectrophotometer, specifically the AAS PERKIN ELMER Analyst 300.

2 EXPERIMENTAL

Non isothermal differential thermal analysis was conducted on a Netzsch STA 409 EP instrument, employing Al_2O_3 powder as the reference material. Each run used 100 mg of sample, heated at 10 °C per minute, and nucleation was examined in glass powders with particle sizes ranging from 0.50 to 0.65 mm. Heating was performed in alumina crucibles at 10 °C/min, starting from room temperature ($T = 20$ °C) up to selected temperatures in the range of 500–620 °C. These target temperatures were then maintained for varying durations of 15, 30, 60, 120, 180, and 300 minutes.

For the thermal treatment, a Carbolite CWF 13/13 furnace was used, offering automatic regulation and precise temperature control within ±1 °C. After annealing, the samples were cooled to room temperature and subsequently reheated in the DTA system at a constant heating rate of 10 °C/min, starting at 20 °C and reaching 800 °C.

To determine phase composition, XRD analysis was performed using a Philips PW 1710 diffractometer. The instrument employed a copper tube running at 40 kV and 32 mA. Patterns were recorded across the 2θ interval of 4–70°, with 0.25 s per step and increments of 0.02°. Divergence and receiving slits were maintained at 1 and 0.1 units, respectively. Measurements were taken at room temperature with the sample mounted in a stationary holder.

3 RESULTS AND DISCUSSION

Chemical analysis confirmed that the obtained glass composition was $22Li_2O\cdot10Al_2O_3\cdot30GeO_2\cdot38P_2O_5$ (mol%). This formulation is close to the stoichiometric NASICON type solid electrolyte $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$. Powder X ray diffraction (XRD) verified that the quenched melt was vitreous. The XRD pattern of samples subjected to thermal treatment at 800 °C for 100 h (Fig. 1) revealed the formation of $LiGe_2(PO_4)_3$ (JCPDS 80 1922) and GeO_2 (JCPDS 83 0543) phases during crystallization. Rietveld profile fitting indicated that the glass transformed into a two phase glass ceramic, consisting predominantly of $LiGe_2(PO_4)_3$ (97.5%) with GeO_2 as a minor secondary phase (2.5%).

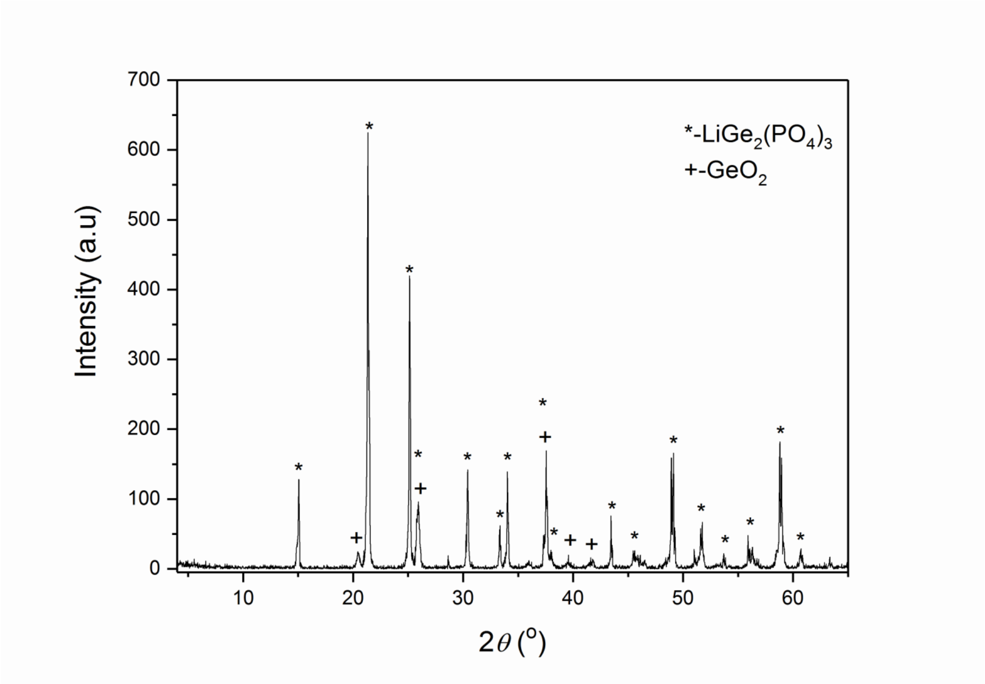

Figure 1 Diffraction pattern obtained from the glass sample after annealing at 800 °C for 100 h.

The results indicate that the trace presence of GeO_2 originates from slight deviations in the glass composition compared to the nominal formulation, caused by batch evaporation during melting. Consequently, only the crystallization of the $LiGe_2(PO_4)_3$ phase was taken into account. According to the JCPDS card, aluminium is not part of the $LiGe_2(PO_4)_3$ structure, although it is generally assumed that Al can enter the lattice as a solid solution. When Al_2O_3 is introduced, Ge^{4+} cations are partially substituted by Al^{3+}, creating a charge imbalance that is compensated by Li^+ ions. This leads to the modified structure $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ and simultaneously enhances the thermal stability of the glass network. For the investigated composition, aluminium was present below the detection limit of XRD analysis (Đorđević et al., 2025).

A straightforward method for evaluating nucleation parameters in glasses was introduced through DTA analysis (Ray and Day, 1990; Kelton, 1992). The technique involves subjecting a small portion of the glass to isothermal treatment at a chosen temperature (T) for a specified duration (t), after which the sample is reheated in a DTA device at a constant rate until crystallization is completed. This procedure was carried out for several values of T, while parameters such as annealing time, heating rate (β), sample mass, and particle size remained unchanged. By plotting the reciprocal of the peak temperature (Tp^{-1}) against the nucleation temperature, a curve resembling the nucleation rate was obtained, enabling determination of the effective nucleation interval and the temperature at which nucleation reaches its maximumThe DTA curves showing the variation of Tp with annealing time at 550 °C are presented in Figure 2.

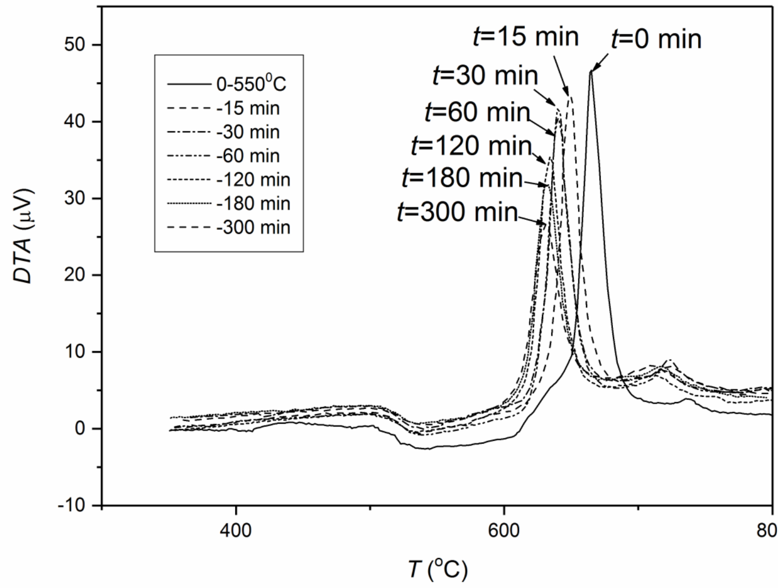

Figure 2 Differential thermal analysis curves of glass powders with particle sizes between 0.5 and 0.65 mm, subjected to annealing at 550 °C for different times.

It can be observed that the peak temperature (Tp) decreases with longer annealing times, and the intensity of the peak also diminishes over time. Such behavior corresponds to polymorphic crystallization, in which prolonged heat treatment raises the number of nuclei and consequently shifts the exothermal peak to lower temperatures (Wakasugi, Kadoguchi, and Ota, 2001). A comparable trend was noted for the parameter ΔTp, defined as the difference between the crystallization peak temperatures of untreated and heat treated samples, although the change occurred in the opposite direction. In contrast, variations in the exothermal peak height (δTp) as a function of annealing time at selected temperatures differ from those observed for Tp^{-1} and ΔTp.

Figure 3 presents the curves showing the dependence of Tp^{-1} on temperature.

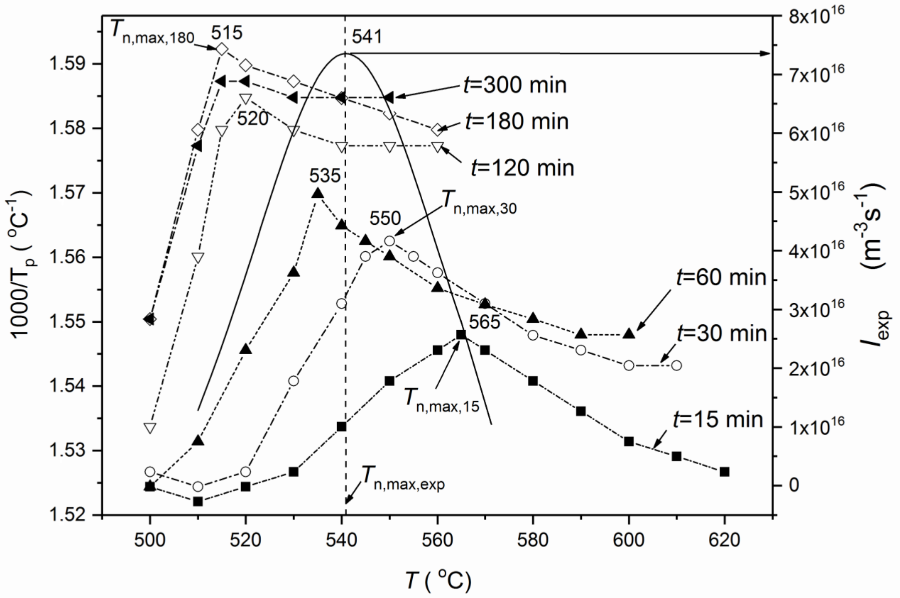

Figure 3 “Variation of parameters with temperature: a) Tp^{-1} plotted on the left ordinate (curves generated by fitting experimental observations).

“b) Right axis. The nucleation curve was measured under isothermal conditions. As depicted in Figure 3, Tp^{-1} shows a complex temperature dependence: it rises, reaches a maximum, and then declines, producing the well known bell shaped profile typical of glasses (Matijašević et al., 2022). For short treatment times below 30 minutes, the maxima were displaced to higher temperatures, while longer annealing progressively aligned them with the temperature of maximum nucleation.

“For annealing durations between 30 and 60 minutes, the curve maxima were located near the temperature corresponding to the highest nucleation rate (Tn,max). This trend reflects transient nucleation. At shorter treatment times, fewer nuclei developed, which caused the crystallization peaks to appear at elevated temperatures. In these cases, a significant portion of the glass phase remained untransformed, producing curves shifted toward higher temperatures. With longer annealing, the crystalline fraction expanded, and the right side of the curves progressively moved to lower temperatures. When t exceeded 120 minutes, a pronounced narrowing of the right-hand side of the curves was evident. Because the nucleation and growth temperature ranges in this glass partly overlap, the crystalline fraction increased quickly with rising temperature, ultimately resulting in complete crystallization of the sample.

The maximum nucleation rate (Iexp = 7.34×10^{16} $m^{-3}s^{-1}$), determined from isothermal experiments, was found at Tn,max = (541 ± 5) °C (Figure 3, solid curve). The obtained glass composition exhibits a remarkably high nucleation rate compared to previously reported inorganic glass systems (Fokin et al., 2006)

4 CONCLUSION

“The nucleation characteristics of $22Li_2O{\cdot}10Al_2O_3{\cdot}30GeO_2{\cdot}38P_2O_5$ (mol%) glass under non isothermal conditions were examined. Results confirmed that the glass undergoes polymorphic crystallization, producing $LiGe_2(PO_4)_3$ phases. Analysis of pre DTA heat treatment effects on the peak temperature (Tp) revealed that, at constant temperatures between 500 and 620 °C, longer annealing times led to a reduction in Tp, approaching values typical of the quenched glass. When annealing times were varied between 15 and 300 minutes, the DTA parameters showed complex behavior. For short treatments ($t < 30$ min), the maxima in Tp^{-1} vs. T plots were shifted above the temperature of maximum nucleation. At intermediate durations (30–60 min), the maxima aligned with the peak nucleation rate, while extended annealing shifted the maxima toward lower temperatures

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