Thermal and optical properties of TeO$_2$–BaO–SrO–Nb$_2$O$_5$ based glasses: New broadband Raman gain media

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Abstract

We systematically added WO$_3$ (up to 10 mol%) and P$_2$O$_5$ (up to 16 mol%) in TeO$_2$–BaO–SrO–Nb$_2$O$_5$ (TBSN) glass system and studied thermal and optical properties of the resultant glasses. The dependences of the additive concentration on glass transition ($T_g$) and crystallization ($T_x$) temperatures are presented. The TBSN glass added with $\geq$4 mol% WO$_3$ and P$_2$O$_5$ showed high stability against crystallization. The changes in optical band gap energy due to WO$_3$ and P$_2$O$_5$ addition was studied using UV–VIS–NIR absorption spectrometry. The WO$_3$ addition shifted the optical band gap to longer wavelengths, whereas P$_2$O$_5$ addition shifted that to shorter wavelengths. Effects of the WO$_3$ and P$_2$O$_5$ addition on the Raman spectra of TBSN glass are clarified. New Raman bands due to WO$_4$ and PO$_4$ tetrahedra formed in the resultant glasses broadened their Raman spectra. Present glasses are characterized by higher thermal stability and wider Raman spectra, therefore, they are promising candidates for fiber Raman amplifiers in photonics systems.

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1. Introduction

Recently considerable efforts have been devoted to materials and design for optical fibers, waveguide devices, and fiber amplifiers to meet demands of present and future telecommunication systems and other data transmitting services. Many attempts have been made on broadening and flattening of gain spectra of Er-doped fiber amplifiers (EDFAs) to expand the usable bandwidth for wavelength division multiplexing (WDM) systems [1–3]. Due to the inherent high energy phonons in silicate-based glasses, usable rare-earth ions which are optically active for optical amplification are limited in silicate-based fibers. Because fluoride and heavy metal oxide glasses have low energy phonons and many rare-earth ions are optically active in them, these glasses have been studied as rare-earth hosts to expand amplification bandwidth in WDM systems [1]. These fibers have contributed much to expand amplification bandwidths of rare-earth doped fiber amplifiers. There is still a need to explore fiber materials that have good thermal stability and optical performances to develop various fiber devices including fiber amplifiers, optical signal processing devices, etc.

Among non-silicate glasses, such as heavy metal oxide and non-oxide glasses, tellurite glasses are promising materials [4] for photonics applications, unifying the following features (i) wide transmission window [5], (ii) good glass stability and durability [4], (iii) high refractive index [6], (iv) higher non-linear optical properties [7], and (v) relatively low phonon energies. In addition, tellurite glasses have low glass transition temperature ($T_g$) and high thermal stability against crystallization which are primary
factors for successful fiber drawing with improved properties. Furthermore, tellurite glasses have been shown to have \(~\sim 30\) times higher Raman gain coefficients and much larger Stokes shifts than the most widely used silica glass \([8,9]\). Therefore, abundant research is focused on producing new tellurite glasses of high stability and improved optical properties.

Recently, we have reported a new group of tellurite glasses in TeO$_2$–BaO–SrO–Nb$_2$O$_5$ (TBSN) system for their use as optical fibers in optical communication systems \([10–12]\). We have reported that addition of alkaline earth and transition metal oxides to the tellurite glasses improve the stability of tellurite glasses against crystallization. Raman scattering cross sections and bandwidths of these glasses are higher than that of the conventional tellurite glasses \([10]\). We note that WO$_3$ and P$_2$O$_5$ forms Raman active tetrahedra in tellurite glasses and likely to widen the Raman spectra of the resultant glasses. Formations of these tetrahedra are expected to enhance their thermal stability also. Therefore, we systematically added WO$_3$ and P$_2$O$_5$ in a TBSN glass and studied their thermal and optical properties. In this paper we report a comprehensive study of thermal and optical characteristics of TeO$_2$–BaO–SrO–Nb$_2$O$_5$–WO$_3$–P$_2$O$_5$ glasses.

2. Experimental details

2.1. Glass preparation

All glasses were prepared following a conventional casting technique using high purity TeO$_2$ (99.9%), BaCO$_3$ (99%), SrCO$_3$ (99.9%), Nb$_2$O$_5$ (99.9%), WO$_3$ (99.9%), and P$_2$O$_5$ (99%). Appropriate amounts of these chemicals were mixed in a zirconia mortar and pestle inside a glove box in nitrogen atmosphere. The mixed powders (~10 g) were melted in a platinum crucible at 900–1000 °C for ~20 min using an electrical furnace under oxy-nitrogen atmosphere. The melt was then quenched onto a preheated copper plate at ~350 °C and subsequently annealed at this temperature for ~10 h to release the thermal stresses developed during quenching. A part of the melt was quenched to room temperature and kept without annealing for thermal measurements. Annealed glasses were cut into rectangular pieces of ~2 mm in thickness and polished for optical measurements.

2.2. Thermal analysis

The thermal analysis was carried out using differential scanning calorimetry (DSC; Thermoplus DSC 8270, Rigaku). Finely powdered as-quenched samples at room temperature were used for DSC measurements. The DSC curves were measured using ~50 mg powder in the 30–900 °C range at a heating rate of 10 °C/min in N$_2$ atmosphere. Glass transition temperature ($T_g$), crystallization temperatures ($T_x$), and melting temperature ($T_m$) of the glasses were obtained from DSC curves. The $T_g$, $T_x$, and $T_m$ were determined from DSC curves by drawing tangents at first endothermic peak corresponding to glass transition, first exothermic peak corresponding to crystallization, and an endothermic peak corresponding to melting, respectively. To eliminate systematic errors in the measurement of $T_g$, $T_x$, and $T_m$, DSC curves of all samples studied here were measured at identical conditions.

2.3. Optical measurements

The refractive indices of the glasses were measured by the prism coupling method (Metricon 2010, USA) at four wavelengths, 633, 974, 1320, and 1544 nm, at accuracy better than ±0.001. The absorption spectra of the glasses were recorded using a UV–VIS–NIR spectrophotometer (Perkin–Elmer Lambda 900) in the 200–3300 nm spectral range. The wavelength accuracy was ±0.8 nm in the UV–VIS range and ±0.32 nm in the NIR range. The optical band gap energy was calculated from the experimental absorption spectra. The Raman spectra of the glasses were measured by a Raman spectrometer (JASCO, NRS 2100) in the 25–1700 cm$^{-1}$ range. The samples were excited with a solid state laser at 532 nm with power of ~100 mW. The spectrum was recorded in the quasi-back scattered mode with the v/v polarization.

3. Results and discussion

3.1. Glass formation

Fig. 1 is a ternary diagram showing compositions of glasses in this study. The glass compositions studied were bound by 56 ≤ TeO$_2$ ≤ 78; 2 ≤ Nb$_2$O$_5$ ≤ 8; 0 ≤ WO$_3$ ≤ 10; 0 ≤ P$_2$O$_5$ ≤ 16 mol%. Partial crystallization were observed for compositions containing 16 mol% P$_2$O$_5$ and >6 mol% WO$_3$. Partially crystallized glasses are eliminated from the discussion of the present report. The BaO–SrO ratio was kept constant at 1:3 (total 14 mol%) for all compositions.
considered in the present study. A reason why we kept them constant is that both BaO and SrO do not exhibit active mode in Raman spectra of glasses containing them [13]. Role of these alkaline earth oxides are explained to cleave one of the Te–O bonds in TeO₄ trigonal bipyramid thereby increase the concentration of TeO₃ trigonal pyramid [11].

The glasses produced in this work could be categorized in to primary series and secondary series. The primary series of glasses takes the general formula (78–x–y) TeO₂–3.5BaO–10.5SrO–8Nb₂O₅–xWO₃–yP₂O₅, (x = 0, 2, 4, 6, 8, 10; y = 0, 4, 8, 12, 16). The first composition in the primary series was 78TeO₂–3.5BaO–10.5SrO–8Nb₂O₅ and the second was 76TeO₂–3.5BaO–10.5SrO–8Nb₂O₅–2WO₃. The seventh composition in this series was 74TeO₂–3.5BaO–10.5SrO–8Nb₂O₅–4P₂O₅, the eighth was 72TeO₂–3.5BaO–10.5SrO–8Nb₂O₅–2WO₃–4P₂O₅, and so on. The primary series consisted of 28 glasses. The secondary series of glasses takes the general formula (74–y) TeO₂–3.5BaO–10.5SrO–mNb₂O₅–(12–m)WO₃–yP₂O₅ (m = 2, 4, 6, 8). In the secondary series we partially replaced Nb₂O₅ by WO₃ to find out relative contribution of these transition metal oxides on thermal and optical properties of the resultant glasses. The secondary series consisted of 20 glasses.

3.2. Thermal analysis

Fig. 2(A) shows DSC curves of a representative group in the primary series with 8 mol% of P₂O₅, viz. (78–x–8) TeO₂–3.5BaO–10.5SrO–8Nb₂O₅–xWO₃–8P₂O₅ (mol%), where x = 0 to 10 at an interval of 2 mol%. These curves features successive events of a normal glass, viz. small broad endothermic peak corresponding to Tₕ followed by relatively intense exothermic peaks corresponding to Tₓ. Glasses with a lower (<4 mol%) content of WO₃ showed three crystallization peaks in DSC curves, whereas the ones with higher (>4 mol%) content of WO₃ showed a single broad crystallization peak. The DSC curves showed similar behavior in the number of crystallization peaks for all members of the primary series except when the P₂O₅ content was 16 mol%. Fig. 2(B) shows the DSC curves of a representative group in the secondary series, (74–x) TeO₂–3.5BaO–10.5SrO–mNb₂O₅–(12–m)WO₃–4P₂O₅ (mol%), where m = 2 to 8 at an interval of 2 mol%. For the secondary series, the number of crystallization peaks increased from one to three when the Nb₂O₅ content was increased from 2 to 8 mol% (Fig. 2(B)). Note that in the primary series also, there were three crystallization peaks for 4 mol% of WO₃ and 8 mol% of P₂O₅.

Fig. 3(A)–(B) show variation in Tₕ and Tₓ, where Tₕ is the onset of first crystallization temperature in the DSC curve, as a function of amount of WO₃ for the primary series. Both Tₕ and Tₓ of TBSN increased due to WO₃ and P₂O₅ addition. In the first group of the primary series, i.e., TBSN–WO₃ system, the Tₕ increased from ~387 to ~408 °C and Tₓ increased from ~471 to ~586 °C as the WO₃ content increased from 0 to 10 mol%. For TBSN–P₂O₅ system, Tₕ increased from ~387 to ~429 °C and Tₓ increased from ~471 to 642 °C as the P₂O₅ content increased from 0 to 16 mol%. The highest value of Tₕ and Tₓ observed in this study was ~444 °C and ~683 °C for a composition that contain 16 mol% P₂O₅ and 6 mol% WO₃ in TBSN. Note that in the primary series we added WO₃ and P₂O₅, both are characterized by different chemistry, to TBSN glass. The results of our experiment show that increase in Tₕ is slightly higher for WO₃ addition compared to P₂O₅ addition. For example, the Tₕ increased from ~387 to ~405 °C for 8 mol% WO₃ addition in TBSN, whereas the increase in Tₕ for 8 mol% P₂O₅ addition in TBSN was from ~387 to ~398 °C. However, crystallization behavior showed an opposite trend due to the WO₃ addition and P₂O₅ addition. The P₂O₅ addition shifted Tₓ to higher temperatures than WO₃ addition. The Tₓ increased from ~471 to ~553 °C for 8 mol% P₂O₅ addition, whereas it increased from ~471 to ~543 °C for 8 mol% WO₃ addition.

Fig. 3(C)–(D) shows the variation in Tₕ and Tₓ as a function of the amount of Nb₂O₅ for the secondary series. The Tₕ and Tₓ showed a small increment due to partial

Fig. 2. (A) DSC curves for (70–x) TeO₂–3.5BaO–10.5SrO–8Nb₂O₅–xWO₃–8P₂O₅ (mol%, primary) series, where x = 0 to 10 mol% in steps of 2 mol%. The starting member (a) is for x = 0 mol% and the ending member (f) is for x = 10 mol%. (B) DSC curves for 70TeO₂–3.5BaO–10.5SrO–mNb₂O₅–(12–m)WO₃–4P₂O₅ (mol%, secondary) series, where m = 2 to 8 mol% in steps of 2 mol%. The starting member (a) is for m = 2 mol% and ending member (d) is for m = 8 mol%.
substitution of Nb$_2$O$_5$ for WO$_3$. The $T_g$ increased from $\sim$375 to $\sim$394 °C, $\sim$393 to 397 °C, $\sim$394 to 415 °C, $\sim$408 to $\sim$429 °C, and $\sim$428 to 437 °C, respectively for 0, 4, 8, 12, and 16 mol% P$_2$O$_5$ when the Nb$_2$O$_5$ content was increased from 2 to 8 mol%. The increase in $T_x$ was from $\sim$453 to $\sim$491 °C, $\sim$502 to $\sim$555 °C, $\sim$516 to $\sim$583 °C, $\sim$534 to $\sim$640 °C, and $\sim$615 to $\sim$677 °C, respectively for 0, 4, 8, 12, and 16 mol% P$_2$O$_5$ when the Nb$_2$O$_5$ content was increased from 2 to 8 mol%. No gradual variation in $T_m$ was observed due to addition of WO$_3$ and/or P$_2$O$_5$ in TBSN. In general the $T_m$ varied between 790–840 °C.

The thermal stability of glasses against crystallization could be evaluated from the characteristic temperatures, $T_g$, $T_x$, and $T_m$ determined from the DSC curves. Two parameters have been commonly employed to evaluate thermal stability of glasses, viz. $(T_x - T_g)$ and Hruby parameter [14], $K_{gl}$, defined as

$$K_{gl} = \frac{T_x - T_g}{T_m - T_x}$$  \hspace{1cm} (1)

The larger differences between crystallization and glass transition temperatures and the smaller differences between crystallization and melting temperatures slow down crystallization process and facilitate glass formation. Fig. 4(A) shows variation in $(T_x - T_g)$ as a function of the WO$_3$ content for the primary series; whereas Fig. 4(B) is the variation in $(T_x - T_g)$ as a function of the Nb$_2$O$_5$ content for the secondary series. In both of these figures $(T_x - T_g)$ was increased with increase in WO$_3$, P$_2$O$_5$, and Nb$_2$O$_5$. The desirable $(T_x - T_g)$ for fiber drawing is understood to be greater than 100 °C. Glasses with P$_2$O$_5 \geq 4$ mol% meet this criterion both in primary and secondary series. In the absence of P$_2$O$_5$, the WO$_3$ content more than 6 mol% was required to obtain $(T_x - T_g) \geq 100$ °C in the primary series. Members in the secondary series showed $(T_x - T_g) \geq 100$ °C only for P$_2$O$_5 \geq 4$ mol%. Increase in $T_g$, $T_x$, and $(T_x - T_g)$ due to WO$_3$ and P$_2$O$_5$ addition could be understood as due to the formation of polyhedra in glasses. The WO$_3$ and P$_2$O$_5$ form tetrahedra in glasses, whereas Nb$_2$O$_5$ forms octahedra. An enhancement of the amount of these oxides leads to an increase in concentration those polyhedra. More thermal energies are required to distort these polyhedral configurations, which accounts the higher thermal stabilities in these glasses. Therefore, glasses with higher WO$_3$, Nb$_2$O$_5$, and P$_2$O$_5$ content are advantageous for thermal stability.

Thermal stability of glasses is an important property both fundamentally and technologically. It is a measure of degree of disorder of glassy state. During the fiber fabrication process the preform is subjected to various heating cycles above $T_g$. If the glass has a poor thermal stability, then crystallization occurs in the glasses during the heating cycles. The crystals thus formed scatter the input signals and contribute to attenuation rather than amplification. Thus, evaluation of thermal stability of glass is important to examine the suitability of a glass to be used as an optical fiber. The higher thermal stability of these glasses was reflected in the calculated $K_{gl}$ also. The value of $K_{gl} > 0.1$ for glasses with higher thermally stability [14]. The $K_{gl}$

![Fig. 3. (A) Glass transition temperature and (B) crystallization temperature of the primary series of glasses; (C) glass transition temperature and (D) crystallization temperature of the secondary series of glasses; a, b, c, d, and e are for 16, 12, 8, 4, and 0 mol% of P$_2$O$_5$, respectively.](image-url)
for both primary and secondary series are >0.4 for all glasses presented here, thereby, confirming the thermal stability of these glasses against crystallization.

3.3. Optical characterization

3.3.1. Refractive index

Fig. 5 (A)–(B) summarizes the trends in the variation of refractive index primary series. Though we measured the refractive index of the samples at all the four wavelengths that our prism coupler is equipped, for simplicity results of 633 nm is presented here. The refractive index of all the samples showed the standard Cauchy’s variation with wavelength. Results of refractive index measurements can be summarized as:

(i) The refractive index of all the samples increased in the primary series monotonously with increasing the WO3 content. In the case of no phosphorous, refractive index varied from 2.114 to 2.118 when the WO3 content varied from 0 to 10 mol%. Corresponding increments for P2O5 contents of 4, 8, 12, and 16 mol% were from 2.078 to 2.094; 2.038 to 2.066; 2.000 to 2.005; and 1.971 to 1.987, respectively.

(ii) The refractive index decreased linearly with increase in the P2O5 content.

(iii) No observable variation in refractive indices was noted for the secondary series.

3.3.2. Absorption spectra

Fig. 6(A)–(C) shows the absorption spectra of the TBSN glasses added with WO3 (Fig. 6A), P2O5 (Fig. 6B), and jointly added with WO3 and P2O5 (Fig. 6C). All these glasses had good transparency from 3300 nm, the highest possible wavelength with the equipment, down to ~400 nm. The samples started to absorb strongly at a characteristic wavelength called ultraviolet transmission cut off (λcutoff). The WO3 and the P2O5 addition exhibited opposite behaviors in the λcutoff. The WO3 addition shifted the λcutoff of TBSN to longer wavelengths (red shift), whereas the P2O5 addition shifted it to shorter wavelengths (blue shift). It was observed that the blue shift due to the P2O5 addition was compensated by the WO3 addition. For example, the λcutoff of TBSN was 422 nm. A 4 mol% P2O5 addition in TBSN blue shifted it to 415 nm and a subsequent 2 mol% WO3 addition brought λcutoff to 423 nm. The joint addition effect is clearly demonstrated in Fig. 6(C). A 16 mol% P2O5 addition in TBSN blue shifted the λcutoff to 384 nm. A 6 mol% WO3 addition was required to bring the λcutoff to ~415 nm. Thus WO3 and P2O5 addition in TBSN could be utilized to tailor the λcutoff. The total shift in λcutoff observed in this study is 56 nm from ~384 nm to ~440 nm.

The optical band gaps of WO3 and P2O5 added TBSN glasses were calculated from the experimental absorption spectrum using the Tauc equation [15]  

\[ax = C \left( \frac{h \nu - E_g}{h \nu} \right)^{1/2} \]  

where C is a constant, hν is the photon energy and \(E_g\) is the band gap energy. The value of \(E_g\) was determined from absorption onset of \([a(h \nu)^{1/2} vs. h \nu]\) curves. The optical band gap energy of TBSN was 2.99 eV which was decreased to 2.75 eV on 10 mol% WO3 addition and increased to 3.18 eV on 16 mol% P2O5 addition. The observed red and blue shifts due to the WO3 and P2O5 additions, respectively, could be understood in terms of the variation in non-bridging oxygen (NBO) ion concentrations. In metal oxides, the valence band maximum (VBM) mainly consists of O(2p) orbital and the conduction band minimum (CBM) mainly consist of M(ns) orbital. The NBO ions contribute to the VBM. When a metal-oxygen bond is broken, the bond energy is released. The non-bonding orbitals have higher energies than bonding orbitals.
Increase in concentration of the NBO ions results in the shifting of the VBM to higher energies and reduces the band gap. Thus, the lowering of band gap energy due to increase in the WO$_3$ content suggests that non-bridging oxygen ion concentration increases with increase in the WO$_3$ content that lowers the band gap energy. On the other hand, increase in the P$_2$O$_5$ content causes a decrease in NBO concentration to decrease that increases the band gap energy.

3.3.3. Raman spectra

Fig. 7 (A)–(C) shows measured Raman spectra of the primary series of glasses grouped as TBSN–WO$_3$ (Fig. 7(A)), TBSN–P$_2$O$_5$ (Fig. 7(B)), and TBSN–WO$_3$–P$_2$O$_5$ (Fig. 7(C)) systems. Fig. 7(D) is a Raman spectrum of a representative group of the secondary series. The Raman spectra of all glasses in this study show major bands in the 25–350 cm$^{-1}$ and 350–1250 cm$^{-1}$. The intense band at $\sim$50 cm$^{-1}$ is the Boson peak, a characteristic feature of the vitreous state, associated with light scattering of due to acoustic-like vibrations of the ordered micro-regions within the glass [16]. Spectral shape of this peak is the same for different glasses and does not depend on their chemical composition [16]. This peak obeys the Bose–Einstein statistics and thus popularly known as Boson peak. Reader may refer to references [11] for assignments of the Raman bands of TBSN, [13] for that of TeO$_2$–alkaline earth oxide, and [17] for TeO$_2$–WO$_3$ and TeO$_2$–P$_2$O$_5$ glass systems.

The intensity and/or bandwidth of the Raman spectrum in the 550–900 cm$^{-1}$ increased due to WO$_3$ and P$_2$O$_5$ addition. In the case of TBSN–WO$_3$ system, Raman spectral intensity increased due to WO$_3$ addition. Also, in addition to the bands due to TBSN [12], a new band centered at $\sim$920 cm$^{-1}$ due to the vibrations of due to W–O and W=O in WO$_4$ tetrahedra [17] was observed in the Raman spectra of TBSN–WO$_3$ system. Intensity of the band at $\sim$920 cm$^{-1}$ increased with WO$_3$ content. Bandwidth of TBSN–WO$_3$ Raman spectra did not increase appreciably due to the new WO$_4$ tetrahedra.

In the case of TBSN–P$_2$O$_5$ system, Raman spectral intensity decreased due to P$_2$O$_5$ addition. Also, in addition to the bands due to TBSN [12], a new band centered at $\sim$920 cm$^{-1}$ due to the vibrations of due to W–O and W=O in WO$_4$ tetrahedra [17] was observed in the Raman spectra of TBSN–P$_2$O$_5$ system. Intensity of the band at $\sim$920 cm$^{-1}$ increased with WO$_3$ content. Bandwidth of TBSN–WO$_3$ Raman spectra did not increase appreciably due to the new WO$_4$ tetrahedra.

In the case of TBSN–P$_2$O$_5$ system, Raman spectral intensity decreased due to P$_2$O$_5$ addition. Also, in addition to the bands due to TBSN [12], a new band in the range 1000–1250 cm$^{-1}$ was observed in the Raman spectrum whose intensity steadily increased with increase in P$_2$O$_5$ content. A recent comprehensive investigation of P$_2$O$_5$–TeO$_2$ system using neutron and high energy X-ray diffraction determined that maximum oxygen coordination
number of P atom in tellurite glasses is four; and therefore, forms PO$_4$ tetrahedra [18]. The bands at $\sim$1020 and 1100 cm$^{-1}$ could be from PO$_4$ tetrahedra [17].

When WO$_3$ and P$_2$O$_5$ were co-doped in TBSN, the intensity and width of the Raman spectrum increased. A detailed analysis using reduced Raman spectra showed that
bandwidth of the Raman spectrum in one of the glasses in this study is more than 70% of silica glass. This value is the highest bandwidth so far achieved in tellurite glasses. In the present study, no commendable differences in the Raman spectra of the secondary sample were observed in the spectral range 25–860 cm$^{-1}$. A decrease in intensity of the band at $\sim$920 cm$^{-1}$ due to WO$_4$ tetrahedra was observed, as expected. A Raman spectral and gain coefficient analysis of these glasses may be found elsewhere [19].

4. Conclusions

We systematically added WO$_3$ (up to 10 mol%) and P$_2$O$_5$ (up to 16 mol%) in TeO$_2$–BaO–SrO–Nb$_2$O$_5$ (TBSN) glass system and studied thermal and optical properties of the doped glasses. Both the additives, i.e., WO$_3$ and P$_2$O$_5$, increased the $T_g$ and $T_x$. The TBSN glass added with $\geq$4 mol% WO$_3$ and P$_2$O$_5$ showed high stability against crystallization. The increase in $T_g$ and $T_x$ are understood as due to the formation of WO$_4$ and P$_2$O$_5$ tetrahedra. The $T_x$–$T_g$ was greater than 100 °C for the glasses with the P$_2$O$_5$ content more than 4 mol%. The WO$_3$ addition shifted the optical band gap to longer wavelengths, whereas P$_2$O$_5$ addition shifted that to shorter wavelengths. This feature suggests that the WO$_3$ and P$_2$O$_5$ addition would influence on the non-linear optical properties of this glass system. Effect of the WO$_3$ and P$_2$O$_5$ addition on the Raman spectra of TBSN glass is clarified. New Raman bands due to WO$_4$ and PO$_4$ tetrahedra are observed in the Raman spectrum of the added glasses that widened the Raman spectrum. The WO$_3$ and P$_2$O$_5$ addition is expected to improve the Raman gain properties of the glass system. The present doped glasses are characterized by higher thermal stability and wider Raman spectra. These features make them new promising candidates for photonic device materials for optical systems.

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