High Electronically Conductive Tungsten Phosphate Glass-Ceramics

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Received: 19 November 2020; Accepted: 12 December 2020; Published: 15 December 2020

Abstract: High electronically conductive tungsten phosphate glass-ceramics have been prepared by the controlled crystallization of binary 60WO3–40P2O5 glass in the temperature range from 700 to 935 °C and for 1 to 24 h. The substantial increase in the conductivity for four orders of magnitude is a result of the formation of electronically conductive W2O3(PO4)2 and WO3 phases. At low crystallization temperature the dominant W2O3(PO4)2 phase is created, whereas at 935 °C for 24 h the formation of semiconducting WO3 crystallites of an average size of 80 nm enhances the conductivity to the highest value of 1.64 × 10−4 (Ω cm)−1 at 30 °C. The course of the crystallization and its impact on this exceptionally high electronic transport of binary tungsten phosphate glass-ceramics has been discussed in detail. Since such highly electronically conductive WO3-based glass-ceramics have a great potential as cathode/anode materials in solid state batteries and as electrocatalysts in fuel cells, it is of interest to provide a novel insight into the improvement of their electrical properties.

Keywords: binary tungsten phosphate glass-ceramics; crystallization; electronic transport; W2O3(PO4)2 phase; semiconducting WO3 phase

1. Introduction

The interest in glass-ceramics has grown exponentially in the recent years due to the novel and useful physical properties that can be obtained by controlling the crystallization process in the glass. Glass-ceramics 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 nano- and micro-structures [2]. The physical properties of glass-ceramics are strongly dependent on the size, type, morphology, and distribution of crystalline phases inside the glass matrix, all of which can be tuned by changing the crystallization conditions. For this reason, many functional glass-ceramics with improved mechanical, electrical, magnetic, and optical properties have been developed through the controlled glass crystallization. In particular, a significant scientific effort has been made to develop glass-ceramics which are applicable in the field of electronics and solid-state batteries as electrolytes or cathode/anode materials. However, ionic as well as electronic transport through the glass-ceramic material is by no means simple. Both conduction mechanisms depend on various structural and morphological characteristics of the material. For example, a study by Schirmeisen et al. [3] on lithium-ion conducting silicate glass-ceramics revealed a pivotal role of the
interfacial regions that act as local electrical short circuits leading to an increase of the ionic conductivity of nanostructured glass-ceramics as compared to the corresponding glass.

Likewise, the electronically conductive oxide glasses containing transition metal oxides such as WO₃, MoO₃, V₂O₅, and Fe₂O₃ appear to be versatile materials whose transport properties can be readily tailored by crystallization. In these glasses, electronic conduction occurs by the electron transfer between transition metal ions in different valence states following the small polaron hopping mechanism [4–10]. Expectedly, the crystallization strongly influences the formation of polarons and course of their transport. For instance, Garbarczyk and coworkers performed a series of studies on V₂O₅-P₂O₅-based glass-ceramics [11–16] and demonstrated that the polaronic transport can be greatly enhanced by the formation of interfacial regions around nano-crystalline grains. The authors postulated that these interfacial regions have a higher fraction of V⁴⁺–V⁵⁺ pairs and form an extensive network of electronic conduction paths which increases polaronic conductivity. On the other hand, our studies on the crystallization of Fe₃O₄-P₂O₅-based glasses [17,18] highlight the importance of nature of the phases that crystallize from the glass matrix. By widely varying the temperature and time of the heat-treatments, we were able to assign the changes in the conductivity to the interplay between amorphous glassy phase and crystalline mixed-valent iron and single-valent iron phosphate phases. In these systems, the conductivity decreases in the early stage of nano-crystallization due to the impoverishment of the continuous amorphous phase with Fe²⁺–Fe³⁺ pairs but increases with further formation of the interfacial region along well-defined interconnected crystalline grains.

Considering the crystallization processes in phosphate glasses containing WO₃, there are many reports on tungsten oxide-based and tungsten fluorophosphate glass-ceramics, and their structural and optical properties [19–22]. Also, there are several reports on the transport mechanisms of the crystalline monophosphate tungsten bronze of the general formula (PO₄)₄(WO₃)₂m [23–25] and tungsten oxide, WO₄; crystals [26,27]. Recently, Moore et al. [28] revisited highly conductive WO₃-TiO₂-P₂O₅ glass-ceramic systems which were first reported by Aitken [26]. They showed that at low crystallization temperature tungsten oxide and titanium pyrophosphate are formed whereas at high temperature (PO₂)₄(WO₃)₂m (m = 4–7) phases are created. Therefore, they concluded that the electrically conducting phases in these glass-ceramics are tungsten phosphates rather than tungsten suboxides reported hitherto.

Most recently, we investigated electrical transport in zinc phosphate glasses which contain alkali [29] and silver [30] oxides in combination with WO₃. Our study showed that the exceptionally high electrical conductivity of WO₃-rich glasses is a result of the formation of tungsten clusters of WO₆ octahedra that facilitate the mobility of polarons. Further, our study on the controlled crystallization of 5Li₂O-5ZnO-40P₂O₅-50WO₃ (mol%) glass demonstrated that heat-treatments up to 800 °C induce crystallization of two polymorphs of W₂O₅(PO₄)₂ and a minor W₁₂P₈O₅₂ phase [31]. The conductivity of obtained glass-ceramics is purely polaronic and close in value to that of the parent glass.

The present work aims to investigate the effect of the controlled crystallization on the electrical conductivity of binary 60WO₃-40P₂O₅ (mol%) glass. The crystallization processes were induced by heat-treatments at different temperatures and times which enabled us to prepare glass-ceramics with various amounts of crystalline phases and comprehensively examine their role in electrical transport. According to our best knowledge, this is the first systematic study on the crystallization of binary tungsten phosphate glasses and its role in the enhancement of their transport properties.

2. Materials and Methods

The parent glass 60WO₃-40P₂O₅ (mol%) was prepared by a conventional melt-quenching technique using an analytical grade of H₃PO₄ and WO₃. The mixture of raw materials was firstly homogenized, calcined up to 600 °C, and held for 2 h in order to remove the water. The reaction mixture was then melted at 1350 °C in a platinum crucible with a lid and held at that temperature for 20 min. The melt was subsequently poured into a preheated graphite mold and annealed for 2 h at 515 °C (5 °C below T_g). After cooling to room temperature (RT), the amorphous character of obtained dark blue glass was checked by X-ray diffraction analysis.
Based on the glass transition temperature ($T_g$) and glass crystallization temperature ($T_c$), heat-treatment temperatures for induced crystallization of glasses were selected as 700, 800, and 935 °C. The induced crystallization was performed in Nabertherm LHT 04/17 furnace with 10 °C/min heating rate and in steady air atmosphere. In the first series of experiments, the powder of 60WO$_3$-40P$_2$O$_5$ glass was pressed in ~0.7 mm thick pellets and heat-treated for 1 and 6 h at 700 and 800 °C and 1, 12, and 24 h at 935 °C. The obtained glass-ceramics were mechanically strong and their color changed from blue to green with increasing crystallization time and temperature. In order to compare crystallization of the pelleted glass powder and bulk glass, the second set of experiments included the crystallization of 60WO$_3$-40P$_2$O$_5$ glass in the form of ~1 mm thick discs for 1 and 12 h at 935 °C. However, the obtained glass-ceramics had much lower mechanical strength and were more prone to cracking in contrast to those prepared from pellets. The as-prepared glass-ceramics were labelled in accordance with their crystallization time and temperature where P and B stand for pellet and bulk crystallization, respectively. For example, P-935-1h glass-ceramic was prepared by heating glass pellet at 935 °C for 1 h.

X-ray diffraction data was collected at RT on Bruker D8 Discover diffractometer equipped with LYNXEYE XE-T detector, in Bragg-Brentano geometry. Rietveld structure refinement was performed in HighScore Xpert Plus program 3.0. Vesta was used for crystal structure visualization [32]. Refinement was carried out by using the split-type pseudo-Voigt profile function and the polynomial background model. Isotropic vibration modes were assumed for all atoms. During the refinement, a zero shift, scale factor, half-width parameters, asymmetry, and peak shape parameters were simultaneously refined. Microstructural information was also obtained in the course of Rietveld refinement with LaB$_6$ used as instrumental broadening standard.

The microstructure and elemental analysis of the prepared glass-ceramics were studied by field emission scanning electron microscopy FE-SEM JSM 7000 (JEOL, Welwyn Garden City, UK) equipped with the Oxford Instruments EDS/INCA 350 energy dispersive X-ray analyzer (EDS).

The density of the selected glass-ceramic samples, P-935-1h and P-935-24h, was determined at RT by the Archimedes method. Deionized water was used as buoyancy liquid. Measurements were done on three samples of both glass-ceramics and the average density for each glass-ceramic is reported. The random error in the density values was found to be ±1%. The relative density was estimated by comparing the measured density with the theoretical one calculated by the rule of mixtures considering 5.32 g/cm$^3$ and 7.29 g/cm$^3$ as the theoretical densities of W$_2$O$_3$(PO$_4$)$_2$ and WO$_3$ phases, respectively.

For the electrical measurements, gold electrodes (3.8 mm diameter) were sputtered on both surfaces of the crystallized samples using the Sputter Coater SC7620. The samples were subsequently placed between two brass electrodes and the complex impedance was measured using an impedance analyzer (Novocontrol Alpha-AN Dielectric Spectrometer) in a wide frequency (0.01 Hz–$10^6$ Hz) and temperature (−30 °C to 240 °C) range. The temperature was controlled to an accuracy of ±0.2 °C.

3. Results and Discussion

3.1. Crystallization

According to the DTA results reported in the previous papers [29,30,33] the temperatures of heat treatments of binary 60WO$_3$-40P$_2$O$_5$ glass were chosen to be in the temperature region above glass transition temperature ($T_g = 520$ °C) at 700 °C and 800 °C for 1 and 6 h and at crystallization temperature $T_c = 935$ °C for 1, 12 and 24 h. Additionally, samples in the form of discs were heat-treated at 935 °C for 1 and 12 h as described in the experimental section.

3.2. Structural Characterization

The temperature-induced evolution of crystalline phases was investigated by the X-ray powder diffraction (XRPD). Figure 1 shows the results of Rietveld refinement analysis for glass pellets heat-treated at 700, 800, and 935 °C for the time ranging from 1 h to 24 h.
A wide scattering halo and absence of diffraction lines (Figure 1a,b) indicate that heat treatment at 700 °C, regardless of the heat treatment time, does not induce any crystallization processes and that the P-700 samples are characterized by an amorphous short-range ordering.

Figure 1. Rietveld refinements of glass pellet samples crystallized for (a) 1 h at 700 °C, (b) 6 h at 700 °C, (c) 1 h at 800 °C, (d) 6 h at 800 °C, (e) 1 h at 935 °C, (f) 12 h at 935 °C and (g) 24 h at 935 °C. Experimental data are given by black line, the calculated pattern is shown in blue, while the red line represents the difference curve. Grey vertical marks show the positions of diffraction lines belonging to W2O3(PO4)2 phase while the positions of WO3 lines are given as grey vertical marks. Inset in (c) shows the structure of dominant phase, W2O3(PO4)2; WO6 octahedra are shown in grey while PO4 tetrahedra are pink. The insets in (e,g) demonstrate the differences in the integral line breadths caused by prolonged crystallization period.

Heat treatment at 800 °C for 1 h represents the onset of crystallization with the appearance of diffraction lines corresponding to W2O3(PO4)2 (97.5 wt. %) and WO3 (2.5 wt. %) phases. The W2O3(PO4)2 phase crystallizes in the monoclinic system, P2\_1/m space group, with the refined unit-cell parameters: a = 7.796(6) Å, b = 12.526(5) Å, c = 7.777(6) Å, β = 92.95(2)° similar to those reported by Kierkegaard and Asbrink (24072-ICSD) [34]. The structure consists of W2O3 dimer units (two WO6 octahedra connected in the corner shared manner) surrounded by PO4 tetrahedra (inset in Figure 1c). Each PO4 unit links together four dimer units, also via corner sharing, thus forming the 3D network. From the Figure 1c–g one can observe that monoclinic W2O3(PO4)2 remains the dominant crystalline phase in all the samples (positions of diffraction lines are given as grey vertical marks). However, the pronounced crystallization of WO3 (positions are given as green vertical marks) with a further increase of heat treatment time and temperature is also observed. The WO3 phase also crystallizes in monoclinic system, in space group P2\_1/c with the refined unit-cell parameters: a = 7.317(4) Å, b = 7.523(4) Å, c = 10.568(7) Å, β = 133.05(2)° similar to those reported by Tanisaki (17003-ICSD) [35].

Quantitative compositions of the samples heat-treated at 700, 800 and 935 °C for different times of heat treatment are given in Table 1.

Based on the composition of samples given in Table 1, the general trend can be observed; the crystallization of WO3 phase becomes more pronounced with the increment of temperature but also, at both temperatures, prolongation in the heat treatment time results in the increase of WO3 phase fraction and the decrease in the amount of W2O3(PO4)2 phase.

Moreover, the X-ray line broadening analysis performed on the P-935-1h and P-935-24h samples revealed the pronounced growth of the diffraction domain sizes of the W2O3(PO4)2 phase with the prolonged time of heat treatment as seen from the evident decrease of integral line breadths for the sample annealed for 24 h compared to sample annealed for 1 h in the inset of Figure 1e,g. On the other hand, the WO3 phase does not show any significant difference in coherent diffraction domains
sizes with prolonged heat treatment time; both samples crystallized for 1 h and 24 h contain crystallites with average sizes of ~80 nm.

**Table 1.** Quantitative composition of the samples heat-treated for 1 to 24 h at 700, 800, and 935 °C.

| Sample   | Heat Treatment Conditions | Composition (in wt. %) |  |
|----------|--------------------------|------------------------|---|
|          |                          | W<sub>2</sub>O<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> | WO<sub>3</sub> |
| P *-700-1h | 700 °C 1 h | - | - |
| P-700-6h   | 700 °C 6 h | - | - |
| P-800-1h   | 800 °C 1 h | 97.5(1) | 2.5(1) |
| P-800-6h   | 800 °C 6 h | 96.0(2) | 4.0(1) |
| P-935-1h   | 935 °C 1 h | 95.7(2) | 4.3(1) |
| P-935-12h  | 935 °C 12 h | 90.9(1) | 9.1(1) |
| P-935-24h  | 935 °C 24 h | 82.0(1) | 18.0(2) |
| B *-935-1h | 935 °C 1 h | 76.1(2) (orthorhombic) | 19.1(2) (monoclinic) |
| B-935-12h  | 935 °C 12 h | 91.8(1) | 8.2(1) |

* Labels P and B denote crystallization from pellet and bulk (discs), respectively.

The crystallization from bulk samples have also been investigated by the means of quantitative Rietveld refinement as shown in Figure 2.

**Figure 2.** Rietveld refinements of the bulk glass samples crystallized for (a) 1 h and (b) 12 h at 935 °C. Experimental data are given by black line, the calculated pattern is shown in blue, while the red line represents the difference curve. Grey vertical marks show the positions of diffraction lines belonging to monoclinic W<sub>2</sub>O<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> phase, magenta bars represent reflection of orthorhombic W<sub>2</sub>O<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> phase, while the positions of WO<sub>3</sub> lines are given as green vertical marks.

Interestingly, unlike the sample obtained from pellets, the sample obtained from bulk, when heat-treated at 935 °C for 1 h, shows the dominant presence of orthorhombic W<sub>2</sub>O<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> phase as reported by Hanawa and Imoto (50742-ICSD) [36], accompanied by monoclinic W<sub>2</sub>O<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> phase as well as small amount of WO<sub>3</sub>. With increase in heat treatment time, a polymorphic transition from orthorhombic to monoclinic phase W<sub>2</sub>O<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> is observed, together with increase in the fraction of WO<sub>3</sub> phase. The presence of the mixture of W<sub>2</sub>O<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> polymorphs in B-935-1h indicates the difference in crystallization processes which occur within the bulk and surface of the glass. It seems that orthorhombic W<sub>2</sub>O<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> starts to crystallize from the bulk and as crystallization proceeds it transforms to a monoclinic phase. This is in accordance with our study of crystallization of 5Li<sub>2</sub>O-5ZnO-40P<sub>2</sub>O<sub>5</sub>-50WO<sub>3</sub> (mol%) glass where the heat treatments of the glass in the form of disc at 800 °C for 1 and 6 h also resulted in glass-ceramics containing both W<sub>2</sub>O<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> polymorphs [31].

**SEM Analysis**

The insight into the microstructural features of glass-ceramics and crystalline grains was gained using scanning electron microscopy (SEM). Figure 3 exhibits the SEM micrographs of tungsten phosphate glass-ceramics obtained at various temperatures and for different times.
Within the grains have the average size of ~80 nm.

The EDS analysis shows that the chemical composition of the large grains corresponds to that of the parent glass, whereas smaller particles having relatively narrow size distribution of ∼0.30 μm are stoichiometrically close to W2O3(PO4)2 phase, see tables in the upper-middle panel in Figure 3. Considering that the PXRD data do not show any diffraction lines it can be assumed that the small grains are amorphous, and, in fact, they act as precursors for further crystallization of W2O3(PO4)2 crystals.

At higher heat treatment temperature, namely 800 °C for 6 h, the microstructure shows better-defined grains with sharp edges and apexes which, according to PXRD, can be identified as dominant W2O3(PO4)2 phase. Also, large, elongated crystals, prismatic in shape, which appeared after crystallization at 935 °C for 1 h, are identified as W2O3(PO4)2 phase, see Figure 3c. When heat treatment at 935 °C is prolonged to 24 h, the W2O3(PO4)2 phase grows in size into large regular crystals of perfectly formed prismatic habit, Figure 3d. In accordance with PXRD results, this sample also contains sporadically distributed small grains of an irregular shape whose chemical composition matches WO3 phase, see EDS spectrum and table in the lower panel in Figure 3d. The size of WO3 grains is approximately ~1 μm, however, the X-ray line broadening analysis revealed that the crystallites within the grains have the average size of ~80 nm.

Figure 3. SEM micrographs of glass-ceramics prepared at (a) 700 °C for 6 h, (b) 800 °C for 6 h, (c) 935 °C for 1 h, and (d) 935 °C for 24 h. EDS spectra and tables with chemical composition from selected areas of the samples are shown in the insets (i) and (ii).

From Figure 3a, it can be seen that the P-700-6h sample contains grains of different sizes with no defined morphology. The EDS analysis shows that the chemical composition of the large grains corresponds to that of the parent glass, whereas smaller particles having relatively narrow size distribution of ~0.30 μm are stoichiometrically close to W2O3(PO4)2 phase, see tables in the upper-middle panel in Figure 3. Considering that the PXRD data do not show any diffraction lines it can be assumed that the small grains are amorphous, and, in fact, they act as precursors for further crystallization of W2O3(PO4)2 crystals.

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Noteworthy, the experimental densities of P-935-1h and P-935-24h glass-ceramics are significantly smaller than the corresponding theoretical values, P-935-1h: ρ_{exp} = 4.43 g/cm³ vs. ρ_{theo} = 5.37 g/cm³ and P-935-24h: ρ_{exp} = 4.68 g/cm³ vs. ρ_{theo} = 5.58 g/cm³, giving the relative densities of 82% and 84%, respectively. This indicates high porosity of the obtained glass-ceramics which is in line with the SEM micrographs shown in Figure 3c,d.

3.3. Electrical Transport

The conductivity spectra for P-935-1h glass-ceramics, as typical spectra for all samples in this study, is shown in Figure 4. Each isotherm exhibits a frequency-independent conductivity (DC conductivity)
over a wide frequency range and a small frequency-dependent part at highest frequencies. These spectral features are characteristic for the electronically conducting materials and indicate fast non-localized electronic transport over a broad range of frequencies and temperatures. According to the PXRD analysis and SEM micrographs, samples heat-treated at 700 °C for 1 and 6 h show an amorphous structure with an indication of the stoichiometric rearrangement within the glassy phase whereas at higher crystallization temperatures, 800 and 935 °C, the crystallization processes rise creating two crystalline phases: W$_2$O$_3$(PO$_4$)$_2$ and WO$_3$. Interestingly though, all samples, regardless of their structural and morphological properties, show frequency-independent conductivity over almost entire frequency span which signifies the absence of any blocking effects of the grain boundaries and (crystalline) grains to the conduction process. These effects usually manifest as a characteristic decrease of conductivity at lower frequencies and a corresponding low-frequency plateau. Therefore, it can be concluded that the electronic transport in all prepared glass-ceramics is continuous and uninterrupted.

**Figure 4.** Conductivity spectra at different temperatures of glass-ceramics prepared at 935 °C for 1 h.

For all samples, the DC conductivity exhibits Arrhenius temperature dependence and hence has characteristic activation energy, see Figure 5a. 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 the equation

$$ \sigma_{DC}T = \sigma_0 \exp(-E_{DC}/k_B T), $$

where $\sigma_{DC}$ is the conductivity, $\sigma_0$ is the pre-exponential factor, $E_{DC}$ is the activation energy, $k_B$ is the Boltzmann constant, and $T$ is the temperature (K). The DC conductivity at 30 °C and determined activation energy, $E_{DC}$, for the parent glass and all glass-ceramics are displayed in Table 2.

**Table 2.** DC conductivity, $\sigma_{DC}$, at 30 °C and activation energy, $E_{DC}$, for parent 60WO$_3$-40P$_2$O$_5$ bulk glass and prepared glass-ceramics.

| Sample     | $\sigma_{DC}/(\Omega \text{ cm})^{-1}$ at 30 °C ± 1.0% | $E_{DC}$/eV ± 1.0% |
|------------|--------------------------------------------------------|-------------------|
| B-Glass    | $4.26 \times 10^{-6}$                                   | 0.37              |
| P-700-1h   | $3.18 \times 10^{-8}$                                   | 0.35              |
| P-700-6h   | $6.57 \times 10^{-8}$                                   | 0.35              |
| P-800-1h   | $3.11 \times 10^{-6}$                                   | 0.30              |
| P-800-6h   | $2.38 \times 10^{-6}$                                   | 0.29              |
| P-935-1h   | $1.20 \times 10^{-5}$                                   | 0.18              |
| P-935-12h  | $5.26 \times 10^{-5}$                                   | 0.13              |
| P-935-24h  | $1.64 \times 10^{-5}$                                   | 0.17              |
| B-935-1h   | $1.19 \times 10^{-5}$                                   | 0.29              |
| B-935-12h  | $2.14 \times 10^{-5}$                                   | 0.27              |
The crystalline phase dominates in both samples having the relative proportion of 97.5\% and P-800-6h samples, respectively. From the Rietveld analysis, it is evident that the W conductivity sharply increases to 3.11\times10^{-6} (\Omega\cdot cm)^{-1} and Figure 3a. As can be seen from Figure 5b, the heat treatments at 700 °C for 1 and 6 h result in nearly two orders of magnitude lower DC conductivity (\sigma_{DC} = 6.57 \times 10^{-6} (\Omega\cdot cm)^{-1} for P-700-6h at 30 °C), than the starting bulk glass (\sigma_{DC} = 4.26 \times 10^{-6} (\Omega\cdot cm)^{-1} at 30 °C). At this point, it is important to consider the structure and electrical transport within the parent bulk glass itself. Our recent studies [29,30] show that the exceptionally high DC conductivity of binary 60WO_3-40P_2O_5 glass is a result of the formation of tungsten clusters of WO_5 octahedra which facilitate the mobility of polarons via W^{5+}-O-W^{6+}-O-W^{5+} bonds. Remarkably, in tungsten phosphate glasses the most important factor of polaronic transport is found to be the structure of the glass network and not the fraction of reduced tungsten, W^{5+} ions [29,30]. Considering the high conductivity in starting 60WO_3-40P_2O_5 bulk glass as a result of an easy motion of polarons through the tungsten clusters, it seems that the lower DC conductivity of P-700-1h and P-700-6h samples is related to a subtle rearrangement of the glass network during heating which accompanies breaking of the bonds in the tungsten clusters and formation of two fully amorphous but stoichiometrically different phases as shown by PXRD and SEM-EDS analysis, see Figure 1a,b and Figure 3a.

As the crystallization progresses and crystalline W_2O_3(PO_4)_2 and WO_3 phases appear, the DC conductivity sharply increases to 3.11 \times 10^{-6} (\Omega\cdot cm)^{-1} and 2.38 \times 10^{-6} (\Omega\cdot cm)^{-1} at 30 °C for P-800-1h and P-800-6h samples, respectively. From the Rietveld analysis, it is evident that the W_2O_3(PO_4)_2 crystalline phase dominates in both samples having the relative proportion of 97.5 wt. % (P-800-1h) and
with the monoclinic polymorph being stable at room temperature as also shown by our PXRD results. It undergoes several phase transitions as a function of temperature, with a wide band gap [37–39]. It is well known that WO$_3$ is a dominant phase along with monoclinic and orthorhombic W$_2$O$_5$(PO$_4$)$_2$ as dominant phases in these glass-ceramics keeps the conductivity nearly the same as for the parent glass.

For glass-ceramics heat-treated at 935 °C for various times the DC conductivity increases further reaching the values of $\sigma_{DC} = 1.20 \times 10^{-5}$ (Ω cm)$^{-1}$, $\sigma_{DC} = 5.26 \times 10^{-5}$ (Ω cm)$^{-1}$, and $\sigma_{DC} = 1.64 \times 10^{-4}$ (Ω cm)$^{-1}$ at 30 °C for P-935-1h, P-935-12h, and P-935-24h samples, respectively, see Table 2. According to the Rietveld analysis in these glass-ceramics, the relative amount of WO$_3$ increases gradually from 4.3 wt. % for P-935-1h to 9.1 wt. % for P-935-12h and 18.0 wt. % for P-935-24h glass-ceramics, see Table 1. In line with the PXRD results, the SEM micrographs shown in Figure 3c, reveal long prismatic crystals that correspond to the W$_2$O$_5$(PO$_4$)$_2$ in the microstructure of P-935-1h whereas as crystallization proceeds with prolonged heating time to 24 h, along with the large W$_2$O$_5$(PO$_4$)$_2$ crystals, agglomerates of WO$_3$ crystallites are evidenced, see Figure 3d. Here, it is worth noting that the X-ray line broadening analysis revealed that the size of WO$_3$ crystallites within the grains does not change with the heat treatment time and remains app. 80 nm in all glass-ceramics. Also, the relative density of P-935-1h and P-935-24h glass-ceramics is nearly the same (82–84%), indicating similar porosity and volume fraction of grain boundaries in both samples. Since the DC conductivity systematically increases with prolonged time of the heat treatment it can be concluded that the increase in the amount of nanostructured WO$_3$ crystallites in these glass-ceramics is responsible for the observed rise of DC conductivity.

Let us now consider WO$_3$ crystals. It is well known that WO$_3$ is a n-type semiconductor with a wide band gap [37–39]. It undergoes several phase transitions as a function of temperature, with the monoclinic polymorph being stable at room temperature as also shown by our PXRD results. The electron concentration in WO$_3$ is determined mainly by the concentration of stoichiometric defects such as oxygen vacancies which generate a new energy level below the conduction band. At the generated energy level, the active electrons can be transited to the upper energy levels. The conduction band generates free electrons and WO$_3$ is thus electronically conductive [38,39]. Therefore, with increasing relative amount of WO$_3$ crystallites in the P-935 glass-ceramics the concentration of free electrons also increases leading to the enhancement in DC conductivity. The obtained high DC conductivity, $\sigma_{DC} = 1.64 \times 10^{-4}$ (Ω cm)$^{-1}$ at 30 °C for P-935-24h glass-ceramics, clearly reveals a rapid electron transport through WO$_3$ crystallites as well as electronically conductive W$_2$O$_5$(PO$_4$)$_2$ crystals, resulting in high electronic conductivity.

Further, we analyze the electrical conductivity of the glass-ceramics prepared from the bulk and compare them with those prepared from the pellet. Figure 6 shows the frequency dependence of conductivity for the bulk and pellet samples heat-treated at 935 °C for 1 and 12 h. As can be seen from Figure 6a the electrical conductivity for both, P-935-1h and B-935-1h samples, shows the same values, $\sigma_{DC} = 1.20 \times 10^{-5}$ (Ω cm)$^{-1}$ and $\sigma_{DC} = 1.19 \times 10^{-5}$ (Ω cm)$^{-1}$ at 30 °C, respectively. The PXRD analysis shows that the bulk sample heat-treated for 1 h exhibits an orthorhombic W$_2$O$_5$(PO$_4$)$_2$ as a dominant phase along with monoclinic W$_2$O$_5$(PO$_4$)$_2$ phase and some traces of WO$_3$. Structurally, these two W$_2$O$_5$(PO$_4$)$_2$ polymorphs do not differ substantially, so nearly identical values for the DC conductivity are expected. A slight decrease in the DC conductivity of bulk glass-ceramic crystallized for 12 h if compared with that prepared from the pellet, see Figure 6b, is a result of a slightly smaller amount of WO$_3$ (8.2 wt. % for B-935-12h vs. 9.1 wt. % for P-935-12h) as well as a decrease in the crystals connectivity within the microstructure. In fact, glass-ceramics prepared from the bulk glass were very fragile and much less dense than their counterparts prepared from the pellets which implies that their conduction pathways are reduced and hence electron transport slower.
Figure 6. Comparison of the conductivity spectra measured at 30 °C for glass-ceramics prepared from the bulk glass (black squares) and pelleted glass powder (red triangles) at 935 °C for (a) 1 h and (b) 12 h.

The analysis of the activation energy, $E_{DC}$, for all samples shows an opposite trend to the DC conductivity, implying that the changes in microstructure have an impact on the activation energy. Also, a continuous decrease in the activation energy from 0.35 eV for P-700-1h to 0.17 eV for P-935-24h corresponds well to the previously reported data [40,41] for the n-type semiconductor behavior of WO$_3$. Thus, the low activation energy of P-935 glass-ceramics acts as a facilitating factor in easy conductive pathways through the crystalline WO$_3$ and W$_2$O$_3$(PO$_4$)$_2$ phases. On the other hand, the slightly higher activation energy for B-935-1h and B-935-12h glass-ceramics of 0.29 eV and 0.27 eV, mirrors a less compact microstructural network of the bulk samples.

4. Conclusions

A series of novel electronically conductive glass-ceramics were prepared by heat treatments of polaronic 60WO$_3$-40P$_2$O$_5$ (mol%) glasses at different temperatures (700, 800, and 935 °C) and for various times (1, 6, 12, and 24 h). For glasses heat-treated at 700 °C for 1 and 6 h PXRD measurements show fully amorphous structure, however SEM-EDS micrographs reveal the presence of two types of grains; the large ones with the composition of the parent glass and the small ones which act as precursors for crystallization of W$_2$O$_3$(PO$_4$)$_2$. The heat treatments at higher temperatures induce the crystallization of W$_2$O$_3$(PO$_4$)$_2$ as a dominant phase and minor WO$_3$ phase in all glass-ceramics. The amount of WO$_3$ increases with increasing heat treatment temperature and time and reaches the highest value of 18.0 wt. % for the glass-ceramics prepared at 935 °C for 24 h. The electrical conductivity of prepared glass-ceramics is electronic in nature and shows a strong dependence on the evolution of crystalline phases. While the samples prepared at 700 °C have two orders of magnitude lower conductivity than the parent bulk glass due to the breakage of the tungsten clusters in glass network, the fast electronic transport within the W$_2$O$_3$(PO$_4$)$_2$ and WO$_3$ crystalline grains makes glass-ceramics prepared at higher temperatures highly conductive. In particular, the increase of the amount of semiconducting WO$_3$ crystallites of an average size of ~80 nm enhances the conduction of the glass-ceramics to the order of $\sim 10^{-4}$ (Ω cm)$^{-1}$ at 30 °C.

Author Contributions: Conceptualization, A.Š., A.M.-M.; methodology, A.Š. and S.R.; software, S.B. and T.K.; validation, A.Š.; formal analysis, S.R., T.K. and P.K.; investigation, A.Š., S.R. and P.M.; resources, A.Š. and P.M.; data curation, S.R.; writing—original draft preparation, A.Š., S.R. and A.M.-M.; writing—review and editing, A.Š. and A.M.-M.; visualization, A.Š. and S.R.; supervision, A.Š. and A.M.-M.; project administration, A.Š.; funding acquisition, A.Š. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Hrvatska zaklada za znanost (Croatian Science Foundation), POLAR-ION-GLASS project, grant number IP-2018-01–5425. Czech authors P.M. and P.K. are grateful for the financial support from the Grant Agency of the Czech Republic (Grant No. 18-01976S).
Conflicts of Interest: The authors declare no conflict of interest.

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