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Properties and structures of TiO_2–ZnO–P_2O_5 glasses

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The glass forming region of TiO_2–ZnO–P_2O_5 glasses was investigated at 1400°C, which is lower than the melting temperature of general titanophosphete glasses. TiO_2 could be added up to 15 mol% in the TiO_2–ZnO–P_2O_5 glasses. The glass forming region of 15TiO_2–ZnO–P_2O_5 was quite smaller than that of ZnO–P_2O_5, and the glasses with TiO_2 were colorized by the formation of Ti^{3+}. The refractive index of the glasses increased with increases in the TiO_2 concentrations, and the maximum was 1.656. The glass transition temperature, T_g, of the glasses increased with increased TiO_2 concentrations, although T_g decreased with increases in the ratio of ZnO to P_2O_5. Raman spectra of the glasses suggested that P–O–Ti bonds were formed by the addition of TiO_2. The increase in T_g and the narrow glass forming region were caused by the formation of strong chemical bonds, P–O–Ti.

Key-words : TiO_2–ZnO–P_2O_5 glasses, Glass forming region, Glass transition temperature, Refractive index, Raman spectra

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1. Introduction

Zinc phosphate glass is interesting in the low-melting sealing glasses and molded glasses because of its low melting temperature.[1),2)] The zinc phosphate glass system can contain high ZnO concentrations, exceeding the pyrophosphate compositional limit, and the glass forming region is wide; the molar ratio $(ZnO)/(P_2O_5) = 0$–2.5. In the zinc phosphate system, metaphosphate chains, which are represented as Q^2 units (where n represented in Q^n is the number of bridging oxygens in a PO_4 tetrahedron), were depolymerized by the addition of ZnO. The average number of non-bridging oxygens per PO_4 tetrahedron increased with the increase in ZnO and reached 3: Q^1 units, when $(ZnO)/(P_2O_5) = 2$. The glass transition temperature, T_g, decreased with the increase in ZnO and became the lowest (415°C) at around 60 mol% ZnO, although the T_g increased above 60 mol% ZnO. The refractive index of the glass increased with increasing ZnO concentrations; the highest refractive index was above 1.64, and the T_g was approximately 460°C when the ZnO was 71 mol%.

On the other hand, titanophosphate glasses have generated interest for applications such as photonic devices[3),4)] and electric conduction glasses.[5),6)] The TiO_2–P_2O_5 glasses are generally known to become purple due to the formation of Ti^{3+} during the melting process. Recently, it was found that the reduced Ti^{3+} could be oxidized by the annealing process and that the Ti^{3+}-free glasses were ecologically sustainable optical glasses with a high refractive index and photocatalytic activity.[7)] In these glasses, it has been reported that TiO_2 behaves as an intermediate network former and that the bridging P–O–P network changes to P–O–Ti linkages. The incorporation of TiO_x polyhedra into the structural network has been realized mostly through the formation of TiO_6 octahedra[3),8),9)] or TiO_5 distorted polyhedra.[8),10)] The glass forming region of the TiO_2–P_2O_5 glasses is known to be 30–45 mol% P_2O_5.[5)–7)] However, the melting temperatures of most of the TiO_2–P_2O_5 glasses are high, generally above 1600°C. It is therefore difficult to obtain the titanophosphate glasses at low temperature.

In this paper, zinc titanophosphate glasses were fabricated at a lower melting temperature than 1600°C, and the thermal properties and refractive indices of the TiO_2–ZnO–P_2O_5 glasses were examined. The structural change was investigated based on Raman spectroscopy, and the increase in the melting temperature in response to the addition of TiO_2 is discussed based on the structural changes.

2. Experimental procedure

Glasses of TiO_2–ZnO–P_2O_5 were prepared from reagent-grade ZnO, $NH_4H_2PO_4$, and TiO_2, (Wako Pure Chem. Ind., Ltd.). Raw materials were mixed and melted in silica glass crucibles in air for 2 h at 1400°C. For binary ZnO–P_2O_5 glasses, the mixture was melted at 1200°C. The melts were poured onto a carbon plate and annealed at $T_g + 10$°C for 1 h. Some melts were quenched between a carbon and a steel plate when the glasses were not transparent.

X-ray diffraction of the glasses was measured to estimate the glass formation. The samples were crushed, and the powders were measured by Cu Kα at 40 kV and 30 mA. The patterns were scanned from 10 to 80 deg at intervals of 0.02 deg.

The thermal properties of the glasses were measured by TMA and TG/DTA. TMA was measured by heating at 5°C/min to determine T_g. A silica glass was used as a reference for the TMA measurement. TG/DTA was measured for 20 mg of crushed glasses to measure the crystallization peak temperature (T_p) and the melting temperature (T_m). Alumina powder was used as a reference, and the heating rate was 10°C/min.

The glass compositions were determined by the following measurements: inductively coupled plasma (ICP), energy-dispersive X-ray spectrometer (EDX), X-ray fluorescence spectrometer (XRF), and FT-IR, because the glasses were not completely dissolved in acids. First, the ratio of Zn and P of the glasses was determined by EDX. The glass samples were polished to a

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Table 1. Compositions of TiO_2–ZnO–P_2O_5 glasses (mol%) and some properties of the glasses

Batched			Analysed					T_g	T_p	T_m	n
TiO_2	ZnO	P_2O_5	TiO_2	ZnO	P_2O_5	OH (ppm)	(ZnO)/(P_2O_5)	(°C)	(°C)	(°C)	
0	60	40	0	56	44	300	1.27	430			1.549
10	50	40	10	50	40	150	1.25	508			1.627
15	35	50	Exceed glass formation				0.7*	—	663	1050	—
15	40	45	15	41	44	50	0.93	562	669	1070	1.627
15	45	40	15	44	41	30	1.07	550	—	960	1.632
15	42.5	42.5	15	46	39	60	1.18	545	661	970	1.643
15	47.5	37.5	15	49	36	30	1.36	530	727	970	1.656
15	55	30	Exceed glass formation				1.83*	—	655, 902	950	—

*: Caluculated from composition of baches.

thickness of 1 mm with kerosene and were measured by EDX at 40 kV and 250 μA. The measured values were revised based on a correction curve, which was drawn based on the relationship between ICP and EDX in the purchased powder samples: $Zn_2P_2O_7$ and $Zn_3(PO_4)_2{\cdot}H_2O$ (Kojundo Chem. Lab. Co., Ltd.). EDX of the powders was measured at 40 kV and 250 μA, and ICP was measured for the solution in which the powders were dissolved in HCl aqueous solution. Second, the ratio of Ti and P was measured by XRF. Mixture powder of TiO_2 and $Zn_2P_2O_7$ were prepared for reference. The mixtures and the glass samples polished to a thickness of 1 mm were measured by XRF, and the ratios of Ti and P were determined. Third, the concentrations of the OH groups were determined by a peak at around 3300 cm^{-1} measured for the 1-mm glass samples by FT-IR spectrometry (Shimadzu, 8600PC), because the water generally remained in the phosphate glasses. Finally, the compositions of the glasses were determined.

UV–VIS spectra were measured to estimate the color of the glasses, as the optical properties of the glasses such as refractive index are not sufficient to estimate when the glasses are colorized. In general, the titanophosphate glasses were colorized by the formation of Ti^{3+}.[11),12)] The colorized glasses were heated in O_2 at a flow rate of 300 ml/min at $T_g + 10$°C to bleach. The bleaching was estimated by comparison of the spectra between before and after heating.

Refractive indices of the glass samples polished to a thickness of 1 mm were measured at 633 nm by a prism coupler (Metricon).

Raman spectra of the glasses were measured at room temperature. The details were described in ref. 13). In the experimental setup, second-harmonic pulses of Q-switched Nd:YAG laser (532 nm) were used as an excitation source with a power of 1.68 W. The Raman spectra were measured at a high frequency range between 850 and 1350 cm^{-1} because the P–O stretching vibration in the Q^1 or Q^2 units is located from 900 to 1300 cm^{-1} in zinc phosphate glasses.[1)]

3. Results

The analyzed compositions of the glasses are summarized in **Table 1**. The glasses with TiO_2 looked black. The glasses containing $TiO_2 > 20$ mol% could not melt at 1400°C. The glass forming region of the $15TiO_2$–xZnO–$y$$P_2O_5$ glasses (mol%) was therefore investigated. The concentrations of TiO_2 in the glasses were the same as those of the batch. The ratios of ZnO and P_2O_5 changed a little. The concentrations of the OH groups were below 1%, and water appeared to remain only rarely in the glasses. The OH concentrations decreased with increases in the concentrations of TiO_2, and dipped to below 100 ppm when 15 mol% TiO_2 was added.

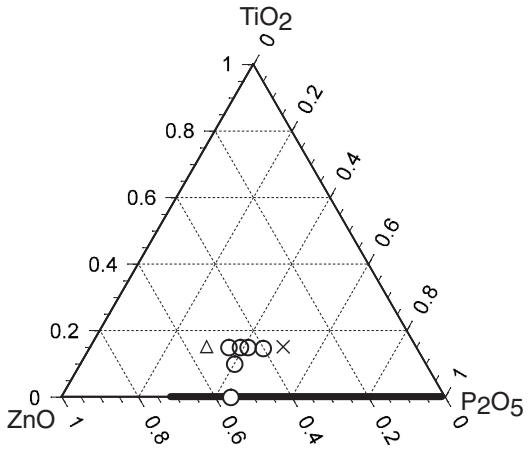

Fig. 1. Glass forming region of the TiO_2–ZnO–P_2O_5 glass system. ○: glass forming, △: phase separation, and ×: crystallization. Bold line represents the glass forming region reported in ref. 1).

Figure 1 shows the glass forming region in which the analyzed compositions of the glasses are plotted and the reported region of binary ZnO–P_2O_5 glasses[1)] is shown by a bold line. In the case of $15TiO_2$–xZnO–$(85 - x)P_2O_5$ glasses, the glasses were formed from $x = 41$ to 49 mol%, however, the bulks containing $x = 35$ mol% and $x = 55$ mol% looked opaque while black. The glass forming region of $15TiO_2$–xZnO–$(85 - x)P_2O_5$ glasses was significantly smaller than that of the binary ZnO–P_2O_5 glass system.

The XRD patterns of the devitrified bulks are shown in **Fig. 2**. The pattern of the prepared $15TiO_2$–35ZnO–$50P_2O_5$ sample had some peaks assigned to TiP_2O_7 crystal (JCPDS No. 38-1468). However, the prepared $15TiO_2$–55ZnO–$30P_2O_5$ glass did not show any peaks. This result suggests that the devitrification of the glass was caused by phase separation due to some kinds of amorphous phases.

The colorization of glasses containing TiO_2 was caused by the redox of Ti^{4+} and the formation of Ti^{3+} ions.[11),12)] The oxidization of Ti^{3+} ions is known to result in decolorization, and the oxidization was carried out by heating in O_2 atmosphere at temperatures above T_g. As an example, the UV–VIS spectra of the $15TiO_2$–49ZnO–$36P_2O_5$ glass before and after heating for 72 h are shown in **Fig. 3**. The spectrum of the glass before heating had a broad peak from approximately 400 to 1000 nm that was assigned to the absorption band of Ti^{3+} ions. After heating, the peak intensity decreased, and the color of the glass changed to transparent. The other glasses changed to transparent after the oxidization the same as the $15TiO_2$–$49ZnO$–$36P_2O_5$ glass.

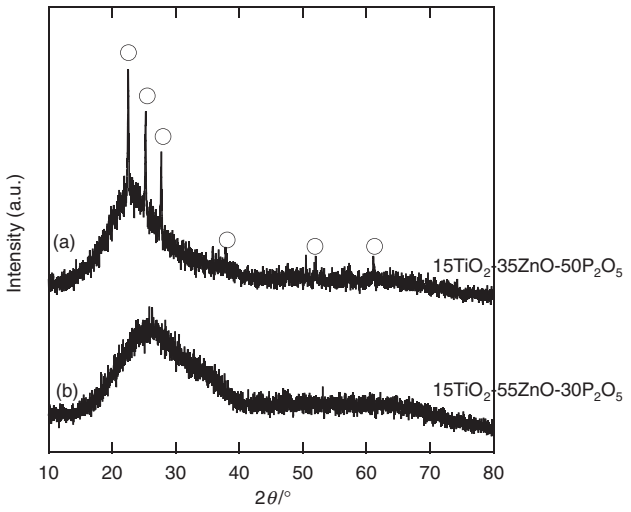

Fig. 2. XRD patterns of opaque samples; (a) $15TiO_2$–$35ZnO$–$50P_2O_5$ and (b) $15TiO_2$–$55ZnO$–$30P_2O_5$. ○: TiP_2O_7 crystal (JCPDS No. 38-1468).

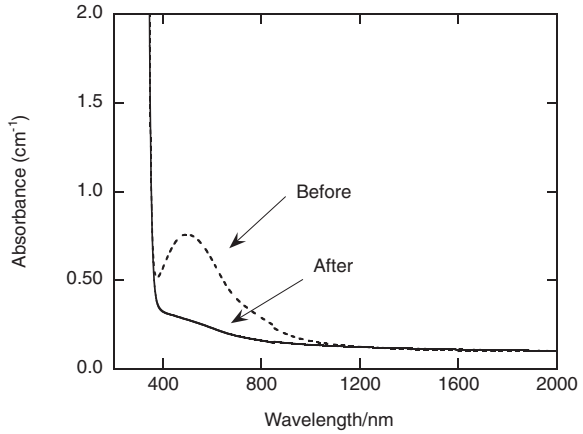

Fig. 3. UV–VIS spectra of $15TiO_2$–$49ZnO$–$36P_2O_5$ glass before and after heating for 72 h.

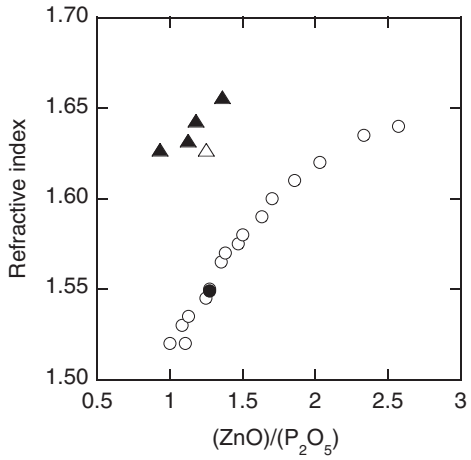

Fig. 4. Refractive indices of for the molar ratio of $(ZnO)/(P_2O_5)$ of ○: $xZnO$–$(100-x)P_2O_5$ (ref. 1)), ●: $56ZnO$–$44P_2O_5$ (this work), △: $10TiO_2$–$50ZnO$–$40P_2O_5$, and ▲: $15TiO_2$–$xZnO$–$(85-x)P_2O_5$.

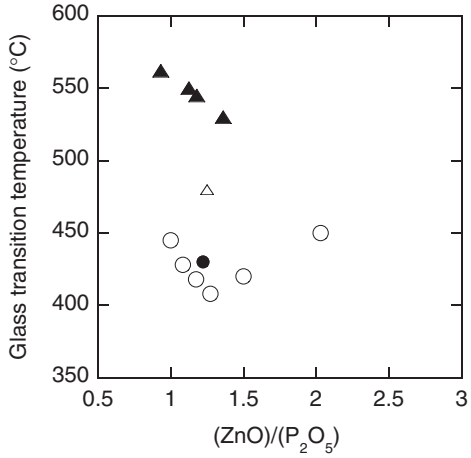

Fig. 5. Glass transition temperatures for the molar ratio of $(ZnO)/(P_2O_5)$ of ○: $xZnO$–$(100-x)P_2O_5$ (ref. 1)), ●: $56ZnO$–$44P_2O_5$ (this work), △: $10TiO_2$–$50ZnO$–$40P_2O_5$, and ▲: $15TiO_2$–$xZnO$–$(85-x)P_2O_5$.

The refractive indices of the glasses are shown in Table 1, and the $(ZnO)/(P_2O_5)$ molar ratio is plotted in **Fig. 4**. The refractive indices of binary ZnO–P_2O_5 glasses are also plotted based on previous reports.[1)] The refractive indices increased with increases in the $(ZnO)/(P_2O_5)$ molar ratio when the TiO_2 concentrations were the same, and were increased by the addition of TiO_2 when the $(ZnO)/(P_2O_5)$ molar ratio was the same. The addition of TiO_2 and ZnO was useful to increase the refractive index of the glasses.

T_g, T_p, and T_m are also shown as thermal properties in Table 1. In **Fig. 5**, the T_gs are plotted for the $(ZnO)/(P_2O_5)$ molar ratio. The T_gs of binary ZnO–P_2O_5 glasses[1)] are also plotted in Fig. 5. In the binary ZnO–P_2O_5 glasses, the T_g decreased with increases in the $(ZnO)/(P_2O_5)$ molar ratio until 1.3, but the T_g increased at ratios above 1.3. In the case of the glasses containing 15 mol% TiO_2, the T_g decreased with increases in the $(ZnO)/(P_2O_5)$ molar ratio, and the T_g reached a minimum at $(ZnO)/(P_2O_5) = 1.4$. The $(ZnO)/(P_2O_5)$ molar ratio of the lowest T_g was similar whether the TiO_2 was contained or not. However, in the case of the glasses containing 15 mol% TiO_2, the glasses were not formed at $(ZnO)/(P_2O_5)$ molar ratios above 1.4 due to the phase separation. The T_g increased with increases in the TiO_2 concentrations when the $(ZnO)/(P_2O_5)$ molar ratios were the same. The increases in the T_g depended on the TiO_2 concentrations, showing that the chemical bonding in the glasses became stronger in response to the addition of TiO_2.

Figure 6 shows the Raman spectra of glasses for which the $(ZnO)/(P_2O_5)$ molar ratio is approximately 1.3, (a) is $56ZnO$–$44P_2O_5$ glass, (b) is $10TiO_2$–$50ZnO$–$40P_2O_5$ glass, and (c) is $15TiO_2$–$49ZnO$–$36P_2O_5$ glass. The Raman spectrum of $56ZnO$–$44P_2O_5$ glass had peaks at around 1180 cm^{-1} and 1250 cm^{-1}, which were assigned to the symmetric and antisymmetric stretching motions of two non-bridging oxygen atoms bonded to phosphorus atoms (PO_2) in the Q^2 phosphate tetrahedra, respectively.[1)] A small peak at around 1000 cm^{-1} was assigned to the phosphorus-oxygen stretching mode in Q^1 phosphate chain terminator groups. In contrast, the two Raman spectra of both glasses with TiO_2 were similar but differed from the spectrum of the $56ZnO$–$44P_2O_5$ glass. The peak at around 1180 cm^{-1} decreased, and the peak at around 1250 cm^{-1} increased. The peak at around 1000 cm^{-1} increased in intensity, and a new peak at around 920 cm^{-1} appeared. These results suggested that the glass structure was changed by the addition of TiO_2.

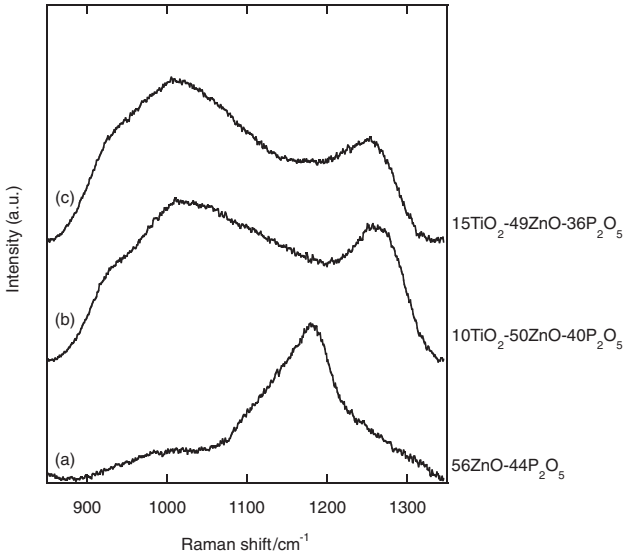

Fig. 6. Raman spectra of (a) $56ZnO–44P_2O_5$, (b) $10TiO_2–50ZnO–40P_2O_5$, and (c) $15TiO_2–49ZnO–36P_2O_5$.

4. Discussion

The glass forming region was narrow, and T_g increased with the addition of TiO_2 to the $ZnO–P_2O_5$ glass system. The Raman spectra showed that the glass structures changed with the addition of TiO_2.

In Fig. 6, it can be seen that the $56ZnO–44P_2O_5$ glass was composed primarily of Q^2 chain networks, and the chains were partially terminated, resulting in that Q^1 units were formed. The spectra shapes of the other glasses with TiO_2 were similar to each other, but looked different from that of $56ZnO–44P_2O_5$ glass. This means that the addition of TiO_2 changed abruptly the glass network composed of ZnO and P_2O_5, resulting in an increase in T_g and a narrow glass forming region. Koudelka et al. have previously reported the glass structure of $50ZnO–10B_2O_3–40P_2O_5 + xTiO_2$ ($x = 0$–24 mol%) glasses based on Raman and NMR spectroscopy.[9] In the Raman spectra, the peak at 1162 cm^{-1} assigned to the PO_2 stretching mode in Q^2 unit shifted to a low wavenumber at 1039 cm^{-1} with increases in TiO_2. This shift could be explained by the depolymerization of phosphate chains because the peak was assigned to the vibrations of Q^1. The increase of the peak at 1000 cm^{-1} in Fig. 6 indicates the depolymerization of phosphate chains and the formation of Q^1 units because the spectrum shape of the $50ZnO–10B_2O_3–40P_2O_5 + 12TiO_2$ glass was similar to the measured spectra. Based on Raman and NMR measurements of $TiO_2–P_2O_5$ and $CaO–TiO_2–P_2O_5$ glasses, Brow has reported that the broad Raman peak at around 1000 cm^{-1} could be assigned to the P–O–Ti linkage.[8] This means that the increase of the peak at around 1000 cm^{-1} was caused by the formation of P–O–Ti and the increase of the Q^1 units coordinated to Ti in the glasses. The electric field strength of Ti^{4+} and Zn^{2+} was calculated as 8.65 and 3.29, respectively, based on the Pauling ionic radius.[14] The difference of the electric field strength caused to form the P–O–Ti linkage easier than the P–O–Zn linkage.

In the case of $56ZnO–44P_2O_5$ glass, the coordination number of Zn was reported to 4 from EXAFS data.[15] In contrast, TiP_2O_7 is known to be a representative stoichiometric compound. Its structure is based on PO_4 tetrahedra in which three 6-coordinated Ti atoms and one P atom bind to four oxygens and a Q^1 unit is formed.[16] The stretching vibration of Ti–O in TiO_5 was reported to appear at around 900 cm^{-1} in Raman spectra.[10] The formation of 6-coordinated or 5-coodinated Ti atoms was caused the increase of the formation of the P–O–Ti linkages and the peak at around 1000 cm^{-1}. The formation of the P–O–Ti linkages would distort the glass network and form three-dimensional networks of P–O–Ti linkages. The three-dimensional network was more stable than the two-dimensional chain network composed of Q^2 units in zinc phosphate glass. The P–O–Ti three-dimensional network would cause the increase in T_g.

In the case of the glasses contained with 15 mol% TiO_2, ZnO could not add more than 1.4 of the $(ZnO)/(P_2O_5)$ molar ratio. In the case of the binary zincphosphate glasses, it is known that the PO_4 chains were depolymerized by the addition of ZnO at the $(ZnO)/(P_2O_5)$ molar ratios until 1.3, resulting in decrease of T_g. The coordination number of Zn changed from 6 to 4 with increase of the ratios until 1.3.[15] The increase of the T_g at the ratio above 1.3 was caused by the structural densification due to sharing two Zn for one terminated oxygen.[15] In the case of the zinc titanophsophate glasses, the P–O–Ti bonds were formed by the addition of the TiO_2 and the coordination number of Ti was 5 or 6. Then, it is difficult to form the P–O–Ti linkages composed of Ti with high coordination number in the zincphosphate glass network, resulting in that the glass was separated to TiO_2-rich glass and ZnO-rich glass when the ZnO added more than 1.4 of $(ZnO)/(P_2O_5)$ molar ratio.

Based on these considerations, the Q^1 units, which were formed by the addition of TiO_2, would bond to Ti octahedra and intersperse themselves in the glass network, resulting in a narrow glass forming region at low melting temperature and an increased T_g.

5. Conclusion

$TiO_2–ZnO–P_2O_5$ glasses were fabricated by melting. The addition of TiO_2 below 15 mol% to the $ZnO–P_2O_5$ glass system was useful in obtaining glasses with a high refractive index and low T_g. However, the glass formation region narrowed and T_g increased with the addition of TiO_2. The Raman spectra measurement suggested that covalent P–O–Ti bonds were formed by the addition of TiO_2, and the chemical bonds were strengthened. Glasses with a high refractive index and low T_g might be obtained by the addition of another oxide with a lower coordination number and a higher refractive index such as SnO.

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