1 *Supplementary Materials*

# Crystallization Behavior of Na2O-GeO2-P2O5 Glass System: (Micro)Structural, Electrical, and Dielectric Study

**Sara Marijan [1], Marta Razum [1], Kristina Sklepić Kerhač [1], Petr Mošner [2], Ladislav Koudelka [2], Jana Pisk [3], Andrea Moguš-Milanković [1], Željko Skoko [4],\* and Luka Pavić [1,\***

[1] Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia; smarijan@irb.hr, mrazum@irb.hr, ksklepickerhac@gmail.com, mogus@irb.hr, lpavic@irb.hr

[2] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, 53210 Pardubice, Czech Republic; petr.mosner@upce.cz, ladislav.koudelka@upce.cz

[3] Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia; jana.pisk@chem.pmf.hr

[4] Department of Physics, Faculty of Science, University of Zagreb, Bijenička 32, 10000 Zagreb, Croatia; zskoko@phy.hr

\* Correspondence: L. P. (lpavic@irb.hr), Ž. S. (zskoko@phy.hr)

## 1. IR-ATR spectroscopy
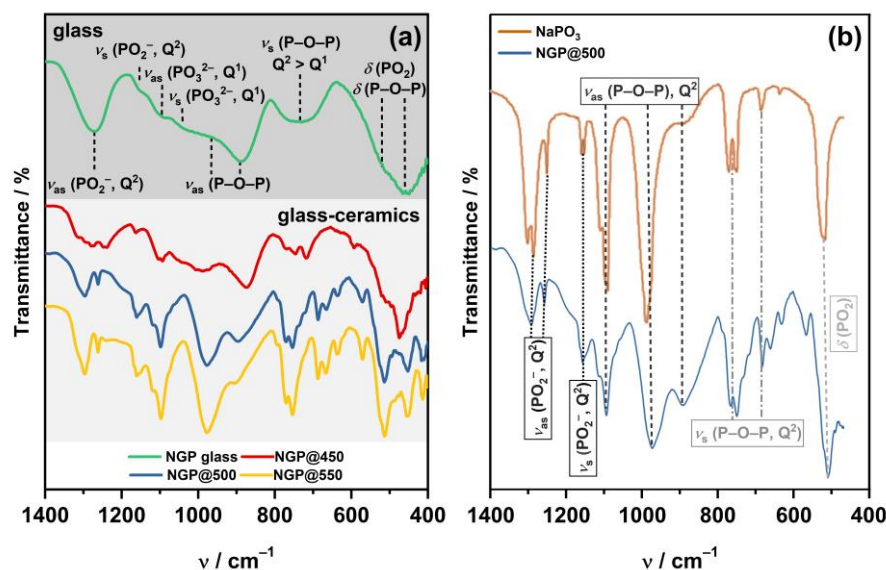


**Figure S1.** (a) IR-ATR spectra of all samples from this study and (b) comparison of IR-ATR apectra of **NGP@500** GC and NaPO3.

The IR-ATR spectrum of NGP glass, see Figure S1(a), exhibits distinct bands characteristic of metaphosphate ($Q^2$) glasses, and it also reveals indications of pyrophosphate units ($Q^1$), which is consistent with the O/P ratio of 3.1 [1]. The intense band observed at 1275 cm$^{-1}$, followed by shoulder at 1110 cm$^{-1}$ is indicative of the asymmetric and symmetric stretching of non-bridging oxygen atoms in $Q^2$ units, respectively [2,3], while the bands at 970 cm$^{-1}$ and 890 cm$^{-1}$ can be attributed to the asymmetric stretching vibrations of P–O–P groups in metaphosphate units, manifesting as chains, rings, and terminal groups [2,3]. Additionally, low intensity shoulders at 1150 cm$^{-1}$ and 1035 cm$^{-1}$ can be assigned to asymmetric and symmetric stretching of non-bridging oxygen atoms in $Q^1$ units, respectively, which presence in small quantities is in accordance with O/P ratio in studied glass. Furthermore, the symmetric stretching vibrations of P–O–P within $Q^2$ and $Q^1$ units are found in the range between 640–810 cm$^{-1}$

[2,3]. Moreover, the bands around ~460 cm⁻¹ and ~520 cm⁻¹ can be ascribed to the bending vibrations of P–O–P and PO₂ units within the metaphosphate framework[2,3]. Notably, the IR-ATR spectroscopy results for the initial glass correlate well with prior Raman spectroscopy findings[1].

In contrast to the broad and diffuse bands observed in the spectrum of the initial glass, the spectra of the prepared glass-ceramics exhibit well-defined, sharp signals characteristic of crystalline materials. As the heat-treatment temperature is elevated from 450°C to 550°C, a notable transformation in the appearance of the spectra becomes apparent. The spectrum of NGP@450 glass-ceramic exhibits initial signs of crystallization and the presence of a glass matrix. In contrast, the spectra of NGP@500 and NGP@550 glass-ceramics display remarkable similarity, reflecting a notably advanced stage of crystallization. Here, it's noteworthy to highlight that the acquired IR-ATR spectra of GC samples, characterized by a substantial amount of NaPO₃ crystal phase, exhibit a striking similarity to the results of the structural analysis of NaPO₃ documented in [4]. Additionally, the strong agreement observed between the IR-ATR spectra of the prepared GCs and the IR spectrum of the NaPO₃ crystal phase (SpectraBase®), see Figure S1(b), provides additional confirmation that NaPO₃ is the predominant phase within the samples.

## 2. SEM-EDS analysis
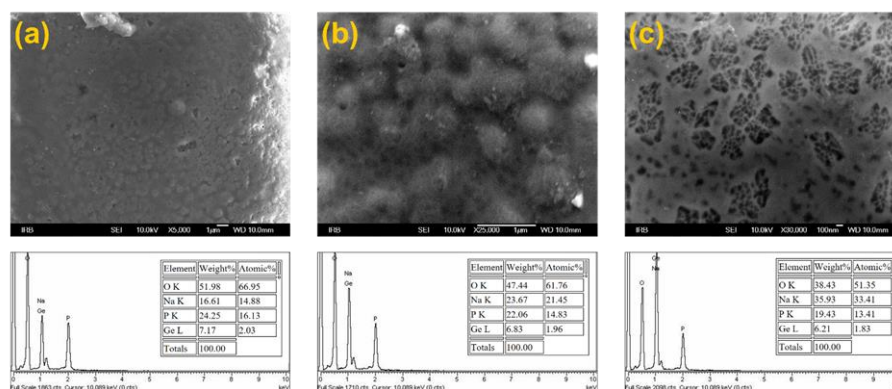


**Figure S2.** SEM images and EDS spectra of the **NGP@450** glass-ceramic surface: (a) area, (b) surface – separation and (c) surface - separation 2.
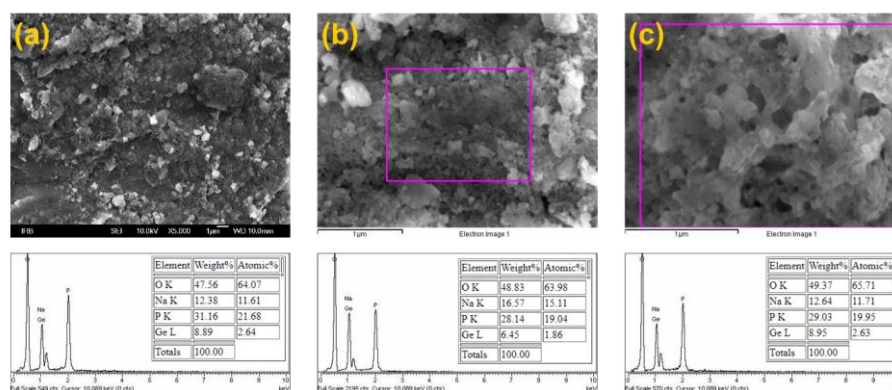


**Figure S3.** SEM images and EDS spectra of the NGP@500 glass-ceramic surface.

## 3. Electrical analysis

*3.1. Complex impedance plane– electrical equivalent circuit modelling*

**Table S1.** Fitting parameters obtained from EEC modeling of complex impedance spectra measured at 150 °C for the initial glass and glass-ceramics from this study

| Parameters | NGP | NGP@450 | NGP@500 | NGP@550 |
|---|---|---|---|---|
| $R_1$[a] ($\Omega$) | $3.65 \times 10^5$ | $3.06 \times 10^6$ | $5.03 \times 10^7$ | $1.96 \times 10^8$ |
| $A_1$[b] ($s^\alpha\ \Omega^{-1}$) | $2.27 \times 10^{-11}$ | $9.41 \times 10^{-12}$ | $4.29 \times 10^{-11}$ | $1.42 \times 10^{-11}$ |
| $\alpha_1$[c] | 0.90 | 0.94 | 0.86 | 0.84 |
| $C_1$[d] (F) | $6.22 \times 10^{-12}$ | $4.92 \times 10^{-12}$ | $1.50 \times 10^{-11}$ | $4.63 \times 10^{-12}$ |
| $R_2$[a] ($\Omega$) | - | $6.51 \times 10^6$ | $3.59 \times 10^8$ | $2.58 \times 10^8$ |
| $A_2$[b] ($s^\alpha\ \Omega^{-1}$) | - | $9.23 \times 10^{-10}$ | $6.56 \times 10^{-11}$ | $2.09 \times 10^{-10}$ |
| $\alpha_2$[c] | - | 0.60 | 0.71 | 0.66 |
| $C_2$[d] (F) | - | $2.95 \times 10^{-11}$ | $1.38 \times 10^{-11}$ | $4.80 \times 10^{-11}$ |
| $R_3$[a] ($\Omega$) | - | - | - | $4.12 \times 10^8$ |
| $A_3$[b] ($s^\alpha\ \Omega^{-1}$) | - | - | - | $2.77 \times 10^{-9}$ |
| $\alpha_3$[c] | - | - | - | 0.49 |
| $C_3$[d] (F) | - | - | - | $3.18 \times 10^{-9}$ |
| $A_4$[b] ($s^\alpha\ \Omega^{-1}$) | $8.85 \times 10^{-6}$ | $2.81 \times 10^{-7}$ | $2.37 \times 10^{-8}$ | $7.16 \times 10^{-8}$ |
| $\alpha_4$[c] | 0.91 | 0.67 | 0.40 | 0.81 |

[a] Individual resistance ($R$) values for each R-CPE circuit element in the proposed model. [b] $A$ – a constant (CPE capacitance) derived from the empirical impedance function, $Z_{CPE}^* = 1/A(i\omega)^\alpha$, measured in $s^\alpha\ \Omega^{-1}$ unit. [c] $\alpha$ – a constant ($0 \leq \alpha \leq 1$) determined from the empirical function, $Z_{CPE}^* = 1/A(i\omega)^\alpha$. When $\alpha = 1$ (true capacitor), the unit becomes $s\ \Omega^{-1} = F$. [d] Individual capacitance ($C$) values calculated for each R-CPE circuit element in the proposed model using the formula $C = A(\omega_{max})^{\alpha-1}$.

## 4. Dielectric analysis

*4.1. Complex Modulus Formalism*
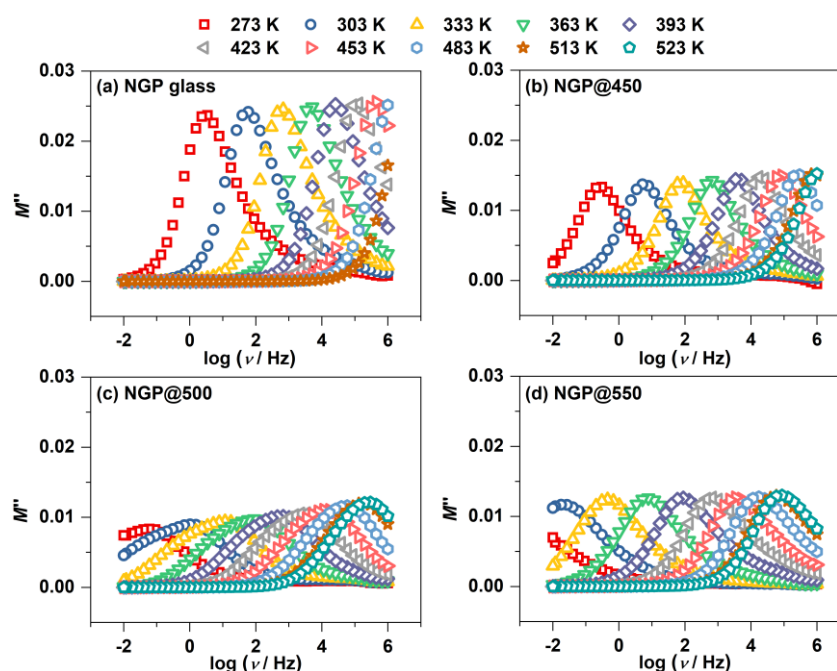


**Figure S4.** Spectra of imaginary moduli, $M''(\omega)$, for all samples.

## References

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