Structural relaxation and viscosity of Al₂O₃ doped magnesium phosphate glasses

Mária Chromčíkováᵃᵇ⁻ˢ, Branislav Hruškaᵇ, Aleksandra Nowickaᵇ, Roman Svobodaᶜ, and Marek Liškaᵃᵇ

ᵃ VILA – Joined Glass Centre of the IIC SAS, TnUAD, FChPT STU, Študentská 2, Trenčín, SK-911 50, Slovakia
ᵇ FunGlass, Alexander Dubček University of Trenčín, Študentská 2, Trenčín, SK-911 50, Slovakia
ᶜ University of Pardubice, Faculty of Chemical Technology, Department of Physical Chemistry, Studentská 573, 532 10 Pardubice, Czech Republic

Abstract

Thermomechanical analysis and differential scanning calorimetry were used to study the viscosity and relaxation behavior of the Al₂O₃-doped magnesium phosphate glasses. Viscosity in the range (10⁷ - 10ⁱ¹) Pa·s was described by the nowadays top performing multiparametric models. A fixed extrapolation of high-temperature viscosity according to the Eyring theory was applied with the exception of the Arrhenius equation. The activation energies of viscous flow were very close to the activation energy of enthalpy relaxation determined in terms of the Tool-Narayanaswamy-Moynihan model. On the contrary, the activation energy of volume relaxation was found to be much lower in comparison with the viscous flow activation energy. In general, the increase of the Al₂O₃ content leads to the increases of the viscosity, of the activation energies of viscous flow and structural relaxation (as well as of the kinetic fragilities calculated from these quantities), and of the temperatures characterizing the glass transition during the viscosity, volume, and enthalpy measurements. The phosphate chains interconnecting effect of the Al³⁺ ions was found to be much stronger than the influence of the MgO modifying oxide. However, the enthalpy changes during the relaxation processes seem to be primarily influenced by the MgO/P₂O₅ ratio. Consistence of the compositional interpretation of the obtained results indicates the benefits of the utilization...
of the correlation coefficients for attributing the structural units responsible for the changes of physico-chemical quantities.

Keywords: viscosity; structural relaxation; fragility; TMA; Al₂O₃-MgO-P₂O₅ glasses

1. Introduction

Amorphous magnesium phosphate (AMP) is an important material for various bio-applications, mostly used as a biomaterial for bioresorbable orthopedic implants. In [1] the AMP was studied with respect to the utilization for bone void filling applications. The mineralization of AMP was shown to mimic the hydroxyapatite-type characteristic morphology on the substrate surface, and to promote the proliferation and differentiation of the osteoblast-like cells. Recently, a biodegradable, non-exothermic, self-setting orthopedic cement based on AMP was developed [2] by incorporation of the water soluble biocompatible polymer (polyvinyl alcohol, PVA), which enables a controlled growth of the final phase via the biomimetic process. The cement composition with 15% of PVA in aqueous medium exhibited clinically relevant setting times, mechanical properties and biodegradability. In another application, the composite film of nanostructured amorphous magnesium phosphate and polylactic acid was spin-coated on the surface of the biodegradable AZ31 magnesium alloy [3], significantly improving corrosion resistance and biomineralization capability. This indicates the great potential of the AMP composites in the protective and bioactive coating applications on biodegradable orthopedic magnesium alloys.

Understanding the structural relaxation processes and viscosity behavior is the key factor for the successful practical application of all glassy materials. These processes not only determine the long-term stability of the materials’ mechanical properties, but they are also closely related to the glass-forming tendency and manufacturing procedures. Unfortunately, since these properties can be tedious to measure, literature usually lacks the data needed for
considering the manufacturing/processing side of the novel biomaterials. In the present study, the relaxation and viscosity behaviors of the Al$_2$O$_3$-doped magnesium phosphate glasses will be reported, where the Al$_2$O$_3$ component was added in order to improve the chemical resistivity and anti-corrosive properties (it is well known that the tetrahedral Al ions cross-link with the neighboring phosphor chains by the formation of AlPO$_4$ species that strengthen the glass network [4, 5]). In addition, the utilization of the correlation coefficients between the composition and various physical quantities will be demonstrated, showing the strengths and also the possible weaknesses of this approach.

2. Experimental

Magnesium phosphate glasses doped with Al$_2$O$_3$ were prepared by the common melt-quenching procedure. The glasses were prepared by melting the p.a. ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$) and magnesium carbonate (MgCO$_3$) in alumina crucibles [6]. Appropriate quantities of these compounds were mixed in an agate mortar and placed into alumina crucible. In the first step, the crucible was heated up to 700 °C in an electrical furnace at slow heating rate to remove the water, ammonia and carbon dioxide (calcination). After the calcination, the reaction mixtures were melted in the temperature range 1100 – 1200 °C, depending on their chemical composition. Composition of the prepared glasses was measured by the X-ray fluorescence elemental analyzer S8 Tiger (Bruker) – the contents of the particular components (Al$_2$O$_3$, MgO, P$_2$O$_5$) are listed in Table 1. The Raman spectrometer inVia Reflex (Renishaw) with Leica DM2500 microscope was used to determine the structure of the prepared glasses. Amorphous nature of the prepared glasses was confirmed by the Panalytical Empyrean DY1098 X-ray diffractometer (XRD) – see the Supplemental online material for the XRD patterns of the prepared amorphous materials. Mass density was measured by the Archimedes method using distilled water. Note that the homogeneity of the
samples was confirmed based on the XRF and Raman measurements performed at various spots on the samples. In addition, the same was done also by DSC, through checking of the glass transition position (which is quite sensitive to the compositional changes).

The volume relaxation and viscosity measurements were realized by the TMA 402 thermomechanical analyzer (Netzsch) – the prismatic samples were cut from the prepared glass ingots (see the Supplemental online material). The dimensions of the prismatic samples were (5x5x20) mm, with the masses approx. (1.5 – 2.0) g. Constant load of 50 mN was applied to the samples in axial deformation during both, the volume relaxation and the viscosity measurements. The volume relaxation measurements were performed by alternating the cooling and heating steps through the glass transition region. The applied heating rates \( q^+ \) and cooling rates \( q^- \) were similar in magnitude (5 °C·min\(^{-1}\)). The temperature ranges for the TMA cyclic experiments were (292 – 600) °C. The isothermal viscosity experiments were realized at temperatures corresponding to the viscosities of approx. (10\(^7\) - 10\(^{11}\)) Pa·s. Note that even for the highest applied heating rates the TMA samples were thermally uniform – the temperature gradients across the sample were under all conditions well below 0.2 °C (as determined based on the numerical simulation of the heat transfer).

The enthalpy relaxation experiments were performed via the differential scanning calorimetry (DSC Q2000; TA Instruments) - samples with masses of approx. 10 mg were measured. The measurements were based on the constant ratio (CR) cycles [7]. The samples were cooled and heated in the (420 – 600) °C range; the heating rates \( q^+ \) were similar as the preceding cooling \( q^- \) rates.

3. Results

The Raman spectra were recorded in the range of (100 – 1500) cm\(^{-1}\); the data were corrected by the Böse-Einstein population factor [8] (see Eq. 1) after the baseline subtraction:
\[ I_{\text{cor}} = I_{\exp} v v_0^3 \left( 1 - \exp \left( \frac{-hc v}{kT} \right) \right) \left( v_0 - v \right)^4 \]  


where \( I_{\exp} \) and \( I_{\text{cor}} \) are the observed and corrected Raman intensities, respectively, \( v \) and \( v_0 \) are the Raman shift and the wavenumber of the excitation laser, respectively, and \( h, k, c, \) and \( T \) represent Planck’s constant, Boltzmann’s constant, the speed of light, and thermodynamic temperature, respectively. In addition, all spectra were normalized for the maximum intensity to equal unity (see Fig. 1). The Raman bands can be assigned as follows [9-15]: the broad band at \(~330\ \text{cm}^{-1}\) corresponds to the bending vibrations of phosphate polyhedra; the bands in the \((650 - 850)\ \text{cm}^{-1}\) spectral region correspond to the vibrations of the bridging oxygen atoms in the P-O-P chains, in particular the band at \(~710\ \text{cm}^{-1}\) corresponds to the P-O-P symmetric stretch in Q\(^2\) structural units and the band at \(795\ \text{cm}^{-1}\) corresponds to the P-O-P asymmetric stretch of the oxygen atom in the Q\(^2\) units; the band at \(1036\ \text{cm}^{-1}\) corresponds to the symmetric stretching vibration of non-bridging oxygen atoms in Q\(^1\) units terminating the metaphosphate chains; the band at \(1210\ \text{cm}^{-1}\) corresponds to the symmetric stretching motions of the two non-bridging oxygen atoms in the Q\(^2\) tetrahedra; the band at \(1280\ \text{cm}^{-1}\) corresponds to the asymmetric stretching motions of the two non-bridging oxygen atoms in the Q\(^2\) tetrahedra. Note that the Q\(^n\) notation expresses the concentration of the bridging oxygen atoms per tetrahedron by varying the superscript \(n\).

The compositional evolution of the bands’ intensities is in a good agreement with the elemental analysis provided by XRF (see Table 1). The structure of the magnesium phosphate glasses largely depends on the magnesium oxide to phosphorous pentoxide molar ratio \(y = n(\text{MgO})/n(\text{P}_2\text{O}_5)\). At the metaphosphate stoichiometry \((y = 1)\), the structure constitutes of chains formed by the Q\(^2\) units (PO\(_4\) tetrahedra where two oxygen atoms are shared/bonded with the neighboring PO\(_4\) tetrahedra). At increasing MgO content (for \(y > 1\)) the structure consists of Q\(^2\) chains terminated by the Q\(^1\) units; the average chain length shortens as the

\[ \text{Eq. 1} \]
MgO/P₂O₅ ratio increases. At the pyrophosphate composition (y = 2) the phosphate dimers, two Q¹ connected by a single oxygen atom, are the dominant structural units. [9] This means that for the present compositions the addition of the Mg²⁺ ions (with coordination number equal to 4 [16]) leads to the formation of more diversified structures – note that MgO is known to be a typical modifier oxide that decreases the degree of crosslinking. As the length of the phosphate chains decreases, the averaged distances between the structural units decrease [17] (with the effect being especially prominent in the polyphosphate region, i.e. for y = 1 – 1.5) and the material’s density increases. For the present glasses, this behavior was confirmed by experimental measurements, as evidenced by the density values listed in Table 1. Regarding the structural arrangements associated with the addition of Al₂O₃, the Al atoms cross-link with the adjacent chains of PO₄ tetrahedra, resulting in the formation of the AlPO₄ units. [5] This largely increases the interconnectivity of the glass matrix, strengthening the network. In addition, the Al³⁺ ions also react with MgO as: Al₂O₃+MgO = Mg²⁺ +2AlO₂⁻. Since the addition of both oxides, MgO and Al₂O₃, contributes to the increase of the density, further analysis will have to be used to determine the dominant structural unit in this regard – see Section 4 for the corresponding discussion.

Using the compositional information from Table 1, the Shakhmatkin and Vedishcheva thermodynamic model [18] was calculated for the present glasses – the detailed calculations and assumptions are included in the Supplemental online material. Based on this model, only Q¹ and Q² structural units are found in the present glasses. The percent representation of the Q² chain-forming tetrahedra is 87.34 % for glass No. 1, 70.78 % for glass No. 2, and 58.49 % for glass No. 3.

The viscosity values were for the studied Al₂O₃-MgO-P₂O₅ glasses determined by TMA based on the following equation:

$$\eta = \frac{Fl}{35(dl/dr)}$$  \hspace{1cm} (2)
where $F$ is the loading force, $l$ is the sample height, $S$ is the cross-section of the sample (perpendicular to the applied force), and $dl/dt$ is the deformation rate. The data are shown in Fig. 2 in dependence on temperature in °C as well as on the reciprocal of the thermodynamic temperature (in K). It is apparent that, as the temperature increases, the viscosity of the glasses with higher MgO and Al$_2$O$_3$ content decreases more rapidly compared to the compositions with lower MgO and Al$_2$O$_3$ contents. Primarily, this is the consequence of the glass matrix being significantly more interconnected via the Al$^{3+}$ ions, which can be confirmed based on the correlation between the composition and log($\eta$/Pa·s). Whereas the correlation coefficient (see Eq. 3 for the definition of correlation coefficient) between the mol.% of Al$_2$O$_3$ and the log($\eta$/Pa·s) values determined at the pre-selected temperatures is $r = 0.99961$, the correlation coefficient between the MgO/P$_2$O$_5$ ratio and the same log($\eta$/Pa·s)-$T$ data is only $r = 0.95965$. This also indicates that the crosslinking caused by Al$_2$O$_3$ has much stronger effect compared to the shortening of the phosphate chains originating from the MgO addition.

$$r = \frac{\sum(x - \bar{x})(y - \bar{y})}{\sqrt{\sum(x - \bar{x})^2 \sum(y - \bar{y})^2}} \quad (3)$$

In order to quantify the viscosity behavior, the data from Fig. 2 were described by the three standard viscosity equations - the Vogel-Fulcher-Tammann [19-21] (VFT; Eq. 4), Avramov-Milchev [22] (AM; Eq. 5) and Mauro-Yue-Ellison-Gupta-Allan [23] (MYEGA; Eq. 6):

$$\log\eta = \log\eta_0 + \frac{B}{T - T_0} \quad (4)$$

$$\log\eta = \log\eta_0 + \frac{B'}{T^{c'}} \quad (5)$$

$$\log\eta = \log\eta_0 + \frac{B''}{T} \cdot \exp\left(\frac{C''}{T}\right) \quad (6)$$
where \( \eta_0, B, B', B'', T_0, C' \) and \( C'' \) are the parameters of the respective models. The model parameters will be later used to extrapolate the viscosity behavior outside of the measured temperature range and to correlate the results with the structural arrangements in the studied glasses. Therefore, during the non-linear optimization we have adopted a fixed value of \( \eta_0 = 4 \cdot 10^{-5} \) Pa.s (in conformity with the Eyring theorem [24]), so that the physically meaningful picture of the viscous flow could be obtained also beyond the data shown in Fig. 2. This option has also the advantage of producing the robust and reliable fits with respect to the possible scatter in the viscosity data. Note that due to the utilization of the Eyring theorem a broad range of viscosities is being described, thus the utilization of the multiparametric equations is both justified and highly necessary. Application of the three models to the present viscosity data is shown in Fig. 3 together with the corresponding sums of squared residuals (SSR). All three models provide similarly good description of the experimental data, with the MYEGA model being very slightly on the top. The fitting parameters of the applied viscosity models are summarized in Table 2. In addition, the viscosity data from Fig. 2 were also fitted by a simple Arrhenius/Andrade equation – see Eq. 7:

\[
\eta = \eta_0 \cdot \exp\left(\frac{E_\eta}{RT}\right)
\]  

(7)

where \( E_\eta \) is the viscous flow activation energy. These fitting parameters are also listed in Table 2. In this case, the \( \eta_0 \) parameter was left free for the optimization, otherwise the fit would be very inaccurate; the linear fit of the \( \log(\eta/\text{Pa}\cdot\text{s})-T^{-1} \) dependence cannot account for the overall curvature of the viscosity-temperature dependences in case of the fragile glasses (this point will be further discussed in Section 4).

Thermomechanical analysis was also used for the measurements of structural relaxation, as depicted in Fig. 4. The left-hand graphs show the TMA data (cyclic temperature
program performed in the glass transition region) fitted by the nowadays most often used structural relaxation model – the Tool-Narayanaswamy-Moynihan (TNM) [25-27] set of equations 8 - 10:

\[ T_f(T) = T(t) - \int_0^t \left( \frac{dT}{dt} \right) M(\xi(t) - \xi(t')) dt \]  

(8)

where \( \xi \) is defined by:

\[ \xi(t) = \int_0^t \frac{d\tau'}{\tau'(t')} \]  

(8a)

\[ M(\xi) = \exp(-\xi^\beta) \]  

(9)

\[ \log \tau(T,T_f) = A' + \frac{\Delta h^*}{RT} + (1 - x) \frac{\Delta h^*}{RT_f} \]  

(10)

where \( T \) is thermodynamic temperature, \( t \) is time, \( T_f \) is the so-called fictive temperature (defined as the temperature of the metastable undercooled liquid with the same structure, at the given moment, as is that of the relaxing glass [25]), \( M \) is the standard relaxation function [28, 29], \( \beta \) is the non-exponentiality relaxation parameter, \( x \) is the non-linearity parameter, \( A' \) is the TNM pre-exponential factor, and \( \Delta h^* \) is the structural relaxation activation energy. In order to accommodate Eqs. 8 - 10 to the effect of simultaneously proceeding viscous flow, the following expression was included in the self-made Fortran non-linear optimization program:

\[ \varepsilon = \frac{l_2 - l_1}{l_1} \approx \int_{T_i}^{T_2} \alpha_g dT + \int_{T_f,2}^{T_f,1} \Delta \alpha dT_f - \left( 1 + \int_{T_i}^{T_2} \alpha_g dT + \int_{T_f,1}^{T_f,2} \Delta \alpha dT_f \right) \int_{T_i}^{T_2} \frac{\sigma}{3\eta(T,T_f)} dt \]  

(11)

where \( \alpha_g \) and \( \alpha_m \) are the thermal expansion coefficients of glass and undercooled liquid/melt, \( \Delta \alpha \) is defined as \( \Delta \alpha = \alpha_m - \alpha_g \), \( \eta \) is viscosity and \( \sigma \) is the axial stress. Note that the relaxation time in Eq. 9 can be replaced by the expression \( \eta(t')/K \), where \( K \) is the shear modulus.

As results from Fig. 4, the TNM model very well describes the volume relaxation data. The right-hand side graphs in Fig. 4 then show the evolution of the fictive temperature \( T_f \).
(as obtained from the non-linear optimization) plotted versus the temperature program of the corresponding cooling-heating cycle. Note that the $T_f$ data exhibit during heating the characteristic behavior typical for the frozen-in glassy structure that requires increased temperature to “catch-up” with the kinetic pseudo-equilibrium of the undercooled liquid. In addition, the volume relaxation data obtained from the TMA were also fitted by the Tool-Narayanaswamy-Mazurin (TNMa) model [30] (Eq. 12 was used instead of Eq. 10 during the non-linear optimization procedure):}

$$\log \eta(T, T_f) = \left( A + \frac{B}{T - T_0} \right) \frac{T_f}{T} + \log \eta_0 \left( 1 - \frac{T_f}{T} \right)$$  \hspace{1cm} (12)

where $A$, $B$ and $T_0$ are the coefficients of the VFT viscosity equation and $\eta_0$ is the limiting dynamic viscosity (tunable parameter in case of the Mazurin’s model). Qualitatively very similar results were obtained for both the TNM and TNMa models. The optimized parameters of both models are listed in Table 3 (graphical representation of the TNMa fits is included in the Supplemental online material). The $T_g$ values determined from the cyclic TMA experiments were approx. 542.6 °C (glass No. 1), 553.5 °C (glass No. 2) and 568.5 °C (glass No. 3).

In addition to the volume relaxation, also the enthalpy relaxation experiments were performed by DSC. These were based on the so-called constant ratio (CR) cycles [31], the example of which is shown in the upper graph in Fig. 5. The CR cyclic measurements can be utilized to evaluate the enthalpy relaxation activation energy $\Delta h^*$ (see Eq. 10 for the TNM model) by employing the following equation (together with the correction factor described in detail e.g. in [31]):

$$-\frac{\Delta h^*}{R} = \left[ \frac{\ln[q^*]}{\ln(1/T_P)} \right]_{q^*/q^{*\text{const}}}$$  \hspace{1cm} (13)
where $T_p$ is the temperature of the relaxation peak (overshoot) maximum, and $q^+ / q^-$ is the heating/cooling rate ratio. The linearization expressed by Eq. 13 is for the present Al$_2$O$_3$-MgO-P$_2$O$_5$ glasses shown in the lower graph in Fig. 5. The enthalpy relaxation activation energies determined according Eq. 13 are listed in Table 3. The $T_g$ values determined from the cyclic DSC experiments were approx. 558.1 °C (glass No. 1), 568.8 °C (glass No. 2) and 577.5 °C (glass No. 3).

4. Discussion

The relation between the relaxation motions and the viscous flow process has been the subject of debate for a long time – see e.g. [32-34]. In general, the activation energies of these phenomena are often considered close or even similar. In the present work, we have tested this hypothesis for the three Al$_2$O$_3$-doped magnesium phosphate glasses. The activation energies of viscous flow $E_\eta$, volume structural relaxation $\Delta h^*_V$ and enthalpy structural relaxation $\Delta h^*_H$ are for the studied glasses shown in Fig. 6; the structural relaxation activation energies are depicted in the temperature ranges corresponding to the measurements present in this study ($\Delta h^*_V$ is further limited to the region of the actual transition between $\alpha_g$ and $\alpha_m$). The $E_\eta$ values were calculated based on Eq. 14:

$$E_\eta = 2.303 \cdot R \cdot \frac{d(\log \eta)}{d(1/T)}$$

(14)

Interestingly, the extrapolation of the viscous flow activation energies outside of the experimentally measured range brings very large differences in dependence on the used viscosity equation (VFT, AM, MYEGA). Despite the relatively small differences in curvatures shown in Fig. 3 (the $\log(\eta/\text{Pa} \cdot \text{s})-T$ fits), the difference between the VFT and AM estimates of $E_\eta$ may reach over 200 % just 100 °C below the experimentally measured range. Naturally, these differences are much larger for extrapolations to lower temperatures (as opposed to the high-$T$ extrapolations).
There is also a good agreement between the \( \Delta h^*_{H} \) and \( E_\eta \) values (particularly those predicted by the VFT model). On the other hand, the \( \Delta h^*_{V} \) values obtained from the curve-fitting of the TMA relaxation experiments are much lower compared to the \( E_\eta \) evaluated in the respective temperature region. Note that the potential issue cannot be the disagreement between the isothermal and non-isothermal conditions and the associated shift of the temperature ranges. For the two activation energies to agree, the volume relaxation measurements would have to be shifted to higher temperatures by approx. 100 °C, which is an unrealistic and physically not meaningful explanation. Theoretically, there is however no reason for the three activation energies to be similar, since each material property (volume, enthalpy, viscous flow) may manifest itself differently in reaction to the similar (or even the same) structural movements.

In addition, the values of activation energies were used to calculate the kinetic fragilities (following the Angell’s concept [35]):

\[
m_{visc} = \left. \frac{d \log \eta}{dT} \right|_{T=T_g} \approx \frac{E_g / R}{T_{12} \ln(10)}
\]

\[
m_{visc} = \left. \frac{d \log \tau}{dT} \right|_{T=T_g} \approx \frac{\Delta h^*_V / R}{T_g \ln(10)}
\]

where the \( T_g \) and \( T_{12} \) were determined from the measurements depicted in Figs. 3 – 5. The fragility values are for the three Al\(_2\)O\(_3\)-MgO-P\(_2\)O\(_5\) glasses plotted in Fig. 7. Each triplet of \( m \) values corresponds to the evaluation based on the different activation energy, as indicated on the \( x \)-axis. In agreement with the findings obtained for the activation energies (Fig. 6), also the fragility values calculated for the viscosity and enthalpy relaxation data are in a good agreement, while the kinetic fragility determined for the volume relaxation data is only of 50 – 60 % magnitude compared to the other depicted values. The average fragility indices \( m \) calculated from the viscosity values are \( \approx 51, 56, \) and 68 for glasses 1, 2, and 3, respectively.
These values of fragility are considered to be rather on the intermediate-to-fragile side, which corresponds to the chain-like structure of the phosphate glasses (the theoretical limits are 16 and 200 for the strong and fragile materials, respectively).

Lastly, we have considered the compositional trends for the quantities reported in the present study and tried to attribute the structural units/components responsible for the particular physico-chemical processes. Intentionally, for this purpose only three glass compositions were included in the present study to show the possibilities provided by this approach. Similarly as previously for the viscosity, we have calculated the correlation coefficients (see Eq. 3) between the compositional dependences of the selected physical quantities and the content of the non-phosphate oxides - expressed as mol.% for Al₂O₃, and as the n(MgO)/n(P₂O₅) ratio for the magnesium oxide. Note that the different expressions were for the two oxides selected purely based on the custom practice with respect to their overall content. The results and conclusions would be similar also for the unified content calculation of any choice. In Table 4 the correlation coefficients are listed for the density ρ, fragility values calculated from different sources (see Fig.7), activation energies of volume $\Delta h^*_V$ and enthalpy structural relaxation $\Delta h^*_H$, $T_g$ values determined by DSC and TMA, and $T_{12}$ values predicted by the three viscosity models ($T_{12}$ VFT, $T_{12}$ AM, $T_{12}$ MYE). The viscosity, fragilities and activation energies (of structural relaxation as well as of viscous flow) seem to be dominantly driven by the crosslinking caused by the Al³⁺ ions (i.e. the correlation coefficients for the Al₂O₃ content were much higher than for the MgO content). Only moderately higher Al₂O₃ correlation coefficients were obtained for the density, $T_{12}$ and $T_g$ determined from TMA. This is particularly interesting with regard to density, where the density increase is undoubtedly caused by both main oxides (MgO and Al₂O₃). However, based on the correlation coefficients mentioned in Table 4 (in addition to the raw magnitudes of the density changes), the Al₂O₃ content has larger impact on the final density. Interestingly,
the $T_g$s obtained from the DSC measurements show much higher correlation with the MgO content (compared to that of Al$_2$O$_3$).

One of the possible interpretations of these findings is that the heat release/consumption changes are dominantly manifesting in association with the movements of the smaller structural unites (shorter phosphate chains) and breakage of the shared tetrahedral interconnections. On the other hand, the volume relaxation appears to be dominantly manifested through the larger-scale simultaneous movements of several adjacent phosphate chains, where the crosslinking via the Al atoms plays the primary role. Correspondingly, the Al$_2$O$_3$ content would be in such scenario even more crucial for the viscous flow itself as well as for the apparent energy barriers needed for the initiation of the flow and relaxation processes (as is indeed observed in case of our data – see Table 4).

6. Conclusions

The structural relaxation and viscosity behaviors were studied using TMA and DSC for the Al$_2$O$_3$-doped magnesium phosphate glasses. Volume relaxation behavior (measured via cyclic TMA experiments performed in the glass transition region) was described by the TNM and TNMa models in combination with the viscous creep equation. Cyclic enthalpy relaxation measurements were evaluated in terms of the TNM model. The viscosity was described by the MYEGA, AM and VFT models in the $(10^7 - 10^{11})$ Pa·s range. The activation energies (and the corresponding kinetic fragilities) of viscous flow and enthalpy relaxation were found to be similar – the extrapolation from VFT showed a particularly accurate correspondence with $\Delta h^*_H$. On the other hand, the volume relaxation activation energies were found to be significantly lower compared to the $E_\eta$ values.

Based on the correlation between the composition of the phosphate glasses (MgO and Al$_2$O$_3$ contents) and the determined physico-chemical properties, we assume that the enthalpy
changes during the relaxation processes are primarily associated with the movements of the short phosphate chains and disruptions of shared PO₄ tetrahedral units (higher correlation with the MgO/P₂O₅ ratio). The viscous flow and volume changes during the structural relaxation (as well as the activation energies of these processes) then seem to be determined by the crosslinking-driven movements of the adjacent phosphate chains (higher correlation with the Al₂O₃ content). Overall, even a small addition of the Al³⁺ ions was found to result in the large degree of crosslinking, which for the phosphate glasses surpasses the macroscopic manifestation of the modification via MgO. Consistence of the compositional interpretation of the obtained results indicates the benefits of the utilization of the correlation coefficients for attributing the structural units responsible for the changes of physico-chemical quantities.

Acknowledgments
This work was supported by The Slovak Grant Agency for Science under grant No. VEGA 2/0091/20, VEGA 1/0064/18, APVV SK-PL-18-0062 and the project Centre for Functional and Surface Functionalized Glass (CEGLASS), ITMS code is 313011R453, operational program Research and innovation, co-funded from European Regional Development Fund.

References


Figure captions

Fig. 1: Raman spectra of the MgO-P$_2$O$_5$-Al$_2$O$_3$ glasses.

Fig. 2: Viscosity values for the MgO-P$_2$O$_5$-Al$_2$O$_3$ glasses and depicted in dependence on temperature in °C and in dependence on the reciprocal temperature (in K). For each glass, several measurements were done. The error bars are of approximately 1.5 the magnitude of points.

Fig. 3: Viscosity data for the MgO-P$_2$O$_5$-Al$_2$O$_3$ glasses (data from Fig. 2) fitted by the MYEGA, AM and VFT viscosity equations. The error bars are lower than the magnitude of points. Sums of squared residuals attributed to the fits are shown.

Fig. 4: Left column: volume relaxation measurements realized via TMA (points) described in terms of the TNM model (solid line).
Right column: course of $T$ and $T_f$ during the volume relaxation experiments corresponding to the left column graphs.

Fig. 5: Typical enthalpy relaxation cyclic measurement realized via DSC (upper graph) and the evaluation of $\Delta h^*_{H}$ using Eq. 13 (lower graph).

Fig. 6: Viscous flow activation energies $E_\eta$ calculated based on the MYEGA, AM and VFT fits, enthalpy relaxation activation energies $\Delta h^*_{H}$ and volume relaxation activation energies $\Delta h^*_{V}$. Errors for $\Delta h^*_{H}$ are approximately twice the size of the points.

Fig. 7: Values of kinetic fragility $m$ calculated from different activation energies (indicated on the x-axis) using Eqs. 15 and 16.
Fig. 2: Viscosity values for the MgO-P$_2$O$_5$-Al$_2$O$_3$ glasses and depicted in dependence on temperature in °C and in dependence on the reciprocal temperature (in K). For each glass, several measurements were done. The error bars are of approximately 1.5 the magnitude of points.
Fig. 3: Viscosity data for the MgO-P₂O₅-Al₂O₃ glasses (data from Fig. 2) fitted by the MYEGA, AM and VFT viscosity equations. The error bars are lower than the magnitude of points. Sums of squared residuals attributed to the fits are shown.
Fig. 4: Left column: volume relaxation measurements realized via TMA (points) described in terms of the TNM model (solid line). Right column: course of $T$ and $T_f$ during the volume relaxation experiments corresponding to the left column graphs.
Fig. 5: Typical enthalpy relaxation cyclic measurement realized via DSC (upper graph) and the evaluation of $\Delta h^*_H$ using Eq. 13 (lower graph).
Fig. 6: Viscous flow activation energies $E_\eta$ calculated based on the MYEGA, AM and VFT fits, enthalpy relaxation activation energies $\Delta h^*_H$ and volume relaxation activation energies $\Delta h^*_V$. Errors for $\Delta h^*_H$ are approximately twice the size of the points.
Fig. 7: Values of kinetic fragility $m$ calculated from different activation energies (indicated on the $x$-axis) using Eqs. 15 and 16.
### Tables

**Table 1:** The composition (wt.% and mol.%), abbreviation and densities $\rho$ of the studied glasses as determined by XRF. In addition, also the molar volume of the glasses (corresponding to one mole of $P_2O_5$) was calculated.

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>$n(MgO)/n(P_2O_5)$</th>
<th>$P_2O_5$ wt %</th>
<th>$P_2O_5$ mol %</th>
<th>MgO wt %</th>
<th>MgO mol %</th>
<th>Al$_2$O$_3$ wt %</th>
<th>Al$_2$O$_3$ mol %</th>
<th>$\rho$ g·cm$^{-3}$</th>
<th>$V_m^{P2O5}$ cm$^3$·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.16</td>
<td>74.05</td>
<td>45.72</td>
<td>24.33</td>
<td>1.62</td>
<td>1.39</td>
<td>2.415</td>
<td>2.145</td>
<td>79.42</td>
</tr>
<tr>
<td>2</td>
<td>1.33</td>
<td>71.08</td>
<td>42.16</td>
<td>26.89</td>
<td>2.03</td>
<td>1.68</td>
<td>2.456</td>
<td>2.456</td>
<td>81.33</td>
</tr>
<tr>
<td>3</td>
<td>1.48</td>
<td>68.24</td>
<td>39.34</td>
<td>28.65</td>
<td>3.11</td>
<td>2.50</td>
<td>2.521</td>
<td>2.521</td>
<td>82.55</td>
</tr>
</tbody>
</table>

**Table 2:** VFT, AM and MYEGA parameters obtained for the fits of the MgO-P$_2$O$_5$-Al$_2$O$_3$ viscosities. Parameter $\log \eta_0$ in the equations fixed at $\eta_0 = 4 \cdot 10^{-5}$ Pa·s according [24]. The errors of the fitting parameters were in the order of the last displayed digit.

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>VFT model</th>
<th>AM model</th>
<th>MYEGA model</th>
<th>Arrhenius</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\log \eta_0$</td>
<td>$B$</td>
<td>$T_0$</td>
<td>$\log \eta_0$</td>
</tr>
<tr>
<td>1</td>
<td>-4.398</td>
<td>8566</td>
<td>575.5</td>
<td>-4.398</td>
</tr>
<tr>
<td>3</td>
<td>-4.398</td>
<td>6434</td>
<td>659.5</td>
<td>-4.398</td>
</tr>
</tbody>
</table>

**Table 3:** The values of TNM (Table A) and TNMa (Table B) relaxation models parameters determined for the volume relaxation measurements by non-linear regression analysis.

<table>
<thead>
<tr>
<th>A) TNM</th>
<th>Glass No.1</th>
<th>Glass No.2</th>
<th>Glass No.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\log {K/\text{Pa}}$</td>
<td>9.03 ± 0.02</td>
<td>8.85 ± 0.01</td>
<td>8.97 ± 0.02</td>
</tr>
<tr>
<td>$\beta$[-]</td>
<td>0.74 ± 0.01</td>
<td>0.84 ± 0.01</td>
<td>0.76 ± 0.01</td>
</tr>
<tr>
<td>$\Delta h^*{\text{kJ.mol}^{-1}}$</td>
<td>387 ± 0.1</td>
<td>400 ± 0.1</td>
<td>443 ± 0.1</td>
</tr>
<tr>
<td>$\chi$[-]</td>
<td>0.42 ± 0.01</td>
<td>0.31 ± 0.01</td>
<td>0.40 ± 0.01</td>
</tr>
<tr>
<td>$\log A/s$</td>
<td>-54.51 ± 0.01</td>
<td>-55.96 ± 0.01</td>
<td>-61.26 ± 0.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B) TNMa</th>
<th>Glass No.1</th>
<th>Glass No.2</th>
<th>Glass No.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\log {K/\text{Pa}}$</td>
<td>8.31 ± 0.01</td>
<td>8.30 ± 0.01</td>
<td>8.56 ± 0.01</td>
</tr>
<tr>
<td>$\beta$[-]</td>
<td>0.77 ± 0.01</td>
<td>0.88 ± 0.01</td>
<td>0.77 ± 0.01</td>
</tr>
<tr>
<td>$B[\text{K}]$</td>
<td>34419 ± 1</td>
<td>38063 ± 2</td>
<td>45822 ± 1</td>
</tr>
<tr>
<td>$E[\text{kJ.mol}^{-1}]$</td>
<td>286 ± 0.1</td>
<td>316 ± 0.1</td>
<td>381 ± 0.1</td>
</tr>
<tr>
<td>$\log {\eta_0/\text{Pa.s}}$</td>
<td>-16.62 ± 0.24</td>
<td>-8.00 ± 0.21</td>
<td>-16.61 ± 0.20</td>
</tr>
</tbody>
</table>
Table 4: Correlation coefficients between the different thermokinetic quantities and compositional components – mol.% Al₂O₃ content (n(Al₂O₃)) and n(MgO)/n(P₂O₅) ratio. The thermokinetic quantities are denoted as follows: density (ρ), fragility calculated from $\Delta h^*_v (m / \Delta h^*_v)$, fragility calculated from $\Delta h^*_H (m / \Delta h^*_H)$, fragility calculated from Arrhenius $E_\eta (m / E_\eta \text{ AR})$, fragility calculated from AM $E_\eta (m / E_\eta \text{ AM})$, fragility calculated from MYEGA $E_\eta (m / E_\eta \text{ M})$, fragility calculated from VFT $E_\eta (m / E_\eta \text{ V})$, activation energy of enthalpy relaxation ($\Delta h^*_H$), activation energy of volume relaxation ($\Delta h^*_v$), $T_g$ from DSC ($T_g \text{ DSC}$), $T_g$ from TMA ($T_g \text{ TMA}$), $T_{12}$ extrapolated by VFT ($T_{12} \text{ VFT}$), $T_{12}$ extrapolated by AM ($T_{12} \text{ AM}$), $T_{12}$ extrapolated by MYEGA ($T_{12} \text{ MYE}$).

<table>
<thead>
<tr>
<th></th>
<th>$n(\text{MgO})/n(\text{P}_2\text{O}_5)$</th>
<th>$n(\text{Al}_2\text{O}_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>0.98502</td>
<td>0.99028</td>
</tr>
<tr>
<td>$m / \Delta h^*_v$</td>
<td>0.92555</td>
<td>0.99715</td>
</tr>
<tr>
<td>$m / \Delta h^*_H$</td>
<td>0.88842</td>
<td>0.98657</td>
</tr>
<tr>
<td>$m / E_\eta \text{ AR}$</td>
<td>0.96771</td>
<td>0.99831</td>
</tr>
<tr>
<td>$m / E_\eta \text{ AM}$</td>
<td>0.97288</td>
<td>0.99685</td>
</tr>
<tr>
<td>$m / E_\eta \text{ M}$</td>
<td>0.96438</td>
<td>0.99898</td>
</tr>
<tr>
<td>$m / E_\eta \text{ V}$</td>
<td>0.96219</td>
<td>0.99932</td>
</tr>
<tr>
<td>$\Delta h^*_H$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta h^*_v$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_g \text{ DSC}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_g \text{ TMA}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{12} \text{ VFT}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{12} \text{ AM}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{12} \text{ MYE}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$n(\text{MgO})/n(\text{P}_2\text{O}_5)$</th>
<th>$n(\text{Al}_2\text{O}_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.90186$</td>
<td>0.94254</td>
<td>0.99997</td>
</tr>
<tr>
<td>$0.99105$</td>
<td>0.99961</td>
<td>0.94919</td>
</tr>
<tr>
<td>$0.98502$</td>
<td>0.92555</td>
<td>0.88842</td>
</tr>
<tr>
<td>$0.99028$</td>
<td>0.99715</td>
<td>0.98657</td>
</tr>
<tr>
<td>$0.98502$</td>
<td>0.92555</td>
<td>0.88842</td>
</tr>
<tr>
<td>$0.99028$</td>
<td>0.99715</td>
<td>0.98657</td>
</tr>
<tr>
<td>$0.99105$</td>
<td>0.99961</td>
<td>0.94919</td>
</tr>
<tr>
<td>$0.99961$</td>
<td>0.99961</td>
<td>0.94919</td>
</tr>
</tbody>
</table>

26