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Influence of Ho_2O_3 on Optimizing Nanostructured $Ln_2Te_6O_{15}$ *anti*-glass Phases to Attain Transparent TeO_2-based Glass-ceramics for Mid-IR Photonic Applications

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Abstract:

The transparent TeO_2-based glass-ceramics have yet to achieve a significant technological breakthrough in the field of photonics, because of poor understanding in optimizing the growth of nanostructured crystalline phases. In the present investigation, the size effect of phase-separation induced, nanostructured $Ln_2Te_6O_{15}$-based (Ln: Gd, Ho) "*anti*-glass" phase in Ho_2O_3 modified TeO_2-based TTLG (in mol%, $80TeO_2–10TiO_2–5La_2O_3–5Gd_2O_3$) glass has been studied to attain transparent glass-ceramics. Raman study of TTLG glass reveals the presence of TeO_3, TeO_{3+1}, and TeO_4, and TeO_6 units with average Te–O coordination number as 3.49. The formation of nanostructured $Ln_2Te_6O_{15}$ phases in glass-ceramics has been confirmed by XRD and TEM analysis. Furthermore, TEM analysis confirms that the Ho_2O_3 concentration has reduced the size of phase-separated domains in nanoscale by the formation of the superstructure to attain transparent glass-ceramics. The superiority of glass-ceramics as photonic material for NIR to MIR range has been established by the realization of enhanced luminescence intensities and bandwidth at ~2900 nm (Ho^{3+}: $^5I_6 \rightarrow {}^5I_7$) and ~2050 nm ($Ho^{3+}$: $^5I_7 \rightarrow {}^5I_8$). The present study offers an opportunity to fabricate the various accessible lanthanide ions doped and/or co-doped TTLG glass with control over nanostructure, to design a series of transparent glass-ceramics from visible to MIR range.

Introduction:

Transparent glass-ceramics have been the most promising and well-accepted material for various photonic and optical applications such as large telescope mirror blanks, liquid crystal displays, solar cells, and other photonic devices. It has been further identified that transparent glass-ceramics are the most appropriate alternative to single or polycrystalline transparent materials, which are being utilized in many optical and photonic applications, for example-temperature sensor, frequency upconverter, white light-emitting diodes,, etc. The major advantages of transparent glass-ceramics over single or polycrystalline materials have been its simple synthesis technique, the flexibility of chemical composition to tailor and optimize its thermal, mechanical and optical properties, as well as the opportunity for large scale production at relatively low cost.

Low phonon energy (750 – 780 cm^{-1}), lower melting temperature (850 – 950 ^{o}C) and substantial thermal stability (60 – 120 °C) with considerable mechanical and chemical durability offering the Tellurium oxide (TeO_2) based glass systems as the most appropriate candidates for the development of transparent glass-ceramics for the various photonic and optical applications. However, the emphasis on the development of transparent tellurium oxide-based glass-ceramics for various applications is limited to date owing to the difficulties in identifying the suitable chemical composition of glasses to achieve transparent glass-ceramics. For example, attempts have been made on the development of transparent tellurite glass-ceramics from $70TeO_2–15Nb_2O_5–15R_2O$ (mol %) (R: Li, Na, and K) glass system for their application as nonlinear optical materials. Nevertheless, transparent glass-ceramic has been achieved from (mol%) $70TeO_2–15Nb_2O_5–15K_2O$ based glass system, which can exhibit the second harmonic generation (SHG) as well. In another study, $10BaO–10Ln_2O_3–80TeO_2$ (Ln: La, Pr, Sm, Eu, Er) series of glass have been considered for the development of transparent glass-ceramics. It has been reported that glasses containing Sm_2O_3, Eu_2O_3 and Er_2O_3 are capable to provide transparent glass-ceramic materials, whilst glass samples containing La_2O_3 and Pr_2O_3 are unsuitable to attain the transparent glass-ceramics. Transparent glass-ceramic through the growth of TeO_2 and $Zn_2Te_3O_8$ crystalline phases have been developed for their applications as efficient upconversion materials from ErF_3-doped TeO_2–ZnO–ZnF_2 glass. On the other hand, as an alternative to transparent glass-ceramics attempts to produce transparent ceramics is being made through implementing the full and congruent crystallization of desired polycrystalline phases in the nanoscale range from parent glass. Bertrand *et al.*, have developed scalable and formable $Bi_{0.8}Nb_{0.8}Te_{2.4}O_8$-based transparent ceramics from $75TeO_2–12.5Nb_2O_5–12.5Bi_2O_3$ glass for near-infrared applications. Dolhen *et al.* have reported Nd^{3+}-doped transparent ceramics from congruent crystallization of $75TeO_2–12.5Nb_2O_5–12.5Bi_2O_3$ glass, which has demonstrated lasing action with ~50% slope efficiency and ~67 mW as threshold pump power.

Interestingly, it has been reported that with the controlled growth of metastable tellurium rich nano-crystalline phases having defective CaF_2 fluorite type crystal structure, generally called as *anti*-glass phases, led to transparent glass-ceramics. Here, an *anti*-glass can be defined as a solid with obvious long-range order of cation, but the partial vacancies of anions have statistically distributed in the short-range order. Nevertheless, the formation of tellurium rich crystalline phase from the glassy matrix upon heating primarily depends on the concentration of the type of network structural units such as TeO_4, TeO_{3+1}, and TeO_3 as well as the linkages between these structural units. A transparent glass-ceramics with the growth of nanostructured $Bi_{0.5}Nb_{0.5}Te_3O_8$ (an analogous to the β-$Bi_2Te_4O_{11}$ fluorite type *anti*-glass phase) crystalline phase has been achieved owing to the controlled heat treatment of $7.14Bi_2O_3–7.14Nb_2O_5–85.72TeO_2$

glass system, which contains chains of corner linked TeO_3 and TeO_4 units with NBOs coordinating NbO_6 and BiO_6 units. It could be understood that the presence of chains of corner linked TeO_3 and TeO_4 coordination polyhedral at an equal proportion and the presence of modifier cations surrounded by NBOs in the form of octahedral units lends the formation of tellurium rich *anti*-glass phase. Therefore, it is apparently clear that selecting more appropriate tellurium based glass composition and executing the controlled crystallization process supports the development of nanostructured crystalline phases to obtain transparent glass-ceramics, which can further be utilized in non-linear and NIR/MIR photonic applications.

Among the various *anti*-glass phases, *lanthanide tellurite* phases with the general formula of $Ln_2Te_6O_{15}$ or $Ln_2Te_5O_{13}$, (where Ln: La, Pr, Nd, Sm, and Dy) have also been well reported. The lanthanide ions have considerable technological importance, because of their magnetic, photonic, catalytic and electrochemical properties. Moreover, lanthanides have been the constituent of *lanthanide tellurite* (i.e. $Ln_2Te_6O_{15}$ or $Ln_2Te_5O_{13}$) kind of *anti*-glass phases. Therefore, the fabrications of optically transparent glass-ceramics containing lanthanide tellurite phases have significant technological importance. Moreover, the basis of oxygen vacancy ordering for *lanthanide tellurite* type of *anti*-glass phases is yet to be explored. However, significant efforts have not been paid on the development and controlled growth of *lanthanide tellurite* type of *anti*-glass phases in the TeO_2 glass to achieve transparent glass-ceramics.

In view of the above discussions, the present study aims to develop transparent TeO_2-based glass-ceramics containing *lanthanide tellurite* ($La_2Te_6O_{15}$) type nano-crystalline phase. In the previous attempt, authors have reported $La_2Te_6O_{15}$ type '*anti*-glass' phase from (mol%) $80TeO_2$–$10TiO_2$–$10La_2O_3$ (TTL10) glass composition upon ceramization at 450 °C for 3 h and 24 h. Nevertheless, the glass-ceramic was opaque in nature. According to Fujimoto *et al.*, the crystalline sizes of *anti*-glass ($Ln_2Te_6O_{15}$) phases reduce with the reduction of the cationic radius of lanthanides. Therefore, to achieve transparent glass-ceramics, the chemical composition of TTL10 glass was further modified to $80TeO_2–10TiO_2–5Gd_2O_3–5La_2O_3$ (TTLG) and considered as parent glass composition in the present study. In addition, foremost efforts have been made in understanding and controlling the retention of transparency in the TTLG glass-ceramics through the modification of glass composition by substituting Holmium oxide (Ho_2O_3) for Lanthanum oxide (La_2O_3). Heat treatment temperature for glass materials to produce transparent glass-ceramics was evaluated using differential scanning calorimetry. The prepared tellurite glass-ceramics have been thoroughly examined through X-ray diffraction (XRD), transmission electron microscopy (TEM) and micro-Raman spectroscopy techniques for phase identification, microstructure, and local structure respectively. Furthermore, Oxygen deficiency ordering in $Ln_2Te_6O_{15}$-based '*anti*-glass' phase has been confirmed via selected area electron diffraction (SAED) technique. It is to be further highlighted those luminescence properties of $Ln_2Te_6O_{15}$-based '*anti*-glass' phase containing transparent glass-ceramics are very little explored. Therefore, considering their technological importance for NIR/MIR photonic applications, the photoluminescence properties in the region ranging from visible (500 nm) to MIR (3500 nm) of Ho^{3+} ion has also been explored for TeO_2-based glass and transparent glass-ceramics.

Experimental:

Glasses and glass-ceramics corresponding to the compositions (80 TeO_2 – 10 TiO_2 – 5 Gd_2O_3 – (5-x) La_2O_3 – x Ho_2O_3 (in mol %)), where x = 0, 1 and 2, which are designated as TTLG for x=0, TTLGH1 and TTLGH2 for x= 1, 2, respectively; have been prepared by using a conventional melt-quenching technique. Commercially available, starting powders of TeO_2 (Alfa Aesar, 99.99%), TiO_2 (Sigma-Aldrich, 99.999%), Gd_2O_3 (Sigma-Aldrich, 99.99%), La_2O_3 (Alfa Aesar, 99.99%) and Ho_2O_3 (Sigma-Aldrich, 99.99%) were weighed of appropriate quantities so that 20 g glass block can be yielded. The detailed synthesis procedure of glass and glass-ceramics and their characterization using Prism coupler for refractive index measurements, DTA-DSC for thermal analysis, XRD for crystalline phase evaluation and Raman for structural characterizations are mentioned in the supplementary Information. Glass-ceramics (GCs) were synthesized by isothermal heat treatment of glasses at 450° C (standardized using thermokinetic analysis) for 3 h and 24 h in a precision microprocessor-controlled electric furnace under ambient condition. The nanostructures of glass and glass-ceramic samples were investigated by using a transmission electron microscope (TEM; FEI Model Tecnai G2 30ST; Hillsboro, OR, USA). Detailed sample preparation procedure for the TEM measurement is provided in Supplementary Information. The distribution of the constituent elements within the glass-ceramic sample was investigated using a Tecnai G^2 30ST TEM operating at 300 kV and equipped with a LaB_6 thermionic electron source. Scanning transmission electron microscopy–high angle annular dark field (STEM-HAADF) images were acquired with a camera length of 120 cm and a probe size of 5 nm. The contrast of these dark-field images is linked to the square of atomic number (Z) of the constituent elements and thus allows one to obtain a chemical contrast. Attempts were also made to obtain Elemental distribution maps by employing the

STEM-EDX spectrum an imaging technique using an EDX Spectrometer (EDAX Inc., USA) detector and a probe size of 5 nm in order to have better insight into the phase separation in the glass-ceramic system. Transparency, as well as related absorption spectra, have been verified in 200 – 2500 nm spectral region by UV-Vis-NIR spectrophotometer (Model: 3101 from Shimadzu, Japan). The transmission spectra in the MIR region (2.5 – 25 μm) has been recorded using FTIR spectrophotometer (Model: Frontier FIR MIR from Perkin-Elmer, USA). The emission and excitation spectra of the sample were recorded at room temperature on a spectrofluorimeter (Model: Quantum Master enhanced NIR from PTI, USA) fitted with double monochromators on both excitation and emission channels. The Visible-NIR (500 – 1500 nm), NIR (1500 – 2500 nm) and MIR (2500 – 5000 nm) emission spectra were recorded using LN_2 cooled NIRPMT, solid-state InGaAs and LN_2 cooled InSb detectors respectively with Xenon lamp operating as the excitation source. All the measurement were carried out by placing the sample at 60° to the incident beam and signals were collected from the same surface at the right angle (90°) to the incident beam. Appropriate low-pass and high-pass filters from Edmund Optics, Inc, of USA were used at excitation and emission channels to avoid excitation and emission wavelength's higher-order harmonics in the recorded emission spectrum.

Results:

Transmission spectra for the series of glass have been shown in Figure 1(a). The spectra show that the series of glass has optical transparency from the visible to MIR wavelength range. Inset of Figure 1(a) presents the photograph of as prepared glass materials. The X-ray Diffraction (XRD) patterns of powdered glass samples have been presented in Figure 1(b), which reveal their X-ray amorphous nature. The morphology of glass powders has been observed using bright-field transmission electron microscopy (BF-TEM). Figures 1(c), 1(d), and 1(e) have been depicting the micrograph of TTLG, TTLGH1, and TTLGH2 glass samples respectively. The insets depict the selected area electron diffraction (SAED) pattern of the relevant sample. It can be noticed from bright-field micrographs that there has been the no obvious formation of noticeable phase-separated domains. Also, the presence of halo rings in the SAED patterns have confirmed the amorphous nature for the glass samples, which is well corroborating with the XRD pattern.

Figure 2 reveals the differential scanning calorimetric (DSC) curves at a heating rate (β) of 10 K/min of TTLG, TTLGH1, and TTLGH2 glass samples. Characteristic temperatures such as glass transition region (T_g), onset crystallization temperature (T_x) and peak crystallization temperature obtained from DSC thermographs are provided in Table 1.[9] For the present series of glass, the glass transition temperature (T_g) is around 430 °C, while 470 – 472 °C is the range of onset crystallization temperature (T_x).

It is well-known that nanostructured bulk nucleation in a glass is a necessary condition to achieve transparent glass-ceramic. In general, due to high nucleation rate at about the glass transition region (T_g), heat treatment of glass at the T_g region might result in the formation of a large number of nuclei in nanoscale. Therefore, the selection of appropriate heat-treatment schedule for glass at around T_g offers control on the size of the crystallites and as a consequence produces transparent nanostructured crystalline phases. Moreover, according to Rayleigh-Gans-Debye and Hendy, nano-crystals of the size of less than 40 nm are good enough to avoid any light scattering. For the uniformity based on DSC curves, all the glass samples have been heat-treated at 450 °C (close to T_g value) for 3 h (short period) and 24 h (long period) to attain nanostructured transparent glass-ceramics. The obtained glass-ceramics (GC) have been labeled as the glass name followed by time duration and GC. For example, the glass-ceramic sample obtained after the heat treatment of TTLG glass at 450 °C for 3 h has been labeled as TTLG-3h-GC.

Transmission spectra extended from UV (300 nm) to MIR (7000 nm) region for the as-prepared glass-ceramics heat-treated for 3 h and 24 h duration have been shown in Figure 3(a) and (b), respectively, and insets depict the photograph of respective glass-ceramics. Figure 3(a) reveals the significant reduction in transparency from 80% to <10% for TTLG-3h-GC sample due to the formation of large-sized crystals. On the other hand, TTLGH1-3h-GC and TTLGH2-3h-GC have exhibited their maximum transparency of 65% and 75%, respectively at 1500 nm wavelength. The ability of the retention in the transparency of Ho_2O_3 substituted glass-ceramics, unlike TTLG-3h-GC sample, has implied that the substitution of Ho_2O_3 in the network might be facilitating the monitoring and controlling the size of crystalline phases. However, further increase of ceramization duration from 3 to 24 h has reduced the transparency of TTLGH1-24h-GC sample to 48%; while, transparency of TTLGH2-24h-GC sample has been 73%. The decrease in transparency with the increase of heat treatment duration has correlated with the enhancement of refractive index for transparent glass-ceramics. The dispersion curves of TTLGH1 and TTLGH2 based glass and respective glass-ceramics have been depicted in Supplementary Information (S-I (a) and (b)). The dispersion curves of the synthesized transparent glass-ceramics have exhibited higher refractive indices than commercially available CaF_2 crystals (n=1.42 at 1064 nm), which are comparable to the polycrystalline ZrO_2 as well as TeO_2–Nb_2O_5–Bi_2O_3 based glass-ceramic. The high refractive indices (i.e., $n \sim 2.1$) of transparent glass-ceramic has useful applications in the development of NIR/MIR lens.

X-ray diffraction (XRD) patterns of the powdered glass-ceramics, obtained after heat treatment at 450 °C for 3 h and 24 h have been presented in Figure 4 (a) and (b), respectively. The patterns have confirmed very sharp and intense diffraction peaks which indicate the formation of crystalline phases upon heat treatment. The qualitative analysis reveals the formation of fluorite-type *lanthanide tellurite* ($Ln_2Te_6O_{15}$) phases in all the glass-ceramics. Further analysis reveals that TTLG glass-ceramics comprise $Gd_2Te_6O_{15}$ (00-037-1400 PDF4+ database card number) as dominant crystalline phase. Nevertheless, in TTLGH1 and TTLGH2-based glass-ceramics $Ho_2Te_6O_{15}$ (00-043-0553) crystalline phase has evolved as the dominant crystalline phase. Further, the broadening of Bragg reflection peaks observed for 3h and 24 h heat-treated glasses indicating that the formation of both $Ho_2Te_6O_{15}$ and $Gd_2Te_6O_{15}$ phases in TTLGH1 and TTLGH2-based glass-ceramics.

To elucidate further on the morphology of the nanocrystalline phase, the TEM studies have been carried out. Figures 5 (a-c) have been depicting the bright-field images of TTLG-24h-GC, TTLGH1-24h-GC, and TTLGH2-24h-GC samples, respectively. TEM bright-field micrograph of TTLG-24h-GC (Figure 5 (a)) reveals the presence of a highly interconnected large size (order of 150 – 200 nm) domain. The nanostructure of TTLGH1-24h-GC and TTLGH2-24h-GC (Figure 5 (b) and (c)) disclose the existence of randomly dispersed isolated spherical domains with diffused phase boundaries. The sizes of the domains are significantly reduced from ~25 nm to ~10 nm with increasing Ho_2O_3 substitution for La_2O_3 from 1 mol% to 2 mol% in TTLG glass composition. The reduction in the size of phase-separated domains (from around 200 nm to 25 nm) of TTLGH1-24h-GC is confirming its translucent character in contrast to TTLG-24h-GC sample which is showing opacity. Similarly, further reduction in domain sizes (10 nm) is responsible for the retention of transparency in TTLGH2-24h-GC. The compositional partitioning in the glass-ceramics has been established using scanning transmission electron microscopy through high angle annular dark field (STEM-HAADF) images. The STEM-HAADF images of TTLG-24h-GC, TTLGH1-24h-GC, and TTLGH2-24h-GC have been presented in Figure 5 (d-f), respectively. Figure 5 (d) reveals the nanostructures have large-sized (150 – 200 nm) interconnected domains in the base glass matrix. In contrast, Figures 5 (e) and (f) reveal the poorly resolved and diffused spherical domains (domain size 10 – 25 nm) that have been dispersed in the matrix, where spherical phases have appeared to be slightly brighter than the matrix. The intensity of STEM-HAADF images represents atomic number contrast ('Z-contrast'), which indicates that the separated domains have large Z-number difference for TTLG-24h-GC as compared to TTLGH1-24h-GC and TTLGH2-24h-GC. Elemental identification participated in the phase-separated domains have also been carried out using EDX point analyses in order to identify the elements participated in the formation of domains. Supplementary Information (S-II (a), (b), and (c)) have shown the distribution of Ti, Gd, Te, La, O and Ho elements present in TTLG-24h-GC, TTLGH1-24h-GC, and TTLGH2-24h-GC samples respectively. Figure S-II (a) reveals that interconnected domains in TTLG-24h-GC are primarily due to the precipitation of gadolinium (Gd), titanium (Ti) and Oxygen (O). This confers that, in STEM-HAADF image of TTLG-24h-GC (Figure 5 (d)), the brighter regions are rich in gadolinium and the darker regions are relatively titanium-rich. However, STEM-EDX elemental maps for TTLGH1-24h-GC (Figure S-II (b)) and TTLGH2-24h-GC (Figure S-II (c)) could not reveal the clear presence of isolated domains.

Figures 6 (a), (b), and (c) have depicted the SAED pattern along $[001]_F$*, $[110]_F$* and $[111]_F$* zone-axis of TTLGH1-24h-GC sample. The high-resolution TEM (HRTEM) image along $[001]_F$*, $[110]_F$* and $[111]_F$* zone-axis has been shown in Figure 6 (d), (e), and (f) respectively; whilst, inset of each HRTEM micrograph are depicting their respective fast Fourier transformation (FFT) patterns. Supplementary information S-III (a) and (b) have been presenting the SAED patterns of TTLGH2-24h-GC and TTLG-24h-GC samples respectively. The SAED patterns of TTLGH1-24h-GC (Figures 6 (a-c)) have confirmed the superstructure formation. The superstructure formation has also been confirmed via HRTEM images of TTLGH1-24h-GC sample (Figures 6 (d-f)). Further, Figure 6(a) reveals that $½\{200\}_{F}*\equiv \{100\}_{F}*$ and $½\{220\}_{F}*\equiv \{110\}_{F}*$ satellite reflections are appearing for the $[001]_{F}*$ zone axis. Whereas, $¼\{220\}_{F}*$ and $½\{200\}_{F}*$ satellite reflection are appeared along $[110]_{F}*$ zone axis (Figure 6 (b)) and $¼\{220\}_{F}*$ appeared along $[111]_{F}*$ zone-axis (Figure 6 (c)). The ring pattern of the SAED has been realized for TTLGH2-24h-GC which has been signifying the smaller size of phase-separated domains for the respective sample. Interestingly, for TTLG-24h-GC sample satellite reflections did not appear in SAED pattern.

The measured Raman spectra of glass and respective glass-ceramics under 785 nm laser excitation is presented in Fig. S. Experimentally measured Raman spectra has been processed for baseline correction with the equation given by Kalampounias *et al.* The obtained spectra after the baseline correction is further normalized at 663 cm^{-1} and are presented in Figure 7. Present series of glass have shown two distinct spectral regions as, (a) 550 – 900 cm^{-1}, and (b) 200 – 550 cm^{-1} respectively. Supplementary Information S-IV has been depicting the deconvoluted Gaussian line profiles of Raman spectra of the glass samples, as proposed by Barney *et al.* The region (a) 550 – 900 cm^{-1} has been fitted with four Gaussian line profiles. For the present study, Raman peak appeared in the region of 775 − 795 cm^{-1} is related to Te-O^{-} stretching vibration of TeO_{3+1} polyhedron or TeO_3 (trigonal pyramid, *tp*) structural units. The peak appeared in the region of 720 − 740 cm^{-1} is attributed to the symmetric stretching vibration between Tellurium and nonbridging Oxygen (NBO) of TeO_{3+1} polyhedron and TeO_3 *tp* in which NBO interacts with adjacent Tellurium atom. The band appeared in 655 – 665 cm^{-1} is assigned to the antisymmetric stretching vibrations of Te–O–Te linkages because of two non-equivalent Te–O bonds (i.e. $Te_{IV}-{}_{ax}O_{eq}-Te_{IV}$) in TeO_4 (trigonal bipyramid, *tbp*) units. Peak observed in 500 – 470 cm^{-1} range is attributed to the symmetric stretching and bending vibrations of continuous Te–O–Te linkages in the vertex sharing of TeO_3 or TeO_{3+1} and TeO_4 structural units. Figure 7 (a) have confirmed that the peaks have appeared less than 450 cm^{-1}. To verify the base of peaks less than 450 cm^{-1}, Raman spectra have also been recorded at 488 nm excitation and shown in Supplementary Information (SI- V). Significantly, the shape function of Raman spectra of 200 – 450 cm^{-1} range has altered significantly with the change of excitation wavelength. This confirms that the peaks appeared in 200 – 450 cm^{-1} range has associated to the intrinsic fluorescence intensities of Ln^{3+} ions doped in the glass sample. SI- V (b) has revealed the appearance of sharp peak at 470 cm^{-1} in the glass-ceramics. With the increase of ceramization duration, the bandwidth of peak at 470 cm^{-1} has reduced steadily (see SI- V (b)). But, the addition of 1 mol% of Ho_2O_3 in the TTLG network has broadened the peak of 470 cm^{-1} in GCs (see SI- V (c)). In case of GCs of TTLGH2, the sharp peak at 470 cm^{-1} has completely disappeared (see SI- V (d)).

Luminescence spectra of Ho^{3+} ions doped glasses (TTLGH1 and TTLGH2) and respective transparent glass-ceramics are depicted in Figure 8. Significant enhancement in luminescence intensity in the spectral region from 1.5 μm to 3.5 μm has been realized for transparent glass-ceramics compared to glass counterparts. Figures 8 (a) and (b) are depicting the signature NIR (Ho^{3+}: ${}^5I_7 \rightarrow {}^5I_8$, λ_p: 2050 nm) emission band for Ho_2O_3 substituted samples; while Figure 8 (c) and (d) are representing the MIR (Ho^{3+}: ${}^5I_6 \rightarrow {}^5I_7$, λ_p: 2900 nm) luminescence for

1194 nm excitation. Unlike glass, the luminescence bands have revealed the variation of shape function for the glass-ceramics.

Discussions:

Increasing the concentration of modifier components in the tellurite glass composition increases the conversion of TeO_4 structural units into TeO_3 structural units containing NBOs that are coordinated to the modifier cations.[38][40][41] The structural evolution of the glass network caused by the addition of various lanthanide ions in the *titanium tellurite glass* (in mol%, $90TeO_2–10TiO_2$) network has been studied here by Raman spectroscopic technique, under 785 nm laser excitation. The measured and baseline corrected Raman spectra of *titanium tellurite glass* have been presented in Supplementary Information (S-VI (a) and (b)). The Raman spectrum of *titanium tellurite glass* reveals the strongest peak at 630 and 660 cm^{-1} (S-VI (b)). However, in the earlier effort authors have observed the gradual enhancement of the relative intensity of peaks at 730 and 780 cm^{-1} with the systematic inclusion of La_2O_3 in the *titanium tellurite glass* (TTL) network by the formation of TeO_3 and TeO_{3+1} units, over TeO_4.[9] To formulate TTLG glass, La_2O_3 has partially been substituted by Gd_2O_3 in the TTL10 (i.e. $80TeO_2–10TiO_2–10La_2O_3$) network. The partial substitution of La_2O_3 by Ho_2O_3 in the TTLG network has been causing an increase of intensity of peak at 790 cm^{-1}. The increase of the intensity at 790 cm^{-1} has been attributing to the steady formation of TeO_3 units over TeO_4 units. The area of decomposed Gaussian line profiles of the modified Raman spectra for glass samples has been utilized to estimate the average Te–O coordination number (n_{TeO}) and presented in Supplementary Information (S-VII). The *titanium tellurite glass* has n_{TeO}-value as 3.65. Nevertheless, the average coordination number (n_{TeO}) of TTLG, TTLGH1, and TTLGH2 has been estimated to be 3.49, 3.45, and 3.46, respectively. For the pure amorphous TeO_2 sample, [38] the n_{TeO} has been reported to be 3.64, which is almost identical to the estimated value for *titanium tellurite glass* in the present study. The similarity of the n_{TeO} values for pure amorphous TeO_2 and *titanium tellurite glass* is not ambiguous; because of the Te^{4+} (network former) ions have successfully been substituted by the Ti^{4+} (network modifier) ions. The progressive inclusion of Holmium oxide in the TTLG network has confirmed the larger formation of terminal oxygen (i.e. Te=O) containing TeO_{3+1} (polyhedron) and TeO_3 (*tp*) structural units, which has reduced their respective average coordination number. Furthermore, the corrected Raman spectra of glass-ceramic samples have been showing elevated baseline (Figure 7 (b)). The coexistence of nano-crystalline and residual amorphous phases in the glass-ceramics has contributed notably in the scattering, which is responsible for the elevated baseline. As a result, Gaussian line profiles are not aptly fitting for the Raman spectra of glass-ceramic samples. However, the tendency to progressively form TeO_3 and TeO_{3+1} unit over TeO_4 has been clear from the corrected Raman spectra of glass-ceramic samples. The peak at 470 cm^{-1} has assigned to the stretching and bending vibration of TeO_3 *tp* having a weak interaction.[39] For the GCs of TTLG, the phase-separated domains have size of 150 – 200 nm. But, with Holmium oxide addition in the network, domain size and domain connectivity have reduced considerably. As a result, propagation of phonon has reduced significantly in Ho_2O_3 doped GCs. Consequently, with the addition of Ho_2O_3, Raman profile of respective GCs has resembled to amorphous profile.

The concentration of Ho_2O_3 in the TTLG network has influenced the domain size of the *spherulites* [42] and resulting nanostructures. Moreover, the Raman spectra of glass-ceramics have shown the amorphous profiles while, XRD patterns exhibit intense and discrete Bragg-maxima; which confirmed that the formed crystalline phases are *anti*-glass type. The changes in the nanostructure of glass-ceramics with the addition of Holmium oxide have been typical consequence of free energy of the system at ceramization temperature. Therefore, it can be concluded that controlled heat treatment schedule and free energy of the system are the basis for tuning the size of the domains which have converted into the nano-sized crystalline phases. The change in nanostructure of the glass-ceramics can be explained on the basis of free energy of the system. The XRD pattern for TTLG-3h-GC and TTLG-24h-GC (Figure 4(b)) further reveal that interpenetrated crystalline phases decomposed into multiple phases. BF-TEM image (Figure 5(a)) and the significant Z-contrast (atomic number based intensity contrast) image (Figure 5(d)) are also confirming the presence of interpenetrated phases in TTLG-24h-GC. Therefore, XRD, bright field and HAADF studies establish that the thermodynamic instability of the TTLG composition causes diffusion-controlled compositional fluctuation in the phase-separated domains that generates interpenetrated phase, upon ceramization. Nevertheless, during prolong heat treatment for 24 h, spinodal decomposition plays a crucial role and decompose the observed interpenetrated phase into highly interconnected multiple crystalline phases. On the other hand, TEM nanostructure of Ho_2O_3 doped TTLG glass network reveal non-obvious formation of phase-separated domains (Figure 1(d) and (e)). Upon crystallization, the formation of spherical phase separated domains that are randomly dispersed in the matrix has been observed in glass-ceramics of Ho_2O_3 doped TTLG network. This implies that with Ho_2O_3 addition in the TTLG network, binodal decomposition might occur in glass-ceramics.[44] Moreover, the elemental maps presented in figures S-II (b) and (c) could not reveal the compositional fluctuation in the phase-separated domains of Ho_2O_3 substituted glass-ceramics; which confirms that the event of phase separation for relevant samples are governed by density fluctuation only. Further, density fluctuation driven phase separation lead to the controlled crystallization via binodal decomposition. This implies that with Ho_2O_3 addition in the TTLG network, the decomposition process is limited to the binodal decomposition for the selected heat treatment schedule. This resulted into the small domains of nanostructured crystalline phases. In case of the *anti*-glass phase, a metal sub-lattice of the large cationic radius (e.g. Sr^{2+}, Pb^{2+}, Ln^{3+}) along with Te^{4+} ions have formed an ordered array of cations.[25][44] The ordered cationic array has been the reason for the Bragg-diffraction maxima in X-ray diffraction experiments. But, an anion-deficient lattice of the anti-glass structure is incapable of the propagation of phonons; therefore, an amorphous profile has been exhibited for Raman and IR experiments of glass-ceramics. In the present study, the melt-quenched TTLG series of glass (annealed at 350 °C) has not shown any phase-separated domains in the nanoscale (Figure 1 (c-e)). However, heat treatment of the glasses at 450 °C and successive slow rate of cooling have resulted in the liquid-liquid phase transition (LLPT) and simultaneous crystallization.

It is assumed that the identified *anti*-glass crystalline phases are decomposed because of the formation of the *spherulitic* microstructure in the glass. It is well known that fluorite-type crystalline formation in AX_2 type compounds demands the cation (A) to anion (X) radius ratio in the range of 0.73 – 1.00. Though, $R(Te^{4+})/R(O^{-2}) = 0.51$ ratio stand far away from the required value, owing to the suitable $R(Ln^{3+})/R(O^{-2})$ values of 0.86, 0.81 and 0.72 for Ln^{3+}: Gd^{3+}, La^{3+}, and Ho^{3+}, respectively and the possibilities to have irregular Te^{4+} coordination sites fluorite-type Lanthanide tellurite crystalline phases generally forms in TeO_2 glass system.[22] Nevertheless, when the sizes of crystallites are larger than the wavelength of incident light the scattering loss also increases significantly. In accordance to the proposed theories, the retention of transparency in the glass-ceramics can be achieved if the size of crystallites are less than 30 – 40 nm.[45]–[47] BF-TEM analysis (Figure 5(a)) for TTLG-24h-GC clearly revealed that highly interconnected and phase-separated domains are very large in size, nearly 150 – 200 nm. Because of such large domains, the opacity has been induced in TTLG glass-ceramics. The TTLG-3h-GC and TTLG-24h-GC are appeared to be opaque in the whole transmission spectrum (Figure 3(a) and 3(b)). Remarkable retention in transparency has been observed with the addition of Ho_2O_3 in the TTLG glass network due to reduction in domain size of crystallites. The size of phase-separated domains lies in the range of 20 – 25 nm in TTLGH1-24h-GC (Figure 5(b)) and 9 – 12 nm in TTLGH2-24h-GC (Figure 5(c)). This resulted in the retention of the transparency of Holmium doped glass-ceramics. TTLGH1-3h-GC and TTLGH1-24h-GC samples have partially retained their transparency, while, TTLGH2-3h-GC and TTLGH2-24h-GC have retained even more transparency.

Selected area electron diffraction (SAED) pattern of glass-ceramics confirms that the observed droplets are primarily responsible for the formation of nanostructured *anti*-glass phases. The SAED patterns, depicted in Figure 6 (a-c), are resembling the superstructure of FCC lattice of $(1–x)\ ZrO_2 – x\ Ln_2O_3$ (Ln: Ho, Dy, Tb, and Gd) oxide system.[48] Therefore, in analogy to $ZrO_2–Ln_2O_3$ system, the presently reported SAED patterns might have appeared due to the partitioning of lattice structures of δ-TeO_2 (fluorite-type, space group $Fm3m$ and a_F~5.691 Å)[49] and Ln_2O_3 (C-type sesquioxide-type, space group $Ia3$ and $a = 2a_F$). The δ-TeO_2 and C-type sesquioxide structures have almost identical cation arrays, while the anions (i.e. O^{2-}) have occupied the tetrahedral sites in both the cases. In analogy to $ZrO_2–Ln_2O_3$ system, for the δ-TeO_2 structure, the anions have occupied all the tetrahedral sites while for C-type sesquioxide structure, only three-quarters of tetrahedral (i.e. 48(e)) sites have filled in an ordered array. Furthermore, depending upon the composition, the remaining one-quarter of tetrahedral sites (i.e. 16(*c*) sites) have filled partially.[50] Ordering of oxygen vacancy for such lattice have been proposed by Withers *et. al.* [48][51] as well as, Suzuki *et. al.*,[52] via the modulation wave approach. According to which, the local symmetry of lattice depends on the number of locally excited primary ¼$\{220\}_F$*-type modulation waves and their phase relationships. Whereas, structural relaxations are associated with second harmonic $\{001\}_F$*-type modulations with metal atom ordering. The significant difference has been observed in the SAED patterns depicted in Supplementary Information (S-III (a)) where the satellite diffraction maxima are absent for TTLG-24h-GC. Nevertheless, the non-obvious formation of satellite maxima for TTLGH2-24h-GC sample (Supplementary Information S-III (b)) might be owing to the small phase-separated domains. The difference in ionic radius of Ho^{3+} compared to those of Gd^{3+} and La^{3+} ions, possibly helps to introduce higher oxygen vacancy concentration of the structure hence, satellite reflections might have appeared in the SAED patterns of TTLGH1-24h-GC sample. The absence of ¼$\{220\}_F$*-type satellite reflections along $[001]^*_F$ zone axis (Figure 6(a)), has been explained based on the superposition of primary ¼$\{220\}_F$*-type and second harmonic $\{001\}_F$*-type modulation waves. For TTLG-24h-GC sample, La^{3+} and Gd^{3+} ions are present in an equal concentration, with the small difference of ionic radius. Therefore, upon crystallization, lattice structure accommodates La^{3+} or Gd^{3+} in more of random fashion. This prevents the respective structure to orderly distribute their oxygen deficiency which has been the plausible reason for the absence of satellite diffraction maxima in TTLG-GC-24h.

The luminescence intensity of TTLGH1 based glass and glass-ceramics have been superior compared to TTLGH2, implying that for TTLGH2 sample Ho^{3+} ion-ion interactions are affecting its emission properties. The deconvolution of luminescence band of Ho^{3+}: $^5I_7 \rightarrow {}^5I_8$ transition has resolved into 3 Gaussian profiles with peak wavelengths at 1965, 2022 and 2065 nm, respectively. The relative ratio of Gaussian profiles of emission band has altered from glass to glass-ceramics and causing the change in shape function of the emission band. In effect, the emission bandwidth has enhanced in glass-ceramic samples, as shown in Figure 8 (c). For transparent glass-ceramics the coexistence of glass and crystalline phases are prevalent, therefore the possibility of diverse local environments of active (Ho^{3+}) ions is obvious; which effectively enhance the FWHM of Ho^{3+} related NIR luminescence (~2050 nm), band. For glass-ceramics, Ho^{3+} ions are positioned into the lattice of $Ho_2Te_6O_{15}$ phase which has attributed in a considerable variation of the ligand and/or crystal field effect around the chromophore (i.e. Ho^{3+}) ion in the glass-ceramics compare to its glass counterpart. Furthermore, the enhanced luminescence intensity in transparent glass-ceramics has been realized compare to its glass counterpart; the presence crystal field effect for the glass-ceramics is the basis of such enhancement. The enhanced FWHM of ~2050 nm luminescence band is of considerable technological importance, as the ultra-short laser pulse generation necessarily requires enhanced luminescence bandwidth. The luminescence decay dynamics of 550 and 1200 nm emission bands have been studied for present glass and glass-ceramic samples which are depicted in Supplementary Information (S-VIII). Compared to TTLGH1 specimen, the fluorescence lifetime for TTLGH2 has been decreased. The possible reason for this decrease of fluorescence lifetime is concentration quenching due to ion-ion interaction. However, the fluorescence lifetime of glass-ceramics has been superior compared to their glass counterpart; which is attributing to the low phonon crystal-field effect of transparent glass-ceramics. Furthermore, the authors have fabricated the series of transparent glass-ceramics doped with various species of lanthanide ions in the TTLG network but, will be discussed in the upcoming studies.

Conclusions:

A new series of TeO_2 based transparent glass-ceramics by the growth of nanostructured $Ln_2Te_6O_{15}$ *anti*-glass phase have been synthesized and their potential applications have been explored as MIR photonic material. XRD and electron microscopic analysis revealed that crystallization of TTLG glass leads to interpenetrating phase formation with domain size is 150 – 200 nm via spinodal decomposition upon crystallization. This exhibits the formation of opaque glass-ceramic (TTLG-3h-GC and TTLG-24h-GC). Translucent glass-ceramic has been accomplished via crystallization of TTLGH1 glass, where phase-separated domain size is 20 – 25 nm (TTLGH1-24h-GC). Further inclusion of Ho_2O_3 in the network (TTLGH2) has reduced the phase-separated domain size to 9 – 12 nm (TTLGH2-24h-GC) and enhanced the transparency of the glass-ceramics. The rigorous modification in the nanostructure of glass-ceramics with Ho_2O_3 substitution has been attributed to the density-driven LLPT induced binodal decomposition dependent crystallization. The electron diffraction patterns of TTLGH1-24h-GC reveal the satellite diffraction peak formation, which confirms the partitioning of δ-TeO_2 and C-type Ln_2O_3 sesquioxide structure-dependent ordering of oxygen vacancy. The XRD of glass-ceramics reveal intense Bragg reflection peaks but, Raman spectra have been depicting the amorphous profile that confirms the formed phases are *anti*-glass type. The optimized Ho_2O_3 concentration in the glass-ceramics leads to considerable enhancement in the NIR as well as MIR luminescence, which signify the promising performance of transparent glass-ceramics for optical amplification, MIR lasers, and many more NIR and MIR photonic applications.

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Table 1: Glass transition (T_g), onset crystallization (T_x), peak crystallization (T_p), and melting (T_m) temperature in °C with measured refractive index (n) at 1064 nm.

Sample	T_g	T_x	T_p	T_m	n
TTLG	429	472	487	769	1.551
TTLGH1	428	470	485	768	1.552
TTLGH2	433	472	492	780	1.552