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Effect of controlled crystallization on polaronic transport in phosphate-based glass-ceramics

Luka Pavić1 | Juraj Nikolić1 | Manuel P.F. Graça2 | Benilde F.O. Costa3 | Manuel A. Valente2 | Željko Skoko4 | Ana Šantić1 | Andrea Moguš-Milanković1

1Division of Materials Chemistry, Ruđer Bošković Institute, Zagreb, Croatia
2I3N, Physics Department, University of Aveiro, Aveiro, Portugal
3CEMDRX, Physics Department, University of Coimbra, Coimbra, Portugal
4Department of Physics, Faculty of Science, University of Zagreb, Zagreb, Croatia

Correspondence
Andrea Moguš-Milanković, Ruđer Bošković Institute, Zagreb, Croatia
Email: mogus@irb.hr

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Abstract
The effect of induced crystallization on changes in electrical transport of two types of glass-ceramics, pure polaron conductive 40Fe2O3-60P2O5 (F40) (mol%) and predominantly polaronic 5Li2O-5ZnO-40P2O5-50WO3 (Li-50W) (mol%) was investigated. F40 glass-ceramics produced at low heat-treatment temperatures contain single-phase Fe3(P2O7)2 whereas at higher temperatures two more phases Fe4(P2O7)3 and Fe(PO3)3 are formed. Structural modifications strongly depend on the crystallization temperature and time. The appearance of crystalline phases studied by Mössbauer spectroscopy exhibits changes in Fe2+/Fetot ratio in crystalline/glassy phases. The detailed analysis of different iron sites allows their correlation with changes in electrical conductivity as crystallization progresses. Depending on the course of crystallization, the contribution of each phase to the overall conductivity is determined by the frequency dependence of \( Z'(\omega) \) and \( M'(\omega) \). DC conductivity shows a sharp decrease as Fe3(P2O7)2 phase appears and consequently glass matrix remains impoverished in Fe2+-Fe3+ pairs. In the multiphase systems prepared at higher crystallization temperatures, the overall electrical conductivity increases although the continuous grain boundaries along different crystalline grains play a limiting factor. In contrast, the slight conductivity change in Li-50W glass-ceramics upon crystallization is a result of remaining W\(^{5+}\)-W\(^{6+}\) pairs in the residual glassy phase. Independence of electrical transport on Li\(^+\) ions confirms predominantly polaronic transport in Li-50W glass-ceramics.

KEYWORDS
glass ceramics, induced crystallization, iron phosphate glass, Mössbauer spectroscopy, polaronic transport, structural properties

1 | INTRODUCTION

The recently revised definition of glass-ceramics states that the glass-ceramics are inorganic, nonmetallic materials prepared by controlled crystallization of glasses via different processing methods. They contain at least one type of functional crystalline phase and a residual glass.\(^1\) The transformation from glass to glass-ceramics takes place by a controlled process of nucleation and crystals growth giving rise to the evolved nano- and microstructures.\(^2,3\) Properties of glass-ceramics are strongly dependent on size, type, morphology and distribution of crystalline phases inside the glass.
matrix which offer vast possibilities for the development of these materials in diverse fields of applications.

In the past few years, the interest in investigating phosphate glasses and glass-ceramics has been increased. It is well known that phosphate-based glasses are interesting from a scientific and technological point of view due to their low melting temperature, high thermal expansion coefficient, and high ultraviolet transmission.\(^4\)\(^5\) On the other hand, their poor chemical durability can be significantly enhanced by the addition of various transition metal oxides (TMO) such as Fe\(_2\)O\(_3\), MoO\(_3\), or WO\(_3\).\(^6\)\(^9\) As a result, these glass systems are not just highly chemically durable, but also act as electronically conducting glasses with polaronic conduction mechanisms.\(^10\)\(^-\)\(^17\)

Among various TMO-phosphate glass systems, iron phosphates are best known for their exceptional chemical durability and high solubility of various nuclear waste compounds which sets the direction of their application as a host material for vitrification of nuclear wastes.\(^18\) In particular, it has been reported that the glass of molar composition 40Fe\(_2\)O\(_3\)·60P\(_2\)O\(_5\) shows the best combination of high chemical durability\(^7\)\(^,\)\(^19\) and low crystallization tendency.\(^7\)\(^,\)\(^20\)

The focus of so far published studies on induced crystallization of iron phosphate glasses was mainly on the structural changes which depend on glass composition and crystallization conditions but less on their influence on the electrical transport.\(^8\)\(^,\)\(^21\)\(^-\)\(^25\) Our recent investigations, however, show that the controlled crystallization appears to be a powerful tool for tailoring electrical properties of these materials.\(^26\)\(^,\)\(^27\) For instance, our study on the 10ZnO·30Fe\(_2\)O\(_3\)·60P\(_2\)O\(_5\) (mol%) glass system\(^26\) shows that in the initial stage of crystallization, the electrical conductivity decreases, whereas with further crystallization progress it rises as a consequence of an increase in the size of crystal grains and their different distribution within the glass matrix. Further, our investigation on the electrical properties of 40Fe\(_2\)O\(_3\)·60P\(_2\)O\(_5\) (mol%) glass-ceramic\(^27\) reveals that the thermally induced microstructural changes and the formation of various crystalline phases have a significant impact on electrical transport. In this glass-ceramic system, different electrical processes could be identified and their contribution to the overall electrical conductivity could be determined.\(^27\)

Another TMO which is very important for phosphate glasses is tungsten oxide. Several studies have shown that the addition of higher amounts of WO\(_3\) to phosphate glass leads to high thermal stability against crystallization and high glass transition temperatures.\(^28\)\(^-\)\(^30\) These properties are found to be strongly related to the incorporation of WO\(_3\) into phosphate glass.\(^29\)\(^-\)\(^34\) Moreover, glasses with high WO\(_3\) content contain clusters of WO\(_6\) octahedra which play a key role in polaronic transport mechanisms making these glasses highly conductive.\(^31\)\(^\)\(^32\)

Wide compositional flexibility of phosphate glasses offers a possibility to combine ionic conduction with polaronic transport by the introduction of highly mobile cations such as Li\(^+\), Na\(^+\), and Ag\(^+\) ions into TMO-phosphate systems. In such mixed ion-polaron glasses, the polaronic contribution arises from the polaron hopping between transition metal ions in different oxidation states,\(^11\)\(^12\) whereas the ionic conductivity is a result of the monovalent cations migrating through the glass network.\(^35\)\(^36\) From the technological point of view, mixed ion-polaron conduction is highly important for the cathode materials in batteries\(^37\)\(^,\)\(^38\) since the best performance is achieved when ionic transport is less than twice in magnitude than the polaronic one.\(^39\)\(^40\) While in glassy systems contributions of polaronic and ionic conductivity can be controlled by the glass composition and structure, the thermally induced crystallization represents an advantageous procedure for developing new ion-polaron materials due to the possibility of fine-tuning their electrical properties via microstructural changes.\(^41\)\(^,\)\(^42\)

Most recently, we have investigated electrical transport in zinc phosphate glasses which contain alkali\(^31\) and silver\(^32\) oxides in combination with WO\(_3\). The study revealed that the systematic replacement of Li\(_2\)O/Na\(_2\)O/Ag\(_2\)O by WO\(_3\) results in a sharp minimum in DC conductivity, which indicates a transition from predominantly ionic to predominantly polaronic conductivity. This result implies that these glass systems contain significant contributions of two types of charge carriers, ions, and polarons, which can both participate in the conduction process making these glasses prospective mixed conductors.

Considering the crystallization processes in phosphate glasses containing WO\(_3\), there are numerous reports on binary tungsten phosphate and tungsten fluorophosphate glass-ceramics, and their optical properties.\(^43\)\(^-\)\(^46\) However, reports on controlled crystallization of tungsten phosphate glasses containing alkali oxide are very rare.\(^47\)

The aim of this work was to systematically examine the effect of the controlled crystallization on the electrical conductivity of two glass systems: (i) pure polaron conductive 40Fe\(_2\)O\(_3\)·60P\(_2\)O\(_5\) (mol%) and (ii) predominantly polaron conducting 5Li\(_2\)O·5ZnO·40P\(_2\)O\(_5\)·5WO\(_3\) (mol%). The crystallization of the former system was controlled by varying both heat-treatment temperature and time in a wide range, for 1, 6, 12, and 48 h, which allowed us to correlate and supplement the results with our previous study on this system crystallized at different temperatures for 24 hours.\(^27\) On the other hand, crystallization of the latter glass system was achieved by heat treatment at different temperatures for 1 and 6 h. Such variations of the heat-treatment conditions enabled us to prepare glass-ceramics with different types and amounts of crystalline phases and to comprehensively investigate their roles in the electrical transport. Overall, this research provides a novel insight into the changes in electrical properties.
and contributes to a better understanding of mechanisms of charge transfer in the pure electronic and predominantly polaronic glass-ceramics.

2 | MATERIALS AND METHODS

2.1 | Parent glasses and glass-ceramics preparation

A detailed preparation procedure of the parent glasses of molar composition 40Fe₂O₃-60P₂O₅ (F40) and 5Li₂O-5ZnO-40P₂O₅-50WO₃ (Li-50W) has been reported in Refs. 27 and 31, respectively.

Both F40 and Li-50W parent glasses were prepared by standard melt-quench technique. Reagent grade materials for F40 glass were melted for 2 h at 1150-1200°C in Al₂O₃ crucibles. Afterward, melts were poured into preheated molds in the shape of long bars and annealed for 4-6 h in air at 450°C and then cooled to room temperature. On the other hand, reagent grade materials for Li-50W glass were melted at 1350°C in ambient air and then poured into a circular graphite mold. Obtained Li-50W glass was annealed for 3 h at 463°C and slowly cooled to room temperature. Prepared glasses were transparent being black in case of F40 and deep blue for Li-50W, see Figure S1 in Supporting Information.

The amorphous character of the glass samples was confirmed by Powder X-ray Diffraction (PXRD) analysis. The fraction of iron ions in different oxidation states, namely as Fe²⁺ and Fe³⁺, in two prepared glass bars of F40 composition was determined by Mössbauer spectroscopy. We found that for one glass bar the Fe²⁺/Fe₉₀₅ fraction was 0.16, whereas for another it was 0.18. The observed difference is due to the fact that Fe²⁺/Fe₉₀₅ fraction is highly sensitive to the melting conditions. However, since it is expected that such slight difference does not affect the crystallization process nor the electrical properties of as-prepared glass-ceramics, we have used both glass bars in further investigation; glasses from the first bar with 16% of Fe²⁺ were subjected to structural characterization of glass-ceramics by means of Mössbauer spectroscopy and those from the second bar where the concentration of Fe²⁺ was 18% were used for electrical characterization of glass-ceramics.

The fraction of tungsten ions in different oxidation states, namely as W⁵⁺ and W⁶⁺, in Li-50W glass was determined from the magnetization measurements using SQUID magnetometer. The fraction of W⁵⁺ was found to be 1.26%.

The glass transition temperature, T_g, and crystallization temperature(s), T_c, for F40 and Li-50W glasses were determined from their DTA and DSC curves, respectively. It is well known from the literature that F40 glass has a T_g at ≈520°C, and exhibits two wide exothermic peaks at ≈650 and ≈800°C that correspond to the crystallization temperatures.

The first exothermic peak which extends through a broad temperature range from 550 to 700°C is attributed to Fe₅(P₂O₇)₂, while the second one, which extends through somewhat narrower temperature range from 750 to 830°C, corresponds to Fe₄(P₂O₇)₃. It should be pointed out that even though the as-prepared F40 glasses contain slightly different Fe²⁺ concentration either 18% or 16%, the crystalline phases obtained in heat treatments are the same. Also, the temperatures of their emergence are slightly shifted, see Figure S2 in Supporting Information, but that does not influence the overall crystallization processes.

For Li-50W glass, the thermal events were determined from DSC measurements which were performed on powder samples (100 mg) with a diameter of ≈10 μm placed in an open platinum crucible under flowing nitrogen atmosphere at a heating rate of 10°C min⁻¹. The DSC curve shows T_g at approximately ≈470°C and two wide exothermic peaks with centers at ≈600 and ≈725°C, see Figure S3.

The induced crystallization of the parent F40 and Li-50W glasses was performed by thermal treatments of the samples in the form of ≈1-mm thick disks at controlled temperatures and times. F40 glasses were heated in Barnstead Tube Furnace 21100, with 10°C min⁻¹ in steady air atmosphere up to the selected temperature (530, 560, 590, 620, 670, 720, 770, 800°C) and held at that temperature for various times (1, 6, 12, 24, and 48 h).

The controlled crystallization of Li-50W glasses was performed in Nabertherm furnace by heating the sample with 10°C min⁻¹ in steady air atmosphere up to the selected temperature (600, 725 and 800°C) at which the sample was held for 6 h.

In this manuscript, the as-prepared glass-ceramics are labeled in accordance with their glass composition and crystallization time and temperature. For example, the sample F40-6@720 is prepared by heat treatment of F40 glass at 720°C for 6 h.

2.2 | Glass-ceramics characterization

PXRD patterns of prepared glass-ceramics were collected at room temperature (RT) by Philips automatic diffractometer in Bragg-Brentano geometry. In the experiment, Cu Kα radiation was used at 40 kV and 30 mA (PW 1820 model) and 45 kV and 40 mA (X'Pert MPD model). Intensity data were obtained in the 2θ angle range from 10 to 70°, with the step of 0.02°. Crystalline phase identification was done using the ICCD-PDF database. The amount of the crystalline phases was determined by the Rietveld method using an internal standard, ZnO powder. Rietveld analysis was performed with commercial software X’Pert HighScore (Plus).

The microstructure of the glass-ceramics was studied by Scanning Electron Microscopy FE-SEM JSM 7000 (JEOL).
Samples were not coated with an electrically conductive layer and the accelerating voltage was kept low.

$^{57}$Fe Mössbauer spectra were collected to characterize the valence state of iron ions and their coordination environment in the F40 glass-ceramic structures. The spectra were recorded at RT in transmission geometry in a constant acceleration type spectrometer using a $^{57}$Co/Rh source with a strength of 20 mCi. The fitting of the spectra was carried out with a set of Lorentzian lines, determined by least squares minimization. The isomer shifts were referenced to $\alpha$-Fe at RT.

Electrical properties were studied by Impedance spectroscopy (IS). The gold electrodes were sputtered onto both sides of $\approx$1-mm thick sample disks using Sputter coater SC7620. Complex impedance, $Z^*$, was measured using an impedance analyzer (Novocontrol Alpha-AN Dielectric Spectrometer, Novocontrol Technologies GmbH & Co.) over the frequency range from 0.01 Hz to 1 MHz at temperatures between 30 and 250°C. The temperature was controlled to an accuracy of $\pm$ 0.2 K. The data were analyzed using three interrelated formalisms: complex impedance, $Z^*$, complex electrical modulus, $M^*$, and complex conductivity, $\sigma^*$.

3 | RESULTS AND DISCUSSION

3.1 | Polaron glass-ceramics

3.1.1 | Structure of iron phosphate glass-ceramics

According to the DTA results, the temperatures of heat treatments of F40 glass are set to be in the temperature region between 530 and 800°C. Duration of heat treatment at each temperature (530, 560, 590, 620, 670, 720, 770, 800°C) varies from 1, 6, 12, 24 to 48 hours. It was previously reported that the three crystalline phases, namely $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ (PDF No: 01-080-2315), $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ (PDF No: 01-073-6768), and minor $\text{Fe}(\text{PO}_3)_3$ (PDF No: 01-089-8524) are created during crystallization. The appearance of each crystalline phase in the glass matrix depends on the time and temperature of heat treatment.

Figure 1 shows the PXRD patterns for F40 glass and glass-ceramics heat-treated at various temperatures for 6 and 48 hours. For F40 glass crystallized for 6 hours at 530 and 560°C, the PXRD patterns are free of diffraction lines showing a wide halo which confirms the amorphous state. With increasing heating temperatures up to 770°C, the diffraction lines that correspond to the pyrophosphate $\text{Fe}_3(\text{P}_2\text{O}_7)_2$ crystalline phase appear, while at 800°C the beginning of the formation of the second crystalline phase $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ is detected. The PXRD patterns for glass-ceramics prepared by heat treatments for 48 hours show diffraction lines related to the $\text{Fe}_3(\text{P}_2\text{O}_7)_2$ in the temperature range from 560 to 720°C. Furthermore, the increase in crystallization temperatures to 770 and 800°C results in the additional diffraction lines characteristic for $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ and $\text{Fe}(\text{PO}_3)_3$ phases. It should be noted that the heat treatment at higher temperatures causes a massive crystallization, which leads to the presence of all three crystalline phases embedded in a minor residual glassy phase. The appearance of the detected crystalline phase(s) is in accordance with the literature data.

The dependence of total crystallinity upon heat-treatment temperatures and times calculated using Rietveld analysis is exhibited in Figure 2. Generally, with increasing heat-treatment temperature and time, total amount of crystalline...
phase(s) increases. However, it is interesting to note that within the range of single crystalline phase, that is, up to 720°C, see Figure 1, the amount of Fe$_3$(P$_2$O$_7$)$_2$ increases with both time and temperature and reaches maximal value of 40 wt% (marked as a black-dashed line in Figure 2). Also, it should be noted that with increasing duration of heat treatments in this temperature range, the formation of Fe$_3$(P$_2$O$_7$)$_2$ phase is shifted to the lower temperatures. For example, for F40-1 the Fe$_3$(P$_2$O$_7$)$_2$ appears at 620°C while for F40-48, it is formed at 560°C. In the temperature region of 770-800°C, crystallinity sharply increases as a result of the formation of Fe$_4$(P$_2$O$_7$)$_3$ and Fe(PO$_3$)$_3$, see Figures 1 and 2.

Going further into the structural analysis it is important to point out that Fe$_3$(P$_2$O$_7$)$_2$ contains both Fe$^{2+}$ and Fe$^{3+}$ ions where Fe$^{2+}$ is in a specific trigonal prismatic coordination. In contrast, both Fe$_4$(P$_2$O$_7$)$_3$ and Fe(PO$_3$)$_3$ contain only Fe$^{3+}$ ions. Changes in the concentrations of Fe$^{2+}$ and Fe$^{3+}$ ions in the glass-ceramics are especially important for the interpretation of electrical properties.

### 3.1.2 Mössbauer spectroscopy

In order to determine the progress of the crystallization and changes in Fe$^{2+}$/Fe$_{tot}$ ratio of F40 glass-ceramics, Mössbauer spectroscopy was used. The room temperature $^{57}$Fe Mössbauer spectra of starting F40 glass which contains 16% of Fe$^{2+}$ ions and F40 glass-ceramics prepared by heat treatment for 24 hours are shown in Figure 3.

The Mössbauer hyperfine parameters, isomer shift, $\delta$, quadrupole splitting, $\Delta$, line width $\Gamma$, and a fraction of Fe$^{2+}$ are listed in Tables 1 and 2. Mössbauer spectra of starting F40 glass and sample heat-treated at 590°C are similar and can be decomposed into three sets of doublets using Lorentzian shapes. These doublets represent one doublet of Fe$^{2+}$ in an octahedral site and two central superimposed doublets related to the Fe$^{3+}$ in dominantly octahedral sites which do not exclude Fe$^{3+}$ in lower coordination number. These findings are consistent with earlier Mössbauer studies of iron phosphate glasses. The corresponding parameters, isomer shift $\delta = 1.18$ mm s$^{-1}$ and quadrupole splitting $\Delta = 2.25$ mm s$^{-1}$ for Fe$^{2+}$ and two for Fe$^{3+}$ sites of $\delta = 0.38$ mm s$^{-1}$ and $\delta = 0.37$ mm s$^{-1}$ as well as of $\Delta = 1.00$ mm s$^{-1}$ and $\Delta = 0.56$ mm s$^{-1}$ are observed for F40 glass. The difference in $\Delta$ for Fe$^{3+}$ ions in two sites is related to the higher environmental disorder of more intense site of Fe$^{3+}$. It is worth noting that the spectra of glass-ceramic heat-treated at 590°C show a slightly lower fraction of Fe$^{2+}$ having a value of 14%.

With increasing temperature to 620°C along with three doublets for Fe$^{2+}$ and Fe$^{3+}$, a new doublet having parameters $\delta = 1.20$ mm s$^{-1}$ and $\Delta = 4.36$ mm s$^{-1}$ appear in the Mössbauer spectrum. Such a high value of quadrupole splitting corresponds to the trigonal prismatic coordination of Fe$^{2+}$ ions characteristic for Fe$_3$(P$_2$O$_7$)$_2$ crystalline phase. This crystalline phase is formed in the entire temperature range 620-700°C as confirmed by PXRD. Furthermore, Mössbauer spectrum for glass-ceramic heat-treated at 620°C was analyzed by the superposition of five doublets attributed to Fe$^{2+}$ and Fe$^{3+}$ ions in both glass matrix (three doublets) and Fe$_3$(P$_2$O$_7$)$_2$ crystalline phase (two doublets). The difference between Fe$^{2+}$ ions in Fe$_3$(P$_2$O$_7$)$_2$ phase and residual glass matrix is visible in two doublets having values of quadrupole splitting, $\Delta = 2.37$ mm s$^{-1}$ and $\Delta = 4.36$ mm s$^{-1}$, which corresponds to two different Fe$^{2+}$ sites, one in octahedral (glass matrix) and the other one in trigonal prism (Fe$_3$(P$_2$O$_7$)$_2$ phase), Table 1.
### Table 1

Hyperfine parameters determined from the fitting of the spectra for F40 glass and glass-ceramics heat-treated at various temperatures between 590 and 750°C for 24 h.

<table>
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<th>Sample</th>
<th>$\delta$/mm s$^{-1}$</th>
<th>$\Delta E$/mm s$^{-1}$</th>
<th>$\Gamma$/mm s$^{-1}$</th>
<th>Iron ion site</th>
<th>Relative area/%</th>
<th>Attributed phase</th>
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<td>$\text{Fe}^{2+}$</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>$\text{Fe}^{3+}$– site II</td>
<td>—</td>
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<td></td>
</tr>
<tr>
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<td>1.20</td>
<td>4.34</td>
<td>0.30</td>
<td>$\text{Fe}^{2+}$</td>
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<td>$\text{Fe}_3(\text{P}_2\text{O}_7)_2$</td>
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<td></td>
<td>0.44</td>
<td>0.28</td>
<td>0.30</td>
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<tr>
<td></td>
<td>0.42</td>
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<td>0.30</td>
<td>$\text{Fe}^{3+}$</td>
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<tr>
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<td>0.34</td>
<td>0.42</td>
<td>0.35</td>
<td>$\text{Fe}^{3+}$</td>
<td>10</td>
<td></td>
<td>$\text{Fe}(\text{PO}_3)_3$</td>
</tr>
</tbody>
</table>

*Note:* The estimated error in $<\delta>$, $<\Delta E>$, and $<\Gamma>$ is ±0.01 mm/s. The isomer shifts are referenced to $\alpha$-Fe at RT.
As the crystallization temperature increases to 650 and 700°C, the shape of Mössbauer spectra is changed due to an increase in the amount of Fe$_3$(P$_2$O$_7$)$_2$ phase. In fact, doublet related to Fe$^{2+}$ ions in the glass matrix disappears indicating a decrease in the amount of Fe$^{2+}$ whereas doublet for Fe$^{2+}$ ions in Fe$_3$(P$_2$O$_7$)$_2$ phase becomes more intense. On the other hand, quadrupole splitting values for Fe$^{3+}$ ions in glass-ceramics heat-treated at 650 and 700°C decrease to $\Delta = 0.30$ and $\Delta = 0.27$ suggesting a less distorted local environment around the octahedral Fe$^{3+}$ sites. Deformation of the central doublets in Mössbauer spectra is attributed to the Fe$^{3+}$ ions in the glassy and crystalline phase.

Crystallization in the temperature range 750–830°C, see Figure 3B, leads to further changes in the glass-ceramic structures, that is, to the formation of the new crystalline phases, a dominant Fe$_4$(P$_2$O$_7$)$_3$ and Fe(PO$_3$)$_3$. It is evident that the fraction of Fe$^{3+}$ in the glassy phase decreases and finally disappears with the progress of crystallization. Moreover, along with two doublets for Fe$^{2+}$ and Fe$^{3+}$ in Fe$_3$(P$_2$O$_7$)$_2$ every newly formed crystalline phase shows a characteristic contribution observed in Mössbauer spectra. According to literature, the Fe$_4$(P$_2$O$_7$)$_3$ phase contains four Fe$^{3+}$ sites$^{47}$ while three Fe$^{3+}$ sites are found for Fe(PO$_3$)$_3$ phase$^{51}$, Tables 1 and 2.

Mössbauer parameters for Fe$^{3+}$ ions in Fe$_4$(P$_2$O$_7$)$_3$ are $\delta = 0.42$ and $\Delta = 066 \text{ mm s}^{-1}$, whereas for Fe$^{3+}$ ions in the Fe(PO$_3$)$_3$ the values are $\delta = 0.34$ and $\Delta = 0.42 \text{ mm s}^{-1}$. This is consistent with literature data$^{49,51}$ confirming that the Fe$^{3+}$ ions in these phases are situated in distorted octahedral coordination. At the same time, two doublets that correspond to the Fe$^{2+}$ and Fe$^{3+}$ in Fe$_3$(P$_2$O$_7$)$_2$ crystalline phase with a characteristic high value of quadrupole splitting for Fe$^{2+}$, $\Delta = 4.34 \text{ mm s}^{-1}$ are also present in the Mössbauer spectra.

Furthermore, higher values of $\delta = 0.50 \text{ mm s}^{-1}$ and $\Delta = 0.42 \text{ mm s}^{-1}$ for Fe$^{3+}$ in Fe$_3$(P$_2$O$_7$)$_2$ phase is attributed to the increase in environmental disorder around Fe$^{3+}$ ions as crystallization progresses. Concomitantly, for glass-ceramics heat-treated at 800 and 830°C, the deformation of the central doublets that correspond to the Fe$^{3+}$ in the new crystalline phases formed becomes smaller since both Fe$_4$(P$_2$O$_7$)$_3$ and Fe(PO$_3$)$_3$ crystalline phases contain only Fe$^{3+}$ ions. It is worth noting that during crystallization processes and increasing heat-treatment temperatures for all glass-ceramics investigated, there is no considerable change in the overall Fe$^{2+}$/Fe$_{tot}$ ratio, that is, fraction of Fe$^{2+}$ (changes only from 16% to 11%) as listed in Tables 1 and 2. As a conclusion, the evolution of Mössbauer spectra along with PXRD analysis clarify structural modifications and determine Fe$^{3+}$ and Fe$^{2+}$ ions coordination in both glassy and crystalline phases. The step in which the amount of Fe$^{3+}$ and Fe$^{2+}$ ions in each phase, glassy and crystalline, is specified plays a key role in further study of electrical properties of these pure polaronic glass-ceramics. Such a detailed analysis of Mössbauer spectra allows the identification of every Fe$^{3+}$ and Fe$^{2+}$ site and their significance in the electrical conductivity changes.

### 3.1.3 | Electrical properties of iron phosphate glass-ceramics

The effect of structural modifications induced by crystallization on the electrical conductivity spectra of

**TABLE 2** Hyperfine parameters determined from the fitting of the spectra for glass-ceramics heat-treated at 800 and 830°C for 24 hours

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta$/µm s$^{-1}$</th>
<th>$\Delta E_Q$/mm s$^{-1}$</th>
<th>$\Gamma$/mm s$^{-1}$</th>
<th>Iron ion site</th>
<th>Relative area/%</th>
<th>Attributed phase</th>
<th>Fe$^{2+}$/Fe$_{tot}$</th>
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<tr>
<td>@800</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Amorphous phase 0.12</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>0.38</td>
<td>1.00</td>
<td>0.40</td>
<td>Fe$^{2+}$</td>
<td>—</td>
<td>Fe$_3$(P$_2$O$_7$)$_2$</td>
<td></td>
</tr>
<tr>
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<td>1.20</td>
<td>4.34</td>
<td>0.30</td>
<td>Fe$^{2+}$</td>
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<td>Fe$_3$(P$_2$O$_7$)$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.38</td>
<td>0.35</td>
<td>Fe$^{3+}$</td>
<td>28</td>
<td>Fe$_3$(P$_2$O$_7$)$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.42</td>
<td>0.66</td>
<td>0.30</td>
<td>Fe$^{3+}$</td>
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<td>Fe$_4$(P$_2$O$_7$)$_3$</td>
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</tr>
<tr>
<td>@830</td>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>Amorphous Phase 0.11</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>0.38</td>
<td>1.00</td>
<td>0.40</td>
<td>Fe$^{2+}$</td>
<td>—</td>
<td>Fe$_3$(P$_2$O$_7$)$_2$</td>
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</tr>
<tr>
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<td>4.34</td>
<td>0.30</td>
<td>Fe$^{2+}$</td>
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<td>Fe$_3$(P$_2$O$_7$)$_2$</td>
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<tr>
<td></td>
<td>0.50</td>
<td>0.38</td>
<td>0.30</td>
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<td>Fe$_3$(P$_2$O$_7$)$_2$</td>
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<tr>
<td></td>
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<td>0.66</td>
<td>0.30</td>
<td>Fe$^{3+}$</td>
<td>35</td>
<td>Fe$_4$(P$_2$O$_7$)$_3$</td>
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</tr>
<tr>
<td></td>
<td>0.34</td>
<td>0.42</td>
<td>0.35</td>
<td>Fe$^{3+}$</td>
<td>19</td>
<td>Fe(PO$_3$)$_3$</td>
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<tr>
<td></td>
<td>0.29</td>
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<td>0.30</td>
<td>Fe$^{3+}$</td>
<td>1</td>
<td>FePO$_4$</td>
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</tbody>
</table>

*Note: The estimated error in <$\delta$>, <$\Delta E_Q$> and <$\Gamma$> is ±0.01 mm/s. The isomer shifts are referenced to α-Fe at RT.*
glass-ceramics prepared by heat treatments at 590, 620, 720, and 800°C for 48 hours is shown in Figure 4. For F40-48@590 sample, the conductivity spectra show two typical features; a plateau at a low frequency that corresponds to the DC conductivity, $\sigma_{DC}$, and a dispersion at higher frequencies which is related to the short-range polaronic transport within an amorphous glass network. With the increase in heat-treatment temperature, the shape of conductivity dispersion changes. According to the PXRD and analysis of Mössbauer spectra, heat treatments up to 720°C yield glass-ceramics which contain one Fe$_3$(P$_2$O$_7$)$_2$ phase whereas heat treatments at higher temperatures, 770-800°C, produce multiphase systems comprising three crystalline phases Fe$_3$(P$_2$O$_7$)$_2$, Fe$_4$(P$_2$O$_7$)$_3$, Fe(PO$_3$)$_3$, and glass matrix. Therefore, the observed changes in the shape of conductivity spectra can be related to a gradual formation of the abovementioned crystalline phase(s). Similar spectral features which emerged as a result of the progressed crystallization were also observed for glass-ceramics prepared at other heat-treatment times.

For all obtained glass-ceramics the DC conductivity, $\sigma_{DC}$, exhibits an Arrhenius temperature dependence with the characteristic activation energies for DC conductivity, $W_{DC}$, which can be determined from the relation: $\sigma_{DC} = \sigma_0 \exp(-W_{DC}/k_B T)$, where $k_B$ is Boltzmann constant and $T$ is the temperature. The values of $\sigma_{DC}$, $W_{DC}$, and $\sigma_0$ for F40 glass-ceramics prepared at different temperatures for 1 and 6 hours are listed in Table S1. A detailed discussion on the changes in $W_{DC}$ with crystallization of F40 glass is given in the following section.

To understand the impact of heat-treatment duration on polaronic transport, the trends of $\sigma_{DC}$ for all glass-ceramics are exhibited in Figure 5. As can be seen from the figure, three regions can be identified. The first region which is attributed to the lowest crystallization temperatures, <560°C, shows slight changes in $\sigma_{DC}$ due to an early beginning of the crystallization. In the temperature region 590-720°C, here denoted as region II, $\sigma_{DC}$ changes nonmonotonically: first showing a sharp decrease and then an increase with increasing heat-treatment temperature. The minimum in $\sigma_{DC}$ shifts to lower temperature as crystallization time increases from 1 to 48 h. It is interesting to note that the lowest value of $\sigma_{DC}$≈1×10$^{-9}$ (Ω cm)$^{-1}$ is observed for the glass-ceramics in which the relative amount of crystalline Fe$_3$(P$_2$O$_7$)$_2$ phase is 8-15 wt% (F40-6@620, F40-12@590, F40-24@590), compare Figures 2 and 5. On the other hand, the magnitude of minimum in $\sigma_{DC}$ is higher for F40-48 series, that is, for F40-48@560 glass-ceramic in which the amount of Fe$_3$(P$_2$O$_7$)$_2$ phase is 33 wt%.

![FIGURE 4](https://example.com/figure4.png)

**FIGURE 4** Conductivity spectra measured at various temperatures for F40-48 glass-ceramics prepared at (A) 590, (B) 620, (C) 720, and (D) 800°C.

![FIGURE 5](https://example.com/figure5.png)

**FIGURE 5** DC conductivity at 120°C for F40 glass-ceramics prepared at different heat-treatment temperatures and times.
These results indicate that the growth of Fe₃(P₂O₇)₂ phase within the glassy matrix has a dual role in the polaronic transport. First, the sharp decrease in the σ DC is a result of the impoverishment of the concentration of Fe²⁺-Fe³⁺ pairs in the dominant glass matrix. Second, the increase in σ DC with further increase in crystallization temperature up to 720°C is due to the increase of the amount of well-defined Fe₃(P₂O₇)₂ phase to ≈38-40 wt% for F40-24 and F40-48 glass-ceramics. Here, it can be inferred that a better connection of crystalline grains, and, hence, the formation of easier conduction pathways enhances the polaron mobility between Fe²⁺-Fe³⁺ pairs through and along Fe₃(P₂O₇)₂ crystallites.

In the third temperature region, 770-800°C, an additional increase in the σ DC is observed as new Fe₄(P₂O₇)₃ and Fe(PO₃)₃ phases are formed. An enhancement in σ DC with further increase in crystallization temperature up to 720°C is due to the increase of the amount of well-defined Fe₃(P₂O₇)₂ phase to ≈38-40 wt% for F40-24 and F40-48 glass-ceramics. Here, it can be inferred that a better connection of crystalline grains, and, hence, the formation of easier conduction pathways enhances the polaron mobility between Fe²⁺-Fe³⁺ pairs through and along Fe₃(P₂O₇)₂ crystallites.

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3.1.4 | Electrical relaxation and activation energies

As mentioned in the previous section, the occurrence of the crystalline phases in glass-ceramics causes visible changes in the shape of the conductivity spectra, see Figure 4. However, it is not possible to extract information on the electrical processes within different phases (crystalline/glassy) in glass-ceramics from the conductivity spectra. Hence, we attempt to identify them and separate their contributions to the overall electrical conductivity by analyzing relaxation processes detectable in the frequency dependence of imaginary part of impedance, Z'(ω) and electrical modulus, M*(ω). The complex electric modulus M*(ω) is defined as an inverse of complex permittivity, ε*: M*(ω) = 1/ε* = ε'/((ε')² + (ε'')²) + je''/((ε')² + (ε'')²) = M'(ω) + jM''(ω), where j = √−1. This formalism suppresses the contribution of the DC conductivity and electrode polarization effects which dominate at lower frequencies.

It is well known that the spectra of M'(ω) and Z'(ω) may show one or more maxima depending on the presence of different phases within a material. The characteristic frequency of each maximum in M'(ω) and Z'(ω), fₘ and fₙ, is related to the relaxation time, τₘ and τₙ via relation fₘ,Zₙ = 1/(2πτₘ,Zₙ). It should be pointed out that the M'(ω) spectra are dominated by the processes with small capacitance whereas Z'(ω) spectra are related to the processes with high resistivity values.

Figure 6 shows the spectra of normalized M'(ω) and Z'(ω) for F40-24 glass-ceramics prepared at (A) 590°C and (B) 800°C. Considering the relaxation processes in F40-24@590 glass-ceramics, it can be seen that Z'(ω) shows a broad slightly asymmetric peak indicating two relaxation processes, whereas M'(ω) exhibits a single peak located at much higher frequencies. The two contributions in the Z'(ω) spectrum which are related to the Fe₃(P₂O₇)₂ phase and grain boundaries, respectively, are separated using the nonlinear least square method with Lorentzian function approximation and their characteristic relaxation frequencies, f_ZCP₁ and f_Zgb, are
determined. It is important to note that these two maxima are nearly overlapped indicating close relaxation times of contributions from crystalline Fe₃(P₂O₇)₂ and grain boundary. These results are consistent with our previous study where the resistivity values of Fe₃(P₂O₇)₂ crystalline phase and grain boundaries are of the same order of magnitude, ≈3×10⁷ Ω and ≈7×10⁷ Ω, respectively.

On the other hand, the maximum in $M''(ω)$ observed at much higher frequencies corresponds to the phase with the lowest value of capacitance and is attributed to the dominant glassy phase. Here, it should be mentioned that the contribution of the glass matrix cannot be resolved from the complex impedance plot but using electric modulus formalism. From this formalism, the characteristic relaxation frequency for the glassy phase in F40-24@590 glass-ceramic can be easily identified and determined, see Figure 6A.

With increasing heat-treatment temperature to 800°C, the $M''(ω)$ and $Z''(ω)$ spectra behave differently when compared with the previous sample, showing two maxima in $M''(ω)$ at high and intermediate frequencies and one maximum in $Z''(ω)$ at low frequencies, see Figure 6B. The two distinguished maxima in $M''(ω)$ correspond to the relaxation processes in dominant Fe₄(P₂O₇)₃ (higher frequency) and Fe₃(P₂O₇)₂ (lower frequency) phases, whereas maximum in $Z''(ω)$ is related to the process with higher relaxation time associated with grain boundaries. Figure 6C,D represents an Arrhenius plot for $σ_{DC}$ and relaxation frequencies, $f_{M''1}$, $f_{M''2}$, $f_{Z''1}$, and $f_{Z''2}$ from which the activation energies for each contribution, that is, glass matrix, Fe₃(P₂O₇)₂ and Fe₄(P₂O₇)₃ crystalline phases and grain boundaries are calculated and summarized in Table 3.

Figure 7 exhibits the dependence of activation energy of total DC conductivity, $W_{DC}$, and activation energies for different relaxation processes determined using $M''(ω)$ and $Z''(ω)$ spectra on the crystallization temperature for F40-24 glass-ceramics. In the temperature region I, the $W_{DC}$ starts to decrease. At the same time, three contributions to the overall conductivity could be distinguished and their activation energies could be determined; $W_{gm}$ for the glass matrix, $W_{CP1}$ for the Fe₃(P₂O₇)₂ phase and $W_{gb}$ for the grain boundaries, see Table 3 and Figure 7. The values of $W_{CP1}$ and $W_{gb}$ are similar ≈0.65 eV and are higher than $W_{DC} = 0.57$ eV. However, the values of $W_{gm}$ for glass matrix are found to be unexpectedly low ≈0.45 eV in the entire temperature region II.

In the transition from the region I to region II, the $W_{DC}$ starts to decrease. At the same time, three contributions to the overall conductivity could be distinguished and their activation energies could be determined; $W_{gm}$ for the glass matrix, $W_{CP1}$ for the Fe₃(P₂O₇)₂ phase and $W_{gb}$ for the grain boundaries, see Table 3 and Figure 7. The values of $W_{CP1}$ and $W_{gb}$ are similar ≈0.65 eV and are higher than $W_{DC} = 0.57$ eV. However, the values of $W_{gm}$ for glass matrix are found to be unexpectedly low ≈0.45 eV in the entire temperature region II.

With increasing heat-treatment temperature, in the region II, the fraction of Fe₃(P₂O₇)₂ phase increases causing a decrease in $W_{DC}$ down to the plateau of 0.48 eV. Moreover, for F40-24@720 glass-ceramics, the activation energies

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Region</th>
<th>$W_{DC}$/eV</th>
<th>$W_{gm}$/eV</th>
<th>$W_{CP1}$/eV</th>
<th>$W_{CP2}$/eV</th>
<th>$W_{gb}$/eV</th>
</tr>
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<td>F40 glass</td>
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<td>0.62</td>
<td>0.62</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>F40-24@530</td>
<td>(I)</td>
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<td>0.62</td>
<td>—</td>
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<td>—</td>
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<tr>
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<td>0.65</td>
<td>0.63</td>
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<td>—</td>
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<tr>
<td>F40-24@590</td>
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<td>—</td>
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</tr>
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<td>F40-24@770</td>
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<td>0.49</td>
<td>0.33</td>
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<td>0.54</td>
<td>—</td>
<td>0.49</td>
<td>0.32</td>
<td>0.58</td>
</tr>
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</table>

FIGURE 7 Dependence of activation energy of total DC conductivity, $W_{DC}$, and activation energies for each contribution to the total electrical conductivity (glass matrix, crystal phases, and grain boundary) on the heat-treatment temperature for F40-24 glass-ceramics.
$W_{\text{CP1}}$ and $W_{\text{gb}}$ reveal an identical trend, having higher values of 0.52 eV and 0.54 eV, respectively. This result agrees well with the PXRD analysis which showed that a two-phase system comprising glass matrix and Fe$_3$(P$_2$O$_7$)$_2$ crystalline phase, exists in region II. Besides, it seems that the activation energy for glass matrix, $W_{\text{gm}}$, is independent of the heat-treatment temperatures.

The transition from region II to region III is accompanied by an increase in $W_{\text{DC}}$ indicating additional structural changes. The three contributions present here, and their activation energies, $W_{\text{CP1}}$, $W_{\text{CP2}}$, and $W_{\text{gb}}$, are related to the Fe$_4$(P$_2$O$_7$)$_3$, Fe$_3$(P$_2$O$_7$)$_2$ phases and grain boundaries, respectively. In region III, the fraction of glass matrix reduces significantly and Fe$_4$(P$_2$O$_7$)$_3$ becomes a dominant crystalline phase. Therefore, it can be concluded that the formation of Fe$_4$(P$_2$O$_7$)$_3$ phase causes a steep increase in $\sigma_{\text{DC}}$ as shown in Figure 5. Indeed, the corresponding activation energy, $W_{\text{CP2}}$, determined for glass-ceramics prepared at 770 and 800°C shows the lowest values equal to 0.33 and 0.32 eV, respectively. The contribution of Fe$_3$(P$_2$O$_7$)$_2$ phase which appears as a second maximum in $M''(\omega)$, Figure 6B, exhibits activation energy of $\approx$0.49 eV which is slightly lower than that of $W_{\text{CP1}} \approx$0.52 eV in the region II. Both $W_{\text{CP1}}$ and $W_{\text{CP2}}$ values are lower than the activation energy for overall DC conductivity, $W_{\text{DC}}$. The reason for higher $W_{\text{DC}}$ value lies in the high activation energy of grain boundaries, $W_{\text{gb}}$, with a value of $\approx$0.60 eV. It could be concluded that in the multiphase systems obtained at high heat-treatment temperatures, region III, the formation of continuous grain boundaries along different crystalline grains is responsible for high $W_{\text{gb}}$. Thus, the high activation energy of grain boundaries acts as a limiting factor for the overall electrical transport. Nevertheless, the facilitating role of easy conductive pathways through the crystalline phases (Fe$_4$(P$_2$O$_7$)$_3$ in particular) prevails the limiting role of the grain boundary and these highly crystalline multiphase systems exhibit highest DC conductivity among all F40 glass-ceramics, see Figure 5.

### 3.2 Predominantly polaron conductive glass-ceramics

#### 3.2.1 Structural characterization of lithium tungsten glass-ceramics (Li-50W)

Structural changes induced by the heat treatments of Li-50W glass at 600, 725, and 800°C for 6 hours are exhibited in Figure 8. PXRD patterns for Li-50W@600 and Li-50W@725 samples show no diffraction lines which indicate their amorphous structure. However, as can be seen from the SEM micrograph of Li-50W@600 sample, see Figure S4A, well-defined dendritic microstructures related to an initial stage of crystallization are present on the surface of this system. At crystallization temperature of 800°C, the diffraction lines corresponding to the two polymorphs of W$_2$O$_5$(PO$_4$)$_2$, orthorhombic (ICSD no: 50 742) and monoclinic (ICSD no: 24 072), appear in the PXRD pattern. Some barely detectable lines of W$_{12}$P$_8$O$_{52}$ (ICSD no: 24 832) can also be found in this pattern. To gain a better insight into the formation of crystalline phases for this sample, we have crystallized Li-50W glass at the same temperature, 800°C, but only for 1 hour. The PXRD pattern of this sample is also displayed in Figure 8. Interestingly, it seems that all three phases also crystallize when heat treatment lasts for 1 hour and prolonging the heat-treatment time to 6 hours only causes their further simultaneous growth. However, as can be seen from the SEM micrograph in Figure S4B, in the Li-50W glass-ceramic prepared at 800°C for 6 hours along with well-defined W$_2$O$_5$(PO$_4$)$_2$ crystals, a large amount of about 50 wt% of glass matrix is still present despite the high crystallization temperature and relatively long heating time. This is in line with the fact that glasses containing a lower amount of WO$_3$ and higher alkali content do not crystallize.

It should be noted that both W$_2$O$_5$(PO$_4$)$_2$ polymorphs contain tungsten ions in the W$^{5+}$ oxidation state and their structure is built up from corner-sharing PO$_4$ tetrahedra and WO$_6$ octahedra, where two WO$_6$ octahedra are linked together through a bridging oxygen atom to form a W$_2$O$_{11}$ di-octahedral unit. Without going into further details, the main structural difference between the two polymorphic forms is evident in the two terminal W-O bonds arranged in different directions. From the point of view of electrical investigations of glass-ceramics, to identify the contributions of such structurally similar crystalline phases in the overall conduction process is a challenging task.
3.2.2 | Electrical properties

Conductivity spectra for Li-50W@600 sample shown in Figure S5, illustrate the typical spectra for polaronic glasses showing long \( \sigma_{\text{DC}} \) plateau at low frequencies and dispersion at high frequencies. For Li-50W@800 glass-ceramics, changes in the shape of conductivity spectra, which get more pronounced with increasing temperature, are related to the formation of \( W_2O_3(PO_4)_2 \) crystalline phases. The obtained values of activation energy for DC conductivity, \( W_{\text{DC}} \), for Li-50W@600 and Li-50W@800 samples are 0.49 and 0.52 eV, respectively, whereas for parent Li-50W glass \( W_{\text{DC}} \) is found to be 0.45 eV.

Figure 9A shows the dependence of \( \sigma_{\text{DC}} \) measured at 150°C on the crystallization temperatures. The values for \( \sigma_{\text{DC}} \) are \( 3.4 \times 10^{-7} \) (Ω cm)\(^{-1} \) and \( 1 \times 10^{-7} \) (Ω cm)\(^{-1} \) for Li-50W@600 and Li-50W@800, respectively, which is just slightly lower than \( \sigma_{\text{DC}} \) of nontreated parent glass. Thus, it seems that the \( \sigma_{\text{DC}} \) is nearly independent of the heat treatments, that is, the formation of \( W_2O_3(PO_4)_2 \) crystalline phases. While both \( W_2O_3(PO_4)_2 \) polymorphs contain tungsten in \( W^{6+} \) oxidation state, the \( W^{5+}-W^{6+} \) pairs which remain in the residual glassy phase play an important role in keeping the mobility of polarons, and hence \( \sigma_{\text{DC}} \) remains almost unchanged. As mentioned earlier, for Li-50W glass, the \( W^{5+}/W_{\text{tot}} \) fraction is relatively low, 1.26%. However, it was previously reported\(^ {31} \) that despite such a low \( W^{5+} \) concentration, Li-50W glass exhibits very high polaronic conductivity. Thus, it is likely that a slight decrease in the number of \( W^{5+}-W^{6+} \) pairs in the glassy phase due to a formation of crystalline phases is responsible for a slight decrease in \( \sigma_{\text{DC}} \) of Li-50W glass-ceramics.

Considering the composition of the parent Li-50W glass, it can be argued that a small concentration of \( Li^+ \) ions (5 mol%) might have some impact on the electrical conductivity of Li-50W glass-ceramics. However, we have previously reported\(^ {31} \) that the dominant conduction mechanism in Li-50W glass is polaronic and since there are no significant changes in \( \sigma_{\text{DC}} \) for the obtained glass-ceramics, it can be concluded that in these materials, the polaronic transport through the glassy phase has a key role.

Another aspect of the analysis of the electrical properties of Li-50W glass-ceramics is the evaluation of the relaxation times using the frequency response of \( Z''(\omega) \) and \( M''(\omega) \). As mentioned earlier, the \( Z''(\omega) \) and \( M''(\omega) \) spectra are suitable for the identification of the resistive component and the component having high capacitance, respectively.

Figure 9B exhibits the normalized \( Z''(\omega) \) and \( M''(\omega) \) spectra for Li-50W@600 sample showing practically overlapped peaks suggesting that both bulk responses, that is, localized relaxation and nonlocalized conductivity, are due to the same relaxation process. This behavior implies that after heat treatment at 600°C, the electrical relaxation occurs within a dominant glassy phase in a very similar manner as in the parent Li-50W glass. This is in a good agreement with PXRD analysis and SEM microscopy, see Figure 8 and Figure S4. On the other hand, with increasing crystallization temperature to 800°C, the three maxima in \( Z''(\omega) \) and one maximum in \( M''(\omega) \) spectrum are determined, see Figure 9C. The relaxation frequencies and activation energies calculated from each maximum in \( Z''(\omega) \) and \( M''(\omega) \) spectra for Li-50W@600 and Li-50W@800 samples are listed in Table S2a,b.

Comparable values of the relaxation frequency, \( f_{Z''} = 2.0 \times 10^4 \) Hz and \( f_{M''} = 3.2 \times 10^4 \) Hz, for Li-50W@600 sample confirm a single relaxation process which corresponds to the glass matrix. In contrast, for Li-50W@800 glass-ceramics, the three contributions are separated from \( Z''(\omega) \) spectrum. The first relaxation, at the lowest frequency, is related to the grain boundaries having a value of activation energy, \( W_{\text{gb}} = 0.65 \) eV. The second barely detectable relaxation at a higher frequency is probably connected to the formation of one of the \( W_2O_3(PO_4)_2 \) polymorphs with \( W_{\text{Cg1}} = 0.54 \) eV. The most intense \( Z''(\omega) \) maximum at even higher frequencies shows activation energy of \( W_{\text{Cg2}} = 0.63 \) eV and could be attributed to another \( W_2O_3(PO_4)_2 \) polymorph with higher wt%
The crystallization processes in Li-50W glass-ceramics are related to the formation of two polymorphs of W_{2}O_{3}(PO_{4})_{2} phase. DC conductivity slightly decreases upon crystallization due to the decrease in the concentration of W^{2+}-W^{6+} pairs in the residual glassy phase.

Considering the lack of significant change in $\sigma_{DC}$ of glass-ceramics compared to predominantly polaron conducting starting glass, it can be concluded that the electrical transport in these crystallized glasses is also polaronic in nature and independent of Li^{+} ions.

This work combines the course of crystallization processes and determination of each contribution to the overall electrical conductivity in F40 and Li-50W glass-ceramics. The structural modifications caused by induced crystallization have a key role in the polaronic transport mechanism in these two types of glass-ceramics.

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**ORCID**

Luka Pavić [https://orcid.org/0000-0003-2232-6602](https://orcid.org/0000-0003-2232-6602)

Andrea Moguš-Milanković [https://orcid.org/0000-0001-6686-6470](https://orcid.org/0000-0001-6686-6470)

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