

Supporting Information for:

Ionic Conductivity of Lithium Germanium Phosphate Glass-Ceramics

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Raman Spectroscopy

Figure S1 shows the evolution of the Raman spectra of prepared glass-ceramics. The Raman bands are ascribed in accordance with literature data obtained in the previous studies where the assignment of the bands is analyzed in details.³⁰⁻³³ The references refer to the main text.

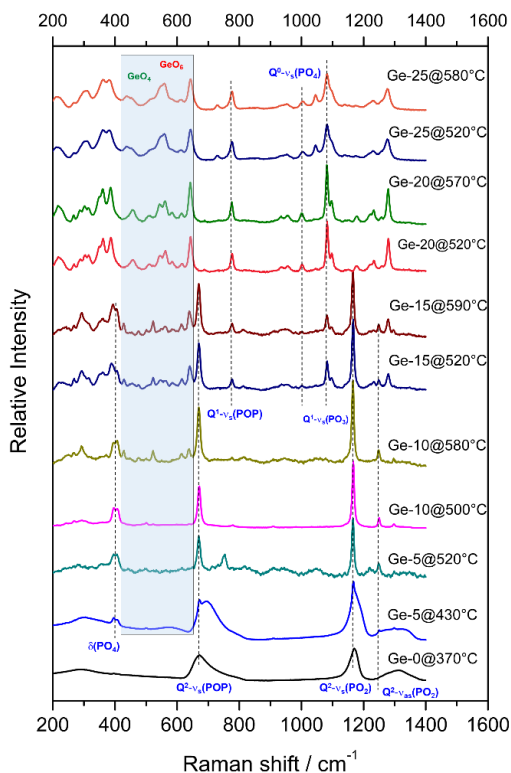


Figure S1. Evolution of Raman spectra of $40\text{Li}_2\text{O}-(60-x)\text{P}_2\text{O}_5-x\text{GeO}_2$, $0 \leq x \leq 25$ mol%, glass-ceramics prepared by heat-treatment at various temperatures for 24 h.

Raman spectra of Ge-0 sample heat-treated at a lower temperature is characteristic for metaphosphate, Q^2 , structure with the most dominant bands at 1173 and 665 cm^{-1} related to the symmetric stretching mode of non-bridging $(\text{PO}_3)_{\text{sym}}$ and bridging $(\text{P-O-P})_{\text{sym}}$ oxygen atoms, respectively. The bands appeared are broad which implies the dominant amorphous structure. In

the concentration range of 5-10 mol% of GeO_2 content, the main Raman bands do not change its position which indicates small changes in the phosphate network. However, in the Raman spectra for Ge-5 and Ge-10 crystallized at higher, T_2 , temperatures, at 520 and 580 °C, respectively, the sharp bands appeared suggesting the formation of the crystalline phases. Beyond this, at T_2 barely detectable band at around 520 cm^{-1} is observed suggesting incorporation of GeO_4 unit.³⁰⁻³³ Furthermore, for samples containing from 15 to 25 mol% of GeO_2 , it can be seen that the band at 650 cm^{-1} increases in intensity as the P-O-P linkage represented by the band at 665 cm^{-1} is replaced. This suggests a formation of P-O-Ge linkages as well as progressive replacement of metaphosphate, Q^2 , chains to pyro- Q^1 and orthophosphate Q^0 units. With the increase of GeO_2 content to 25 mol%, the bands associated to the germanate, GeO_4 and GeO_6 , units are detected. However, although the intensity of Raman bands assigned to the phosphate units decreases, it is evident that the addition of GeO_2 modifies glass-ceramics structure causing an increase of numerous germanate crystalline phases that are created in these samples.

Impedance spectroscopy

Electrical properties were studied by impedance spectroscopy. Samples were prepared by sputtering gold electrodes, as contacts, onto both sides of ~1 mm thick glass-ceramic disks using Sputter coater SC7620. Details about samples geometry (thickness and electrode diameter) for each sample are presented in Table S1.

Table S1. Samples thickness (t) and gold electrode diameter (d) used for electrical characterization by means of Impedance spectroscopy.

Samples	Thickness (t) / mm	Electrode diameter (d) / mm
T_1 -lower crystallization temperature		
Ge-0@370	0.844	3.8
Ge-5@430	2.258	3.8
Ge-10@500	2.383	3.8
Ge-15@520	1.238	3.8
Ge-20@520	1.128	3.8
Ge-25@520	1.406	3.8
T_2 -lower crystallization temperature		
Ge-0@470	1.180	3.8
Ge-10@580	1.446	3.8
Ge-15@590	1.494	3.8
Ge-20@570	1.532	3.8
Ge-25@580	1.598	3.8

*Electrode area, $A = \pi(d/2)^2$

The results of the impedance spectroscopy measurements are presented by the frequency dependence of the AC conductivity at different temperatures. Figure S2 shows the conductivity isotherms of selected glass-ceramics. At low frequency and sufficiently high temperature, the plateau that corresponds to the DC conductivity appears. The DC conductivity exhibits Arrhenius temperature dependence and thus shows characteristic activation energy as listed in Table 5, main text. In addition, with increasing temperature, the DC plateau is shifted to the higher frequencies accompanied by the drop in the conductivity related to the electrode polarization due to the accumulation of mobile lithium ions at the blocking metal electrode.

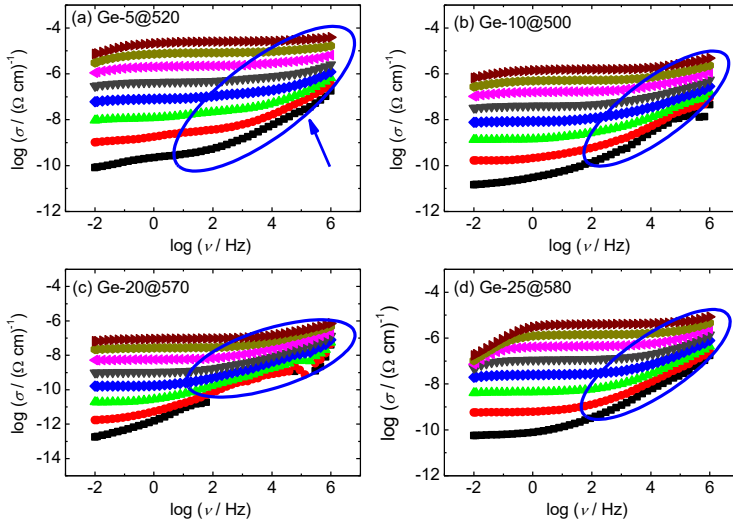


Figure S2. Conductivity spectra at different temperatures for selected $40\text{Li}_2\text{O}-(60-x)\text{P}_2\text{O}_5-x\text{GeO}_2$, $0 \leq x \leq 25$ mol%, glass-ceramics prepared by heat-treatment at various temperatures for 24 h. Note: arrow points the dispersion region where the changes in the conductivity shape are visible which depends on the stage of crystallization.

It is clear from Figure S2 that the investigated glass-ceramics display the dispersive behavior which is attributed to the back-and-forth motion of lithium ions and is more visible at lower frequencies and lower temperatures, shifting to higher frequencies and higher temperatures. Also, the difference in the shapes of isotherms is the most evident in the dispersive part as a result of the various degrees of crystallization in each sample. Figure S2 (a-d) shows a decrease in the DC conductivity for Ge-5@520, Ge-10@500 and Ge-20@570 glass-ceramics whereas the conductivity for Ge-25@580 glass-ceramic increases. This means that the DC conductivity strongly depends on the crystalline phases formed within the glassy phase which is discussed in details in the main text.

The activation energy for DC conductivity, E_{DC} , for each sample was determined from the slope of $\log(\sigma_{DC}T)$ vs. $1000/T$ using equation $\sigma_{DC}T = \sigma_0^* \exp(-E_{DC} / k_B T)$ where σ_{DC} is the total conductivity, σ_0^* is the pre-exponential factor, E_{DC} is the activation energy, k_B is the Boltzmann constant and T is the temperature (K), see Figure S3.

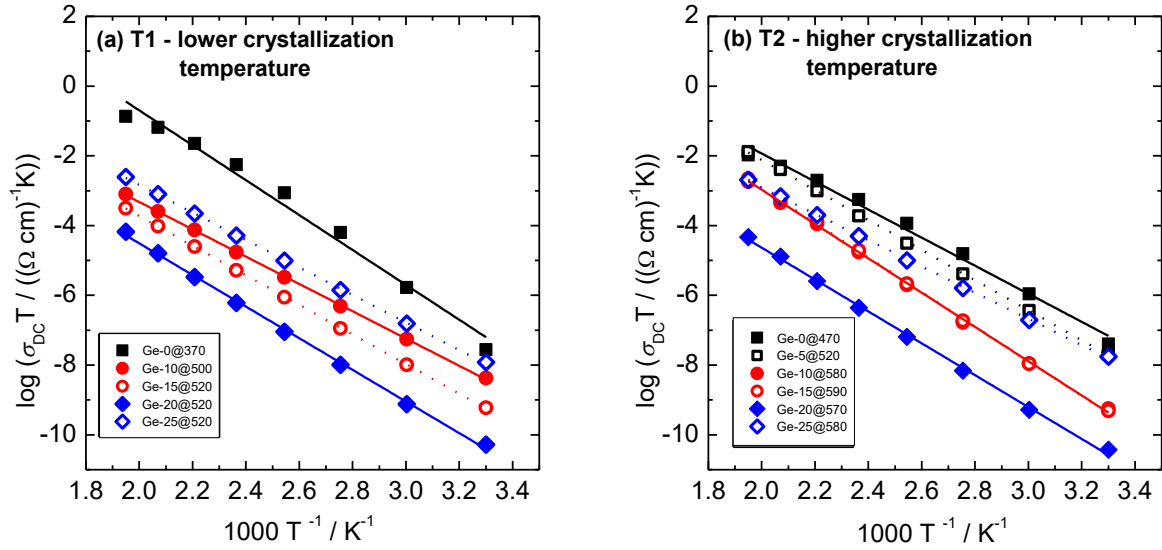


Figure S3. Arrhenius plot of the temperature dependence of DC conductivity for all 40Li₂O-(60-x)P₂O₅-xGeO₂, $0 \leq x \leq 25$ mol%, glass-ceramics prepared by heat-treatment at various temperatures for 24 h.

SEM/ EDS analysis

Figure S4 shows SEM micrographs and EDS analysis for Ge-25 sample heat-treated at 580 °C. The compositional analysis is obtained at two different spots on EDS spectra.

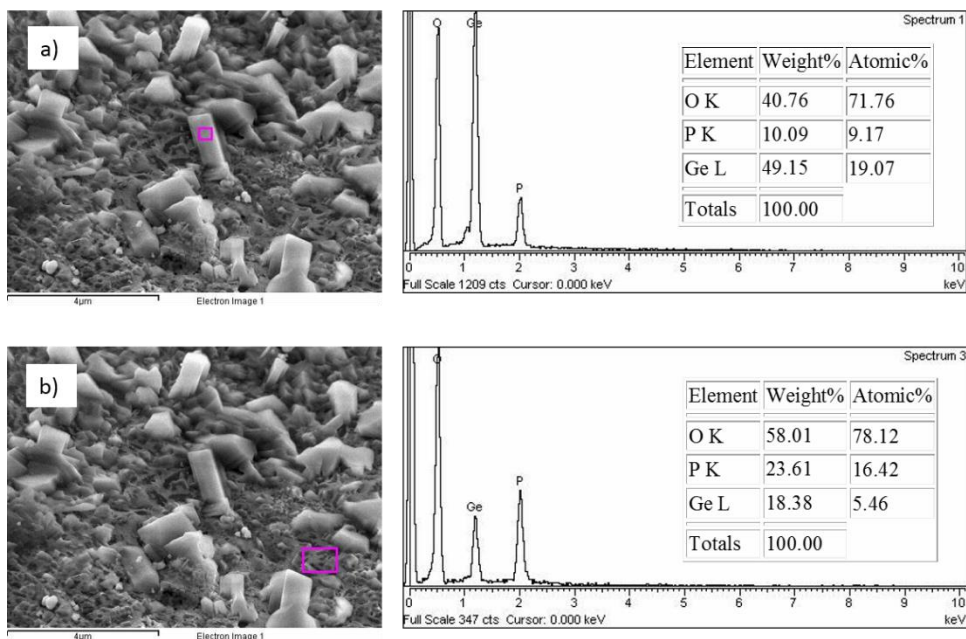


Figure S4. SEM micrographs and EDS analysis for Ge-25@580 sample.

The first spot related to the crystal surface reveals the predominance of O and Ge probably accompanied with a small residual amount of P. This is consistent with the Rietveld analysis that indicates the dominance of GeO_2 crystals, Figure S4(a). On the other hand, EDS data obtained for the bulk of sample contains a substantially higher amount of P than Ge (at%) suggesting germanium-phosphate rich crystalline phases and residual amorphous phosphate matrix, Figure S4(b).

Glasses with GeO_2 above 25 mol%

Glasses that contain >25 mol% of GeO_2 , prepared by the melt-quenching method, are partially crystallized, see Figure S5. This untreated Ge-30 sample exhibits the milky regions suggesting the beginning of spontaneous crystallization, which is an indication that the crystalline nuclei are already formed. Therefore, samples containing >25 mol% of GeO_2 are excluded from the present investigation since our main intention is to investigate the effect of induced crystallization on glasses (from amorphous to crystalline).

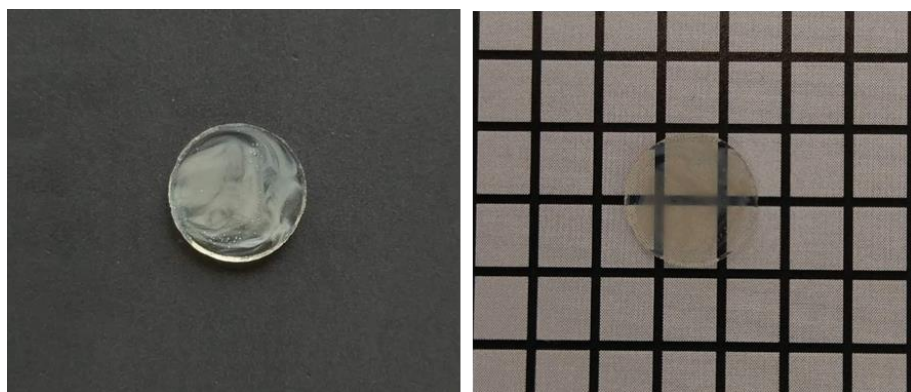


Figure S5. Non-treated Ge-30 sample.

Electronic/ionic contributions to the total conductivity

To further study the type of transport mechanism in studied glass-ceramics, we have performed the thermally stimulated current (TSC) measurements, which allowed us to probe the nature of the transport mechanism. In general, an ionically conducting glass exhibits a polarization in the DC field and thus, the electrical conductivity of such glass with metallic ion blocking electrodes at a constant temperature decreases with time. On the other hand, materials, which exhibit electronic

conductivity, do not show such an effect since metals are not blocking for electrons. In other words, for these electronic materials, DC conductivity is constant with time at a constant temperature.

Therefore, in order to prove that glass-ceramics investigated in this study are ionically conducting, TSC experiments were performed on Ge-25@580 with applied DC voltage, $U = 100$ V, at $200\text{ }^{\circ}\text{C}$ and for 90 min (please see black squares in Figure S6). As can be seen in Figure S6 the conductivity strongly decays for two orders of magnitude in time. Such decay is typical for ionic conductors due to the polarization of the charge carriers, in our case of the lithium ions that are accumulated on the electrodes.

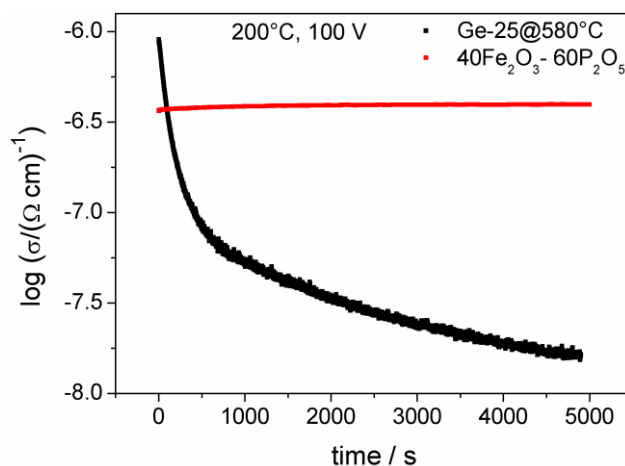


Figure S6. TSC experiments performed on Ge-25@580 glass-ceramic and 40Fe₂O₃-60P₂O₅ glass.

For comparison, pure electronic (polaronic) 40Fe₂O₃-60P₂O₅ glass was polarized using the same experimental conditions: applied DC voltage of 100 V, for 90 min. at $200\text{ }^{\circ}\text{C}$. As can be seen in Figure S6, this glass shows no time-dependent electrical conductivity. Such a behavior is typical for electronically conducting glasses.

The performed TSC experiments confirm that for the glass-ceramics studied in this paper, the electronic contribution to the total electrical conductivity is not identified proving that the nature of the transport mechanism is ionic.