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# Study of structure and properties of $ZnO–Bi_2O_3–P_2O_5$ glasses

**Josef Jirák · Ladislav Koudelka · Jaroslav Pospíšil ·
Petr Mošner · Lionel Montagne · Laurent Delevoye**

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**Abstract** Glasses of the ternary system $ZnO–Bi_2O_3–P_2O_5$ were prepared and studied in two compositional series $50ZnO–xBi_2O_3–(50 - x)P_2O_5$ and $(50 - y)ZnO–yBi_2O_3–50P_2O_5$. Two distinct glass-forming regions were found in the $50ZnO–xBi_2O_3–(50 - x)P_2O_5$ glass series with $x = 0–10$ and 20–35 mol.% $Bi_2O_3$. All prepared $Bi_2O_3$-containing glasses reveal a high chemical durability. Small additions of $Bi_2O_3$ (~5 mol.%) improve thermal stability of glasses. All glasses crystallize on heating within the temperature range of 505–583 °C. Structural studies by Raman and $^{31}P$ MAS NMR spectroscopies showed the rapid depolymerisation of phosphate chains within the first region with $x = 0–15$ and the presence of isolated $Q^0$ phosphate units within the second region with $x = 20–35$. Raman studies showed that bismuth is incorporated in the glass structure in $BiO_6$ units and their vibrational bands were observed within the spectral region of 350–700 $cm^{-1}$. The evolution of properties and the spectroscopic data are both in accordance with a network former effect of $Bi_2O_3$.

## Introduction

Phosphorus pentoxide $P_2O_5$ is known as one of the glass forming oxides. It is able to form glasses also when mixed with considerable quantities of other oxides. Phosphate glasses reveal a low chemical durability, which can be increased by the addition of oxides of trivalent metal cations like $Al_2O_3$, $Fe_2O_3$, or $B_2O_3$ [1, 2]. Also the role of another trivalent oxide $Bi_2O_3$ in phosphate glasses was investigated in several previous papers [2–15]. These studies were devoted mainly to potassium and sodium-phosphate based glasses [3–14]. Peng and Day [2] studied thermal expansion and chemical durability of $K_2O–B_2O_3–P_2O_5$ glasses. Montagne et al. [3] studied the structure of ternary glasses of the $Na_2O–Bi_2O_3–P_2O_5$ system by $^{31}P$ MAS NMR and infrared spectroscopies, whereas Shaim and Et-Tabirou [4] investigated some physical properties and electrical conductivity of the series of sodium phosphate with 40 mol.% $P_2O_5$ and with 0–25 mol.% $Bi_2O_3$. Recently Daviero et al. [5] investigated structural role of $Bi^{3+}$ in $Na_2O–Bi_2O_3–P_2O_5$ glasses by EXAFS, XANES and $^{31}P$ DQ MAS-NMR spectroscopy and found two distinct oxygen shells in the $Bi^{3+}$ environment and a mixed network-former effect of $Bi_2O_3$ in these glasses. The effect of $Al_2O_3$ substitution by $Bi_2O_3$ in the quaternary glasses of the $Na_2O–Bi_2O_3–Al_2O_3–P_2O_5$ system was studied in [6], where the authors concluded that $Bi^{3+}$ exhibits the same structural role in the glass network as $Al^{3+}$ and also improves chemical durability of sodium phosphate glasses. Ahaman et al. [7] studied glass-formation in the system $Na_3PO_4–Pb_3(PO_4)_2–P_2O_5$ and dielectric properties of glasses of this system.

Structural role of $TiO_2$ and $Bi_2O_3$ in $Na_2O–Bi_2O_3–TiO_2–P_2O_5$ glasses was investigated in [8–11]. The authors of [8, 9] came to the conclusion that the incorporation of

J. Jirák · L. Koudelka (✉) · J. Pospíšil ·
P. Mošner
Department of General and Inorganic Chemistry,
Faculty of Chemical Technology, University of Pardubice,
532 10 Pardubice, Czech Republic
e-mail: ladislav.koudelka@upce.cz

L. Montagne · L. Delevoye
Unité de Catalyse et Chimie du Solide, Université des Sciences
et Technologies de Lille, Ecole Nationale Superieure de Chimie
de Lille, BP108, 59652 Villeneuve d’Ascq cedex, France

$BiO_6$ and $TiO_6$ octahedra into the glass structure results in the depolymerisation of phosphate chains and in the glasses with the lowest $Bi_2O_3$ content pyrophosphate groups are prevailing, whereas in $Bi_2O_3$-rich glasses orthophosphate groups become predominant structural units. Ionic conductivity of $Na_2O$–$Bi_2O_3$–$TiO_2$–$P_2O_5$ glasses decreases with increasing concentration of either $Bi_2O_3$ or $TiO_2$ [10], whereas their chemical durability increases. According to the results of $^{31}P$ DQ MAS NMR spectra of these glasses [11] the substitution of $TiO_2$ for $Bi_2O_3$ increases the $Q^2$ fraction of phosphate units, i.e., results in the repolymerisation of the phosphate network [11] which is accompanied by an increase of glass transition temperature.

The investigation of $Na_2O$–CuO–$Bi_2O_3$–$P_2O_5$ quaternary glasses reported in [12–14] showed that additions of CuO or $Bi_2O_3$ increase glass transition temperature and depolymerize phosphate chains [12, 13]. According to [14] $Bi_2O_3$ in these glasses behaves as a network former and is incorporated in the network as $BiO_6$ units.

Glass formation in the ZnO–$Bi_2O_3$–$P_2O_5$ system was reported by Elouadi et al. [15]. The authors [15] determined glass-forming region in this ternary system. There has not been any report on the properties of glasses in this system. Therefore, the aim of this work is the preparation and study of physical and thermal properties and also investigation of structure of glasses from the system ZnO–$Bi_2O_3$–$P_2O_5$.

## Experimental

Glasses of the ZnO–$Bi_2O_3$–$P_2O_5$ system were prepared in the batches of 25 g by the reaction of ZnO, $Bi_2O_3$ and $H_3PO_4$ and slow heating the reaction mixture up to 600 °C to remove water from the reaction mixture and then melted up to 1,050–1,200 °C in high-purity alumina crucibles. After 20 min reaction and mixing at this temperature, the obtained melt was cooled by pouring into a graphite mould of 30 × 30 mm dimensions to form a suitable glass block or quenched between two copper blocks. The obtained glasses were separately annealed for 15 min at a temperature about their $T_g$ and then slowly cooled to the room temperature.

The glass density, $\rho$, was determined at bulk samples by the Archimedes method using $CCl_4$ as the immersion liquid. The molar volume $V_M$ was calculated as $V_M = \bar{M}/\rho$, where $\bar{M}$ is the average molar weight of the glass composition $x$ZnO–$y$$Bi_2O_3$–$z$$P_2O_5$ calculated for $x + y + z = 1$.

Thermal behaviour of the glasses was studied with the Netzsch 404 PC, working in the temperature range of 30–1,100 °C at a scan rate of 10 °C/min in the DSC mode. The measurement was done on powder samples with mean diameter 8–10 μm placed in silica crucibles.

The Raman spectra were measured on bulk samples at room temperature on a FT IR spectrometer, Bruker model IFS 55, with the Raman attachment, FRA 106. The Raman spectra were recorded under excitation with a Nd:YAG laser radiation using a slit width of 4 $cm^{-1}$ with the power of 300 mW at the sample surface.

$^{31}P$ MAS NMR spectra were measured on a BRUKER Avance 400 spectrometer with a 4 mm probe. The spinning speed was 12.5 kHz. The pulse length was 1.2 μs (pi/4), and the recycle delay was 60 s which was sufficient to enable relaxation at this field strength. The Larmor frequency was 162.3 MHz. The chemical shifts of $^{31}P$ nuclei are given relative to 85% $H_3PO_4$ at 0 ppm.

## Results and discussion

Two compositional series of zinc bismuthate–phosphate glasses 50ZnO–$x$$Bi_2O_3$–(50 – $x$)$P_2O_5$ and (50 – $y$)ZnO–$y$$Bi_2O_3$–50$P_2O_5$ were synthesized and studied. Both compositional series are shown in the ternary phase diagram (see Fig. 1) together with glass-forming region determined by Elouadi [12]. In the first glass series 50ZnO–$x$$Bi_2O_3$–(50 – $x$)$P_2O_5$ the samples with $x$ = 0, 5 and 25–35 mol.% $Bi_2O_3$ were prepared by slow cooling, whereas the glasses with $x$ = 10 and 20 mol.% $Bi_2O_3$ were prepared by quenching between copper blocks. The sample with $x$ = 15 mol.% $Bi_2O_3$ was crystalline even when quenching was used. The O/P ratio in this sample is 3.85, i.e., close to the orthophosphate composition. X-ray diffraction analysis revealed that the sample contains crystalline phases $BiPO_4$ and $Zn_2P_2O_7$.

Thus according to our results the glass-forming region in the compositional series 50ZnO–$x$$Bi_2O_3$–(50 – $x$)$P_2O_5$ is

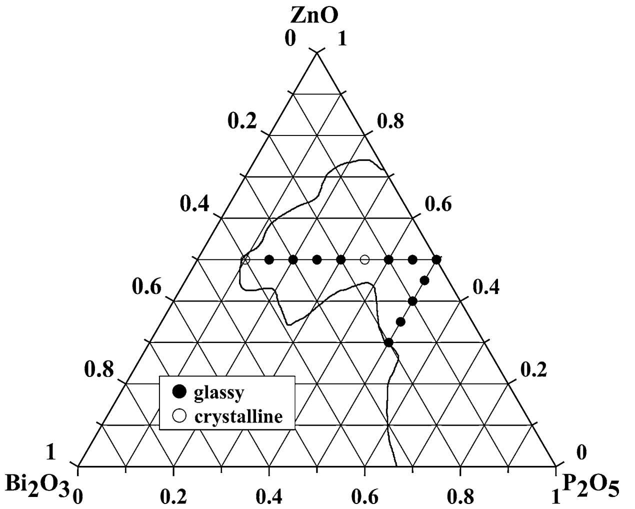

**Fig. 1** Ternary phase diagram of the glass system ZnO–$Bi_2O_3$–$P_2O_5$

split into two regions: the first one at a low Bi$_2$O$_3$ content (0–10 mol.% Bi$_2$O$_3$) and the second one at a higher Bi$_2$O$_3$ content (20–35 mol.% Bi$_2$O$_3$). In the second glass series $(50 - y)$ZnO–$y$Bi$_2$O$_3$–50P$_2$O$_5$ homogeneous glasses with $y = 0$ and 5 mol.% Bi$_2$O$_3$ were obtained by slow cooling of the melt, whereas the glasses with $y$ = 10–20 mol.% Bi$_2$O$_3$ were prepared by quenching between copper blocks. All the prepared glasses were transparent and homogeneous. Glasses of the series $(50 - y)$ZnO–$y$Bi$_2$O$_3$–50P$_2$O$_5$ with a higher content of Bi$_2$O$_3$ were slightly yellowish, glasses of the series 50ZnO–$x$Bi$_2$O$_3$–$(50 - x)$P$_2$O$_5$ with a high Bi$_2$O$_3$ content had an orange-red up to brownish colour. The chemical analysis showed that Al$_2$O$_3$ content in the glasses was less than 1.5 mol.%, which could bring only small changes in the glass properties as shown in Na$_2$O–Bi$_2$O$_3$–Al$_2$O$_3$–P$_2$O$_5$ glasses [5].

The values of the glass density, $\rho$, for both series of glasses are shown in Table 1. The density values of the studied glasses increase with increasing bismuth oxide content in both glass series, but the slope in $\rho$ is higher in the series 50ZnO–$x$Bi$_2$O$_3$–$(50 - x)$P$_2$O$_5$. The observed increase in $\rho$ is monotonous at both compositional series. The reason for this increase in $\rho$ is the addition of heavy metal oxide Bi$_2$O$_3$ replacing lighter oxides P$_2$O$_5$ in the first compositional series with 50 mol.% ZnO or ZnO in the second compositional series $(50 - y)$ZnO–$y$Bi$_2$O$_3$–50P$_2$O$_5$.

The molar volume values, $V_M$ (Table 1), in $(50 - y)$ZnO–$y$Bi$_2$O$_3$–50P$_2$O$_5$ glasses increase almost linearly with increasing Bi$_2$O$_3$ content, whereas in the compositional series 50ZnO–$x$Bi$_2$O$_3$–$(50 - x)$P$_2$O$_5$ the values of $V_M$ slightly decrease within the compositional region $x$ = 0–10 mol.% Bi$_2$O$_3$, while within the compositional range 20–35 mol.% Bi$_2$O$_3$ the values of $V_M$ remain almost unchanged.

Chemical durability of Bi$_2$O$_3$-containing glasses is very high. No measurable mass loss was detected at room temperature even after the immersion of glass samples for 1 month in the distilled water. The measurement of dissolution rate in boiling water for 5 h gave the values from $3 \times 10^{-4}$ g cm$^{-2}$ min$^{-1}$ for the sample 50ZnO–5Bi$_2$O$_3$–45P$_2$O$_5$ up to $1 \times 10^{-7}$ g cm$^{-2}$ min$^{-1}$ for the sample 50ZnO–30Bi$_2$O$_3$–20P$_2$O$_5$ for the first glass series and 2–5 × $10^{-4}$ g cm$^{-2}$ min$^{-1}$ for the glasses of the second series.

The DSC curves of the glass series 50ZnO–$x$Bi$_2$O$_3$–$(50 - x)$P$_2$O$_5$ are shown in Fig. 2. The values of glass transition temperature, $T_g$, of these glasses (see Table 1) are different in the region with a low and a high Bi$_2$O$_3$ content. Within the first compositional region of 0–10 mol.% Bi$_2$O$_3$ the values of $T_g$ slightly increase from 397 to 427 °C and within the second compositional region the $T_g$ values are substantially higher and decrease from 479 to 447 °C at the sample with 35 mol.% Bi$_2$O$_3$. $T_g$ values for glasses from compositional series $(50 - y)$ZnO–$y$Bi$_2$O$_3$–50P$_2$O$_5$ show a slight increase in $T_g$ in the region of 0–10 mol.% Bi$_2$O$_3$ and than $T_g$ slightly decreases (Table 1).

All glasses in the 50ZnO–$x$Bi$_2$O$_3$–$(50 - x)$P$_2$O$_5$ compositional series crystallize on heating within the temperature region of 511–610 °C. The DSC curves of the glass series $(50 - y)$ZnO–$y$Bi$_2$O$_3$–50P$_2$O$_5$ (not shown here) showed that all glasses of this series crystallize on heating in the temperature region of 510–632 °C.

Thermal stability of glasses was evaluated in a first approximation from the values of $T_c - T_g$ (see Table 1). The highest values of $T_c - T_g$ were obtained in both series for the glasses containing 5 mol.% Bi$_2$O$_3$, i.e., their thermal stability is the highest of all studied glasses. With further increase in Bi$_2$O$_3$ content the difference of $T_c - T_g$ decreases in both glass series showing on the decreasing thermal stability of these glasses.

$^{31}$P MAS NMR spectra of four samples of the glass series 50ZnO–$x$Bi$_2$O$_3$–$(50 - x)$P$_2$O$_5$ are shown in Fig. 3

**Table 1** Density, molar volume and glass transition temperature of ZnO–Bi$_2$O$_3$–P$_2$O$_5$ glasses

| ZnO (mol.%) | Bi$_2$O$_3$ (mol.%) | P$_2$O$_5$ (mol.%) | $\rho \pm 0.05$ (g cm$^{-3}$) | $V_M$ (cm$^3$) | $T_g \pm 3$ (°C) | $T_c \pm 2$ (°C) | $T_c - T_g$ (°C) |
|---|---|---|---|---|---|---|---|
| 50 | 0 | 50 | 2.85 | 39.2 | 397 | 531 | 134 |
| 50 | 5 | 45 | 3.50 | 36.5 | 406 | 583 | 177 |
| 50 | 10 | 40 | 4.19 | 34.4 | 427 | 510 | 83 |
| 50 | 20 | 30 | 5.27 | 33.5 | 479 | 564 | 85 |
| 50 | 25 | 25 | 5.90 | 32.7 | 467 | 550 | 83 |
| 50 | 30 | 20 | 6.33 | 33.0 | 468 | 530 | 62 |
| 50 | 35 | 15 | 6.80 | 33.1 | 447 | 528 | 81 |
| 50 | 0 | 50 | 2.85 | 39.2 | 397 | 531 | 134 |
| 45 | 5 | 50 | 3.30 | 39.7 | 407 | 550 | 143 |
| 40 | 10 | 50 | 3.66 | 41.0 | 427 | 565 | 138 |
| 35 | 15 | 50 | 4.09 | 41.4 | 423 | 531 | 108 |
| 30 | 20 | 50 | 4.41 | 42.8 | 422 | 505 | 83 |

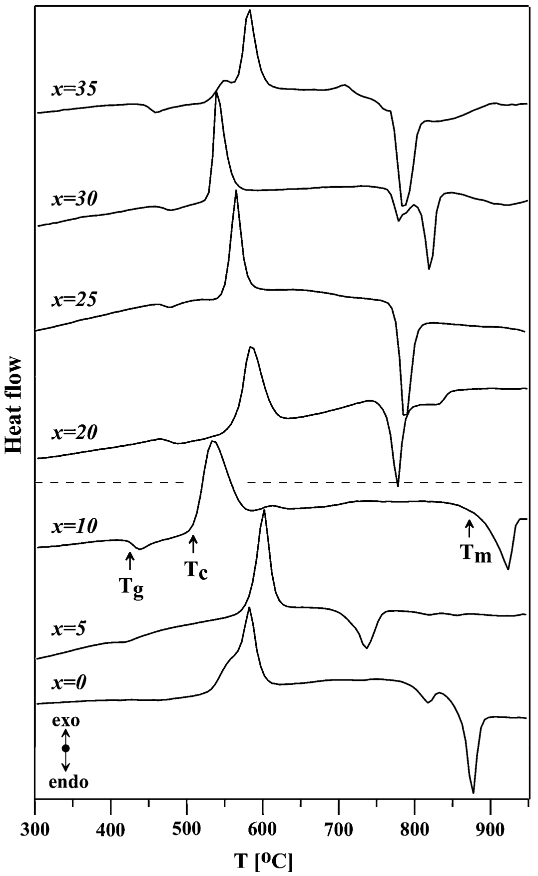

**Fig. 2** DSC curves of the glass series $50ZnO–xBi_2O_3–(50 – x)P_2O_5$

and three samples of the glass series $(50 – y)ZnO–yBi_2O_3–50P_2O_5$ are shown in Fig. 4. These spectra reveal distinct signals of $Q^2$, $Q^1$ and $Q^0$ phosphate groups according to the Van Wazer notation [16], the positions of which are very distinctively separated. Therefore, we have decomposed MAS NMR spectra by the line shape simulation and the results are collected in Table 2.

The spectrum of the metaphosphate glass is dominated by an isotropic peak at –31 ppm (Fig. 3), characteristic of $Q^2$ units with a very small shoulder at –13.4 ppm belonging to the about 2% of $Q^1$ groups terminating metaphosphate chains. Positions of both signals are in a good agreement with the studies of glassy $Zn(PO_3)_2$ by Brow et al. [17] and Wiench et al. [18]. The MAS spectrum of the sample $50ZnO–10Bi_2O_3–40P_2O_5$ from the series $50ZnO–xBi_2O_3–(50 – x)P_2O_5$ is dominated by the signal of $Q^1$ units, with smaller amounts of $Q^2$ and $Q^0$ units, whereas the spectra of glasses containing 20 and 30 mol.% $Bi_2O_3$ reveal dominating signal of $Q^0$ units showing on the presence of isolated orthophosphate units in these glasses.

$^{31}P$ MAS NMR spectra of glass series $(50 – y)ZnO–yBi_2O_3–50P_2O_5$ (Fig. 4) show also the depolymerisation of phosphate chains, but in this case the transformation of $Q^2$ units into $Q^1$ units is slower as the ratio $Bi_2O_3/P_2O_5$ increases not so rapidly as in the previous series. The number of diphosphate units increases steadily with increasing $Bi_2O_3$ content and in the $30ZnO–20Bi_2O_3–50P_2O_5$ glass $Q^1$ units are dominating. The value of

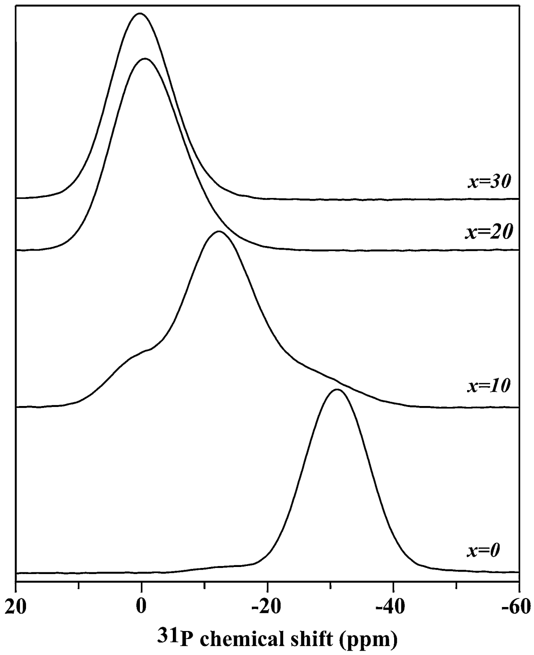

**Fig. 3** $^{31}P$ MAS NMR spectra of the glass series $50ZnO–xBi_2O_3–(50 – x)P_2O_5$

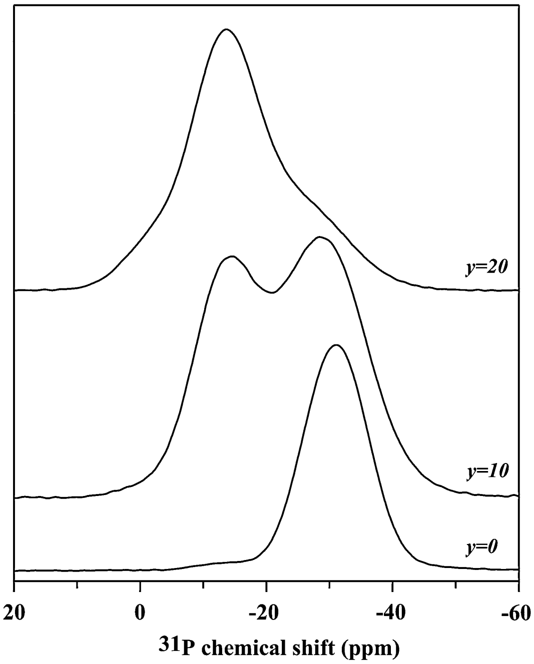

**Fig. 4** $^{31}P$ MAS NMR spectra of the glass series $(50 – y)ZnO–yBi_2O_3–50P_2O_5$

**Table 2** Chemical shifts and relative peak areas of $^{31}P$ MAS NMR spectra of $ZnO–Bi_2O_3–P_2O_5$ glasses

| ZnO | $Bi_2O_3$ | $P_2O_5$ | $Q^2$ | | $Q^1$ | | $Q^0$ | |
|---|---|---|---|---|---|---|---|---|
| (mol.%) | | | (ppm) | Area (% ±2) | (ppm) | Area (% ±2) | (ppm) | Area (% ±2) |
| 50 | – | 50 | –31.0 | 98.2 | –13.4 | 1.8 | – | – |
| 50 | 10 | 40 | –25.9 | 16.4 | –12.1 | 71.1 | +1.5 | 12.5 |
| 50 | 20 | 30 | – | – | –10.7 | 9.0 | –0.4 | 91.0 |
| 50 | 30 | 20 | – | – | –9.2 | 6.3 | +0.4 | 93.7 |
| 50 | – | 50 | –31.0 | 98.2 | –13.4 | 1.8 | – | – |
| 40 | 10 | 50 | –28.9 | 61.9 | –13.4 | 37.2 | –1.4 | 0.9 |
| 30 | 20 | 50 | –25.9 | 27.9 | –13.3 | 63.3 | –1.7 | 8.8 |

chemical shift of $Q^2$ units shifts downfield probably due to an increasing number of P–O–Bi bonds in the glass.

The Raman spectra of the glass series $50ZnO–xBi_2O_3–(50 - x)P_2O_5$ are shown in Fig. 5. In the high-frequency region on the Raman spectrum of the pure zinc metaphosphate glass, there is one dominant very strong narrow band with the maximum at 1,205 $cm^{-1}$ ascribed according to [19] to the symmetrical stretching vibration of non-bridging oxygen atoms between metaphosphate ($Q^2$) structural units. Its position is in agreement with the data on $Zn(PO_3)_2$ by Nelson and Exarhos [20]. Another strong band at 704 $cm^{-1}$ is due to the symmetrical stretching vibration of bridging oxygen atoms between $Q^2$ groups [19]. With the replacement of $P_2O_5$ by $Bi_2O_3$ in the glasses with a low $Bi_2O_3$ content the maximum of this band shifts to lower frequencies up to 1,064 $cm^{-1}$ at the $50ZnO–10Bi_2O_3–40P_2O_5$ glass due to the depolymerisation of phosphate chains and the transformation of $Q^2$ units to $Q^1$ units. This change is also confirmed by the presence of the Raman band at 753 $cm^{-1}$, characteristic of symmetrical stretching vibration between diphosphate ($Q^1$) units [21], on the Raman spectrum of the glass with $x = 10$ mol.% $Bi_2O_3$.

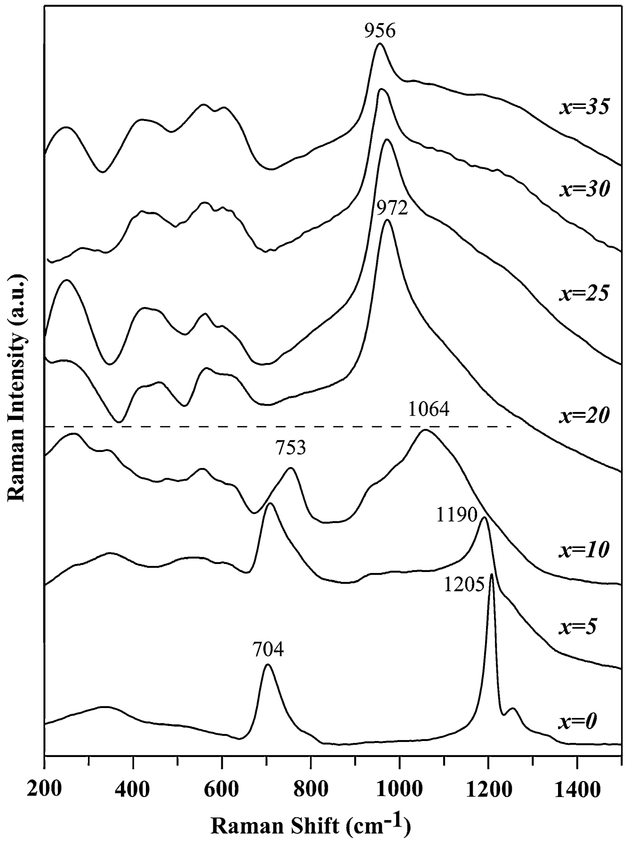

**Fig. 5** Raman spectra of the glass series $50ZnO–xBi_2O_3–(50 - x)P_2O_5$

In the second glass-forming region of $50ZnO–xBi_2O_3–(50 - x)P_2O_5$ glass series with $x = 20–35$ mol.% Raman spectra contain one dominating band in the high-frequency region the position of which shifts only slightly towards shorter wavelength from 972 to 956 $cm^{-1}$. The position of this band in the Bi-rich glasses is close to the values observed for isolated $PO_4$ ($Q^0$) units in orthophosphates [22]. This assignment is in agreement with the results of NMR spectra (Fig. 3), which also revealed dominating role of $Q^0$ units in these glasses. The slight shift of the Raman band from 972 to 956 $cm^{-1}$ reflects also the decrease in the content of $Q^1$ units (see Table 2).

New bands appear in the middle-frequency region of Raman spectra (350–700 $cm^{-1}$) in this compositional region. As their relative intensity increases with increasing $Bi_2O_3$ content in comparison with the intensity of vibrational band of $Q^0$ units, we assume that these bands are associated with the vibrations of Bi–O bonds. In the study of $GeO_2–Bi_2O_3$ glasses Baia et al. [23] considered that $Bi^{3+}$ cations in these glasses are incorporated in the distorted $BiO_6$ octahedral groups. Similar coordination of Bi was considered in $PbO–Bi_2O_3–Ga_2O_3$ glasses [24] as well as in $Na_2O–Bi_2O_3–CuO–P_2O_5$ glasses [12]. A typical peak fitting of the Raman spectrum in the region of 350–700 $cm^{-1}$ is shown in Fig. 6. Two bands observed in the region of 350–500 $cm^{-1}$ can be assigned to overlapping vibrations of Bi–O bonds in distorted $BiO_6$ octahedra with

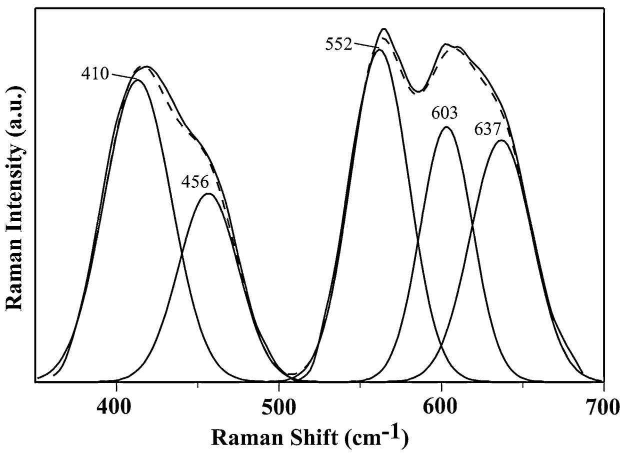

**Fig. 6** Deconvolution of broad Raman bands within the wavelength region of 350–700 cm$^{-1}$ for the $50ZnO–25Bi_2O_3–50P_2O_5$ glass

the deformation vibrations of phosphate groups [13]. The bands observed within the region of 500–700 cm$^{-1}$ are assigned to Bi–O–Bi vibrations similar to $PbO–Bi_2O_3–Ga_2O_3$ glasses [24].

The Raman spectra of the glass series $(50 - y)ZnO–yBi_2O_3–50P_2O_5$ are shown in Fig. 7. With increasing $Bi_2O_3$ content the position of maximum of this dominant peak, which is assigned to stretching vibration of non-bridging oxygen atoms in $Q^2$ structural units, shifts to lower wavelength into the spectral region characteristic of stretching vibrations of non-bridging oxygen atoms on $Q^1$ units. This result is in full agreement with the changes in $^{31}P$ MAS NMR spectra (Fig. 4), where the signal of $Q^2$ units decreases and the signal of $Q^1$ units increases with increasing $Bi_2O_3$ content. This is confirmed also by changes in the shape of the Raman band of vibrations of bridging oxygen atoms between $PO_4$ units at 704–708 cm$^{-1}$, where increasing participation of $Q^1$ units with increasing $Bi_2O_3$ content broadens the band on its high-frequency side and the Raman band of $O_3P–O–PO_3$ vibrations is dominating on the Raman spectrum of $30ZnO–20Bi_2O_3–50P_2O_5$ glass. On the Raman spectra of glasses containing 15 and 20 mol.% $Bi_2O_3$ a broad band of vibrations of Bi–O and Bi–O–Bi bonds can be also observed within the spectral region of 350–680 cm$^{-1}$ like in the previous glass series. As the $Bi_2O_3$ content in these glasses is lower than in the previous series, its intensity is lower and its deconvolution was not possible. Nevertheless, the depolymerisation of phosphate chains, observed in Raman and NMR spectra, reflects the incorporation of $BiO_6$ units into the structural network like in the first glass series.

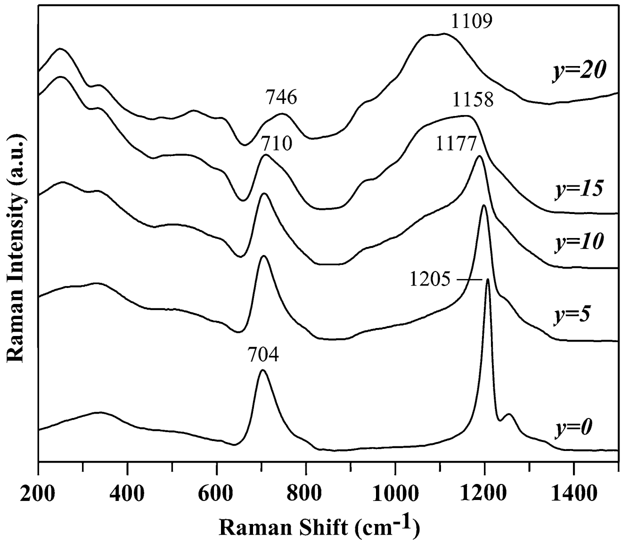

**Fig. 7** Raman spectra of the glass series $(50 - y)ZnO–yBi_2O_3–50P_2O_5$

## Conclusions

The effect of $Bi_2O_3$ addition to $Zn(PO_3)_2$ glass was studied in two compositional series $50ZnO–xBi_2O_3–(50 - x)P_2O_5$ and $(50 - y)ZnO–yBi_2O_3–50P_2O_5$. $^{31}P$ MAS NMR spectra showed that the incorporation of $Bi_2O_3$ into the parent glass structure in $50ZnO–xBi_2O_3–(50 - x)P_2O_5$ results in the depolymerisation of metaphosphate chains, which is almost completed in the first series of glasses with $x = 0–15$ mol.% $Bi_2O_3$, whereas within the compositional region of $x = 20–35$ mol.% $Bi_2O_3$ the presence of isolated orthophosphate tetrahedra in the glass structure was detected both from $^{31}P$ NMR and Raman spectra. The incorporation of $Bi_2O_3$ in the form of $BiO_6$ octahedra into the glass structure was revealed from the Raman spectra by the presence of characteristic Raman bands of vibrations of Bi–O and Bi–O–Bi bonds.

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