

Influence of Ho₂O₃ on Optimizing Nanostructured Ln₂Te₆O₁₅ Anti-Glass Phases to Attain Transparent TeO₂-Based Glass-Ceramics for Mid-IR Photonic Applications

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1 **Influence of Ho₂O₃ on Optimizing Nanostructured Ln₂Te₆O₁₅ *anti*-glass Phases to Attain**
2 **Transparent TeO₂-based Glass-ceramics for Mid-IR Photonic Applications**

3

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15

16 **Abstract:**

17 The transparent TeO₂-based glass-ceramics have yet to achieve a significant
18 technological breakthrough in the field of photonics, because of poor understanding in
19 optimizing the growth of nanostructured crystalline phases. In the present investigation, the size
20 effect of phase-separation induced, nanostructured Ln₂Te₆O₁₅-based (Ln: Gd, Ho) “*anti-glass*”
21 phase in Ho₂O₃ modified TeO₂-based TTLG (in mol%, 80TeO₂–10TiO₂–5La₂O₃–5Gd₂O₃) glass
22 has been studied to attain transparent glass-ceramics. Raman study of TTLG glass reveals the
23 presence of TeO₃, TeO₃₊₁, and TeO₄, and TeO₆ units with average Te–O coordination number as
24 3.49. The formation of nanostructured Ln₂Te₆O₁₅ phases in glass-ceramics has been confirmed
25 by XRD and TEM analysis. Furthermore, TEM analysis confirms that the Ho₂O₃ concentration
26 has reduced the size of phase-separated domains in nanoscale by the formation of the
27 superstructure to attain transparent glass-ceramics. The superiority of glass-ceramics as photonic
28 material for NIR to MIR range has been established by the realization of enhanced luminescence
29 intensities and bandwidth at ~2900 nm (Ho³⁺: ⁵I₆→⁵I₇) and ~2050 nm (Ho³⁺: ⁵I₇→⁵I₈). The
30 present study offers an opportunity to fabricate the various accessible lanthanide ions doped
31 and/or co-doped TTLG glass with control over nanostructure, to design a series of transparent
32 glass-ceramics from visible to MIR range.

33

34 **Introduction:**

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

45 Low phonon energy ($750 - 780 \text{ cm}^{-1}$), lower melting temperature ($850 - 950 \text{ }^\circ\text{C}$) and
46 substantial thermal stability ($60 - 120 \text{ }^\circ\text{C}$) with considerable mechanical and chemical durability
47 offering the Tellurium oxide (TeO_2) based glass systems as the most appropriate candidates for
48 the development of transparent glass-ceramics for the various photonic and optical applications.
49 However, the emphasis on the development of transparent tellurium oxide-based glass-ceramics
50 for various applications is limited to date owing to the difficulties in identifying the suitable
51 chemical composition of glasses to achieve transparent glass-ceramics. For example, attempts
52 have been made on the development of transparent tellurite glass-ceramics from 70TeO_2 -
53 $15\text{Nb}_2\text{O}_5$ - $15\text{R}_2\text{O}$ (mol %) (R: Li, Na, and K) glass system for their application as nonlinear
54 optical materials. Nevertheless, transparent glass-ceramic has been achieved from (mol%)
55 70TeO_2 - $15\text{Nb}_2\text{O}_5$ - $15\text{K}_2\text{O}$ based glass system, which can exhibit the second harmonic generation
56 (SHG) as well. In another study, 10BaO - $10\text{Ln}_2\text{O}_3$ - 80TeO_2 (Ln: La, Pr, Sm, Eu, Er) series of

57 glass have been considered for the development of transparent glass-ceramics. It has been
58 reported that glasses containing Sm_2O_3 , Eu_2O_3 and Er_2O_3 are capable to provide transparent
59 glass-ceramic materials, whilst glass samples containing La_2O_3 and Pr_2O_3 are unsuitable to attain
60 the transparent glass-ceramics. Transparent glass-ceramic through the growth of TeO_2 and
61 $\text{Zn}_2\text{Te}_3\text{O}_8$ crystalline phases have been developed for their applications as efficient upconversion
62 materials from ErF_3 -doped TeO_2 - ZnO - ZnF_2 glass. On the other hand, as an alternative to
63 transparent glass-ceramics attempts to produce transparent ceramics is being made through
64 implementing the full and congruent crystallization of desired polycrystalline phases in the
65 nanoscale range from parent glass. Bertrand *et al.*, have developed scalable and formable
66 $\text{Bi}_{0.8}\text{Nb}_{0.8}\text{Te}_{2.4}\text{O}_8$ -based transparent ceramics from 75TeO_2 - $12.5\text{Nb}_2\text{O}_5$ - $12.5\text{Bi}_2\text{O}_3$ glass for near-
67 infrared applications. Dolhen *et al.* have reported Nd^{3+} -doped transparent ceramics from
68 congruent crystallization of 75TeO_2 - $12.5\text{Nb}_2\text{O}_5$ - $12.5\text{Bi}_2\text{O}_3$ glass, which has demonstrated lasing
69 action with $\sim 50\%$ slope efficiency and ~ 67 mW as threshold pump power.

70 Interestingly, it has been reported that with the controlled growth of metastable tellurium
71 rich nano-crystalline phases having defective CaF_2 fluorite type crystal structure, generally called
72 as *anti-glass* phases, led to transparent glass-ceramics. Here, an *anti-glass* can be defined as a
73 solid with obvious long-range order of cation, but the partial vacancies of anions have
74 statistically distributed in the short-range order. Nevertheless, the formation of tellurium rich
75 crystalline phase from the glassy matrix upon heating primarily depends on the concentration of
76 the type of network structural units such as TeO_4 , TeO_{3+1} , and TeO_3 as well as the linkages
77 between these structural units. A transparent glass-ceramics with the growth of nanostructured
78 $\text{Bi}_{0.5}\text{Nb}_{0.5}\text{Te}_3\text{O}_8$ (an analogous to the β - $\text{Bi}_2\text{Te}_4\text{O}_{11}$ fluorite type *anti-glass* phase) crystalline phase
79 has been achieved owing to the controlled heat treatment of $7.14\text{Bi}_2\text{O}_3$ - $7.14\text{Nb}_2\text{O}_5$ - 85.72TeO_2

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

88 Among the various *anti*-glass phases, *lanthanide tellurite* phases with the general formula
89 of $\text{Ln}_2\text{Te}_6\text{O}_{15}$ or $\text{Ln}_2\text{Te}_5\text{O}_{13}$, (where Ln: La, Pr, Nd, Sm, and Dy) have also been well reported.
90 The lanthanide ions have considerable technological importance, because of their magnetic,
91 photonic, catalytic and electrochemical properties. Moreover, lanthanides have been the
92 constituent of *lanthanide tellurite* (i.e. $\text{Ln}_2\text{Te}_6\text{O}_{15}$ or $\text{Ln}_2\text{Te}_5\text{O}_{13}$) kind of *anti*-glass phases.
93 Therefore, the fabrications of optically transparent glass-ceramics containing lanthanide tellurite
94 phases have significant technological importance. Moreover, the basis of oxygen vacancy
95 ordering for *lanthanide tellurite* type of *anti*-glass phases is yet to be explored. However,
96 significant efforts have not been paid on the development and controlled growth of *lanthanide*
97 *tellurite* type of *anti*-glass phases in the TeO_2 glass to achieve transparent glass-ceramics.

98 In view of the above discussions, the present study aims to develop transparent TeO_2 -
99 based glass-ceramics containing *lanthanide tellurite* ($\text{La}_2\text{Te}_6\text{O}_{15}$) type nano-crystalline phase. In
100 the previous attempt, authors have reported $\text{La}_2\text{Te}_6\text{O}_{15}$ type '*anti*-glass' phase from (mol%)
101 80TeO_2 - 10TiO_2 - $10\text{La}_2\text{O}_3$ (TTL10) glass composition upon ceramization at 450°C for 3 h and
102 24 h. Nevertheless, the glass-ceramic was opaque in nature. According to Fujimoto *et al.*, the

103 crystalline sizes of *anti*-glass ($\text{Ln}_2\text{Te}_6\text{O}_{15}$) phases reduce with the reduction of the cationic radius
104 of lanthanides. Therefore, to achieve transparent glass-ceramics, the chemical composition of
105 TTL10 glass was further modified to $80\text{TeO}_2\text{-}10\text{TiO}_2\text{-}5\text{Gd}_2\text{O}_3\text{-}5\text{La}_2\text{O}_3$ (TTLG) and considered
106 as parent glass composition in the present study. In addition, foremost efforts have been made in
107 understanding and controlling the retention of transparency in the TTLG glass-ceramics through
108 the modification of glass composition by substituting Holmium oxide (Ho_2O_3) for Lanthanum
109 oxide (La_2O_3). Heat treatment temperature for glass materials to produce transparent glass-
110 ceramics was evaluated using differential scanning calorimetry. The prepared tellurite glass-
111 ceramics have been thoroughly examined through X-ray diffraction (XRD), transmission
112 electron microscopy (TEM) and micro-Raman spectroscopy techniques for phase identification,
113 microstructure, and local structure respectively. Furthermore, Oxygen deficiency ordering in
114 $\text{Ln}_2\text{Te}_6\text{O}_{15}$ -based '*anti*-glass' phase has been confirmed via selected area electron diffraction
115 (SAED) technique. It is to be further highlighted those luminescence properties of $\text{Ln}_2\text{Te}_6\text{O}_{15}$ -
116 based '*anti*-glass' phase containing transparent glass-ceramics are very little explored. Therefore,
117 considering their technological importance for NIR/MIR photonic applications, the
118 photoluminescence properties in the region ranging from visible (500 nm) to MIR (3500 nm) of
119 Ho^{3+} ion has also been explored for TeO_2 -based glass and transparent glass-ceramics.

120

121 **Experimental:**

122 Glasses and glass-ceramics corresponding to the compositions (80 TeO₂ – 10 TiO₂ – 5
123 Gd₂O₃ – (5-*x*) La₂O₃ – *x* Ho₂O₃ (in mol %)), where *x* = 0, 1 and 2, which are designated as TTLG
124 for *x*=0, TTLGH1 and TTLGH2 for *x*= 1, 2, respectively; have been prepared by using a
125 conventional melt-quenching technique. Commercially available, starting powders of TeO₂ (Alfa
126 Aesar, 99.99%), TiO₂ (Sigma-Aldrich, 99.999%), Gd₂O₃ (Sigma-Aldrich, 99.99%), La₂O₃ (Alfa
127 Aesar, 99.99%) and Ho₂O₃ (Sigma-Aldrich, 99.99%) were weighed of appropriate quantities so
128 that 20 g glass block can be yielded. The detailed synthesis procedure of glass and glass-
129 ceramics and their characterization using Prism coupler for refractive index measurements,
130 DTA-DSC for thermal analysis, XRD for crystalline phase evaluation and Raman for structural
131 characterizations are mentioned **in the supplementary Information**. Glass-ceramics (GCs) were
132 synthesized by isothermal **heat treatment of glasses at 450° C** (standardized using thermokinetic
133 analysis) for 3 h and 24 h in a precision microprocessor-controlled electric furnace under
134 ambient condition. The nanostructures of glass and glass-ceramic samples were investigated by
135 using a transmission electron microscope (TEM; FEI Model Tecnai G2 30ST; Hillsboro, OR,
136 USA). Detailed sample preparation procedure for the TEM measurement is provided in
137 Supplementary Information. The distribution of the constituent elements within the glass-
138 ceramic sample was investigated using a Tecnai G² 30ST TEM operating at 300 kV and
139 equipped with a LaB₆ thermionic electron source. Scanning transmission electron microscopy–
140 high angle annular dark field (STEM-HAADF) images were acquired with a camera length of
141 120 cm and a probe size of 5 nm. The contrast of these dark-field images is linked to the square
142 of atomic number (*Z*) of the constituent elements and thus allows one to obtain a chemical
143 contrast. Attempts were also made to obtain Elemental distribution maps by employing the

144 STEM-EDX spectrum an imaging technique using an EDX Spectrometer (EDAX Inc., USA)
145 detector and a probe size of 5 nm in order to have better insight into the phase separation in the
146 glass-ceramic system. Transparency, as well as related absorption spectra, have been verified in
147 200 – 2500 nm spectral region by UV-Vis-NIR spectrophotometer (Model: 3101 from
148 Shimadzu, Japan). The transmission spectra in the MIR region (2.5 – 25 μm) has been recorded
149 using FTIR spectrophotometer (Model: Frontier FIR MIR from Perkin-Elmer, USA). The
150 emission and excitation spectra of the sample were recorded at room temperature on a
151 spectrofluorimeter (Model: Quantum Master enhanced NIR from PTI, USA) fitted with double
152 monochromators on both excitation and emission channels. The Visible-NIR (500 – 1500 nm),
153 NIR (1500 – 2500 nm) and MIR (2500 – 5000 nm) emission spectra were recorded using LN₂
154 cooled NIRPMT, solid-state InGaAs and LN₂ cooled InSb detectors respectively with Xenon
155 lamp operating as the excitation source. All the measurement were carried out by placing the
156 sample at 60° to the incident beam and signals were collected from the same surface at the right
157 angle (90°) to the incident beam. Appropriate low-pass and high-pass filters from Edmund
158 Optics, Inc, of USA were used at excitation and emission channels to avoid excitation and
159 emission wavelength's higher-order harmonics in the recorded emission spectrum.

160

161 **Results:**

162 Transmission spectra for the series of glass have been shown in Figure 1(a). The spectra
163 show that the series of glass has optical transparency from the visible to MIR wavelength range.
164 Inset of Figure 1(a) presents the photograph of as prepared glass materials. The X-ray Diffraction
165 (XRD) patterns of powdered glass samples have been presented in Figure 1(b), which reveal
166 their X-ray amorphous nature. The morphology of glass powders has been observed using bright-

167 field transmission electron microscopy (BF-TEM). Figures 1(c), 1(d), and 1(e) have been
168 depicting the micrograph of TTLG, TTLGH1, and TTLGH2 glass samples respectively. The
169 insets depict the selected area electron diffraction (SAED) pattern of the relevant sample. It can
170 be noticed from bright-field micrographs that there has been the no obvious formation of
171 noticeable phase-separated domains. Also, the presence of halo rings in the SAED patterns have
172 confirmed the amorphous nature for the glass samples, which is well corroborating with the
173 XRD pattern.

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

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

190 as the glass name followed by time duration and GC. For example, the glass-ceramic sample
191 obtained after the heat treatment of TTLG glass at 450 °C for 3 h has been labeled as TTLG-3h-
192 GC.

193 Transmission spectra extended from UV (300 nm) to MIR (7000 nm) region for the as-
194 prepared glass-ceramics heat-treated for 3 h and 24 h duration have been shown in Figure 3(a)
195 and (b), respectively, and insets depict the photograph of respective glass-ceramics. Figure 3(a)
196 reveals the significant reduction in transparency from 80% to <10% for TTLG-3h-GC sample
197 due to the formation of large-sized crystals. On the other hand, TTLGH1-3h-GC and TTLGH2-
198 3h-GC have exhibited their maximum transparency of 65% and 75%, respectively at 1500 nm
199 wavelength. The ability of the retention in the transparency of Ho₂O₃ substituted glass-ceramics,
200 unlike TTLG-3h-GC sample, has implied that the substitution of Ho₂O₃ in the network might be
201 facilitating the monitoring and controlling the size of crystalline phases. However, further
202 increase of ceramization duration from 3 to 24 h has reduced the transparency of TTLGH1-24h-
203 GC sample to 48%; while, transparency of TTLGH2-24h-GC sample has been 73%. The
204 decrease in transparency with the increase of heat treatment duration has correlated with the
205 enhancement of refractive index for transparent glass-ceramics. The dispersion curves of
206 TTLGH1 and TTLGH2 based glass and respective glass-ceramics have been depicted in
207 Supplementary Information (S-I (a) and (b)). The dispersion curves of the synthesized
208 transparent glass-ceramics have exhibited higher refractive indices than commercially available
209 CaF₂ crystals ($n=1.42$ at 1064 nm), which are comparable to the polycrystalline ZrO₂ as well as
210 TeO₂-Nb₂O₅-Bi₂O₃ based glass-ceramic. The high refractive indices (i.e., $n \sim 2.1$) of transparent
211 glass-ceramic has useful applications in the development of NIR/MIR lens.

212 X-ray diffraction (XRD) patterns of the powdered glass-ceramics, obtained after heat
213 treatment at 450 °C for 3 h and 24 h have been presented in Figure 4 (a) and (b), respectively.
214 The patterns have confirmed very sharp and intense diffraction peaks which indicate the
215 formation of crystalline phases upon heat treatment. The qualitative analysis reveals the
216 formation of fluorite-type *lanthanide tellurite* ($\text{Ln}_2\text{Te}_6\text{O}_{15}$) phases in all the glass-ceramics.
217 Further analysis reveals that TTLG glass-ceramics comprise $\text{Gd}_2\text{Te}_6\text{O}_{15}$ (00-037-1400 PDF4+
218 database card number) as dominant crystalline phase. Nevertheless, in TTLGH1 and TTLGH2-
219 based glass-ceramics $\text{Ho}_2\text{Te}_6\text{O}_{15}$ (00-043-0553) crystalline phase has evolved as the dominant
220 crystalline phase. Further, the broadening of Bragg reflection peaks observed for 3h and 24 h
221 heat-treated glasses indicating that the formation of both $\text{Ho}_2\text{Te}_6\text{O}_{15}$ and $\text{Gd}_2\text{Te}_6\text{O}_{15}$ phases in
222 TTLGH1 and TTLGH2-based glass-ceramics.

223 To elucidate further on the morphology of the nanocrystalline phase, the TEM studies
224 have been carried out. Figures 5 (a-c) have been depicting the bright-field images of TTLG-24h-
225 GC, TTLGH1-24h-GC, and TTLGH2-24h-GC samples, respectively. TEM bright-field
226 micrograph of TTLG-24h-GC (Figure 5 (a)) reveals the presence of a highly interconnected large
227 size (order of 150 – 200 nm) domain. The nanostructure of TTLGH1-24h-GC and TTLGH2-24h-
228 GC (Figure 5 (b) and (c)) disclose the existence of randomly dispersed isolated spherical
229 domains with diffused phase boundaries. The sizes of the domains are significantly reduced from
230 ~25 nm to ~10 nm with increasing Ho_2O_3 substitution for La_2O_3 from 1 mol% to 2 mol% in
231 TTLG glass composition. The reduction in the size of phase-separated domains (from around
232 200 nm to 25 nm) of TTLGH1-24h-GC is confirming its translucent character in contrast to
233 TTLG-24h-GC sample which is showing opacity. Similarly, further reduction in domain sizes
234 (10 nm) is responsible for the retention of transparency in TTLGH2-24h-GC. The compositional

235 partitioning in the glass-ceramics has been established using scanning transmission electron
236 microscopy through high angle annular dark field (STEM-HAADF) images. The STEM-
237 HAADF images of TTLG-24h-GC, TTLGH1-24h-GC, and TTLGH2-24h-GC have been
238 presented in Figure 5 (d-f), respectively. Figure 5 (d) reveals the nanostructures have large-sized
239 (150 – 200 nm) interconnected domains in the base glass matrix. In contrast, Figures 5 (e) and (f)
240 reveal the poorly resolved and diffused spherical domains (domain size 10 – 25 nm) that have
241 been dispersed in the matrix, where spherical phases have appeared to be slightly brighter than
242 the matrix. The intensity of STEM-HAADF images represents atomic number contrast ('Z-
243 contrast'), which indicates that the separated domains have large Z-number difference for TTLG-
244 24h-GC as compared to TTLGH1-24h-GC and TTLGH2-24h-GC. Elemental identification
245 participated in the phase-separated domains have also been carried out using EDX point analyses
246 in order to identify the elements participated in the formation of domains. Supplementary
247 Information (S-II (a), (b), and (c)) have shown the distribution of Ti, Gd, Te, La, O and Ho
248 elements present in TTLG-24h-GC, TTLGH1-24h-GC, and TTLGH2-24h-GC samples
249 respectively. Figure S-II (a) reveals that interconnected domains in TTLG-24h-GC are primarily
250 due to the precipitation of gadolinium (Gd), titanium (Ti) and Oxygen (O). This confers that, in
251 STEM-HAADF image of TTLG-24h-GC (Figure 5 (d)), the brighter regions are rich in
252 gadolinium and the darker regions are relatively titanium-rich. However, STEM-EDX elemental
253 maps for TTLGH1-24h-GC (Figure S-II (b)) and TTLGH2-24h-GC (Figure S-II (c)) could not
254 reveal the clear presence of isolated domains.

255 Figures 6 (a), (b), and (c) have depicted the SAED pattern along $[001]_{F^*}$, $[110]_{F^*}$ and
256 $[111]_{F^*}$ zone-axis of TTLGH1-24h-GC sample. The high-resolution TEM (HRTEM) image
257 along $[001]_{F^*}$, $[110]_{F^*}$ and $[111]_{F^*}$ zone-axis has been shown in Figure 6 (d), (e), and (f)

258 respectively; whilst, inset of each HRTEM micrograph are depicting their respective fast Fourier
259 transformation (FFT) patterns. Supplementary information S-III (a) and (b) have been presenting
260 the SAED patterns of TTLGH2-24h-GC and TTLG-24h-GC samples respectively. The SAED
261 patterns of TTLGH1-24h-GC (Figures 6 (a-c)) have confirmed the superstructure formation. The
262 superstructure formation has also been confirmed via HRTEM images of TTLGH1-24h-GC
263 sample (Figures 6 (d-f)). Further, Figure 6(a) reveals that $\frac{1}{2}\{200\}_{F^*} \equiv \{100\}_{F^*}$ and $\frac{1}{2}\{220\}_{F^*} \equiv$
264 $\{110\}_{F^*}$ satellite reflections are appearing for the $[001]_{F^*}$ zone axis. Whereas, $\frac{1}{4}\{220\}_{F^*}$ and
265 $\frac{1}{2}\{200\}_{F^*}$ satellite reflection are appeared along $[110]_{F^*}$ zone axis (Figure 6 (b)) and $\frac{1}{4}\{220\}_{F^*}$
266 appeared along $[111]_{F^*}$ zone-axis (Figure 6 (c)). The ring pattern of the SAED has been realized
267 for TTLGH2-24h-GC which has been signifying the smaller size of phase-separated domains for
268 the respective sample. Interestingly, for TTLG-24h-GC sample satellite reflections did not
269 appear in SAED pattern.

270 The measured Raman spectra of glass and respective glass-ceramics under 785 nm laser
271 excitation is presented in Fig. S. Experimentally measured Raman spectra has been processed for
272 baseline correction with the equation given by Kalampounias *et al.* The obtained spectra after the
273 baseline correction is further normalized at 663 cm^{-1} and are presented in Figure 7. Present series
274 of glass have shown two distinct spectral regions as, (a) $550 - 900\text{ cm}^{-1}$, and (b) $200 - 550\text{ cm}^{-1}$
275 respectively. Supplementary Information S-IV has been depicting the deconvoluted Gaussian
276 line profiles of Raman spectra of the glass samples, as proposed by Barney *et al.* The region (a)
277 $550 - 900\text{ cm}^{-1}$ has been fitted with four Gaussian line profiles. For the present study, Raman
278 peak appeared in the region of $775 - 795\text{ cm}^{-1}$ is related to Te-O⁻ stretching vibration of TeO₃₊₁
279 polyhedron or TeO₃ (trigonal pyramid, *tp*) structural units. The peak appeared in the region of
280 $720 - 740\text{ cm}^{-1}$ is attributed to the symmetric stretching vibration between Tellurium and non-

281 bridging Oxygen (NBO) of TeO_{3+1} polyhedron and TeO_3 *tp* in which NBO interacts with
282 adjacent Tellurium atom. The band appeared in $655 - 665 \text{ cm}^{-1}$ is assigned to the antisymmetric
283 stretching vibrations of Te–O–Te linkages because of two non-equivalent Te–O bonds (i.e. Te
284 $_{IV} - a_x O_{eq} - Te_{IV}$) in TeO_4 (trigonal bipyramid, *tbp*) units. Peak observed in $500 - 470 \text{ cm}^{-1}$ range
285 is attributed to the symmetric stretching and bending vibrations of continuous Te–O–Te linkages
286 in the vertex sharing of TeO_3 or TeO_{3+1} and TeO_4 structural units. Figure 7 (a) have confirmed
287 that the peaks have appeared less than 450 cm^{-1} . To verify the base of peaks less than 450 cm^{-1} ,
288 Raman spectra have also been recorded at 488 nm excitation and shown in Supplementary
289 Information (SI- V). Significantly, the shape function of Raman spectra of $200 - 450 \text{ cm}^{-1}$ range
290 has altered significantly with the change of excitation wavelength. This confirms that the peaks
291 appeared in $200 - 450 \text{ cm}^{-1}$ range has associated to the intrinsic fluorescence intensities of Ln^{3+}
292 ions doped in the glass sample. SI- V (b) has revealed the appearance of sharp peak at 470 cm^{-1}
293 in the glass-ceramics. With the increase of ceramization duration, the bandwidth of peak at 470
294 cm^{-1} has reduced steadily (see SI- V (b)). But, the addition of 1 mol% of Ho_2O_3 in the TTLG
295 network has broadened the peak of 470 cm^{-1} in GCs (see SI- V (c)). In case of GCs of TTLGH2,
296 the sharp peak at 470 cm^{-1} has completely disappeared (see SI- V (d)).

297 Luminescence spectra of Ho^{3+} ions doped glasses (TTLGH1 and TTLGH2) and
298 respective transparent glass-ceramics are depicted in Figure 8. Significant enhancement in
299 luminescence intensity in the spectral region from $1.5 \mu\text{m}$ to $3.5 \mu\text{m}$ has been realized for
300 transparent glass-ceramics compared to glass counterparts. Figures 8 (a) and (b) are depicting the
301 signature NIR ($\text{Ho}^{3+}: {}^5\text{I}_7 \rightarrow {}^5\text{I}_8$, λ_p : 2050 nm) emission band for Ho_2O_3 substituted samples; while
302 Figure 8 (c) and (d) are representing the MIR ($\text{Ho}^{3+}: {}^5\text{I}_6 \rightarrow {}^5\text{I}_7$, λ_p : 2900 nm) luminescence for

303 1194 nm excitation. Unlike glass, the luminescence bands have revealed the variation of shape
304 function for the glass-ceramics.

305

306 **Discussions:**

307 Increasing the concentration of modifier components in the tellurite glass composition
308 increases the conversion of TeO_4 structural units into TeO_3 structural units containing NBOs that
309 are coordinated to the modifier cations.^{[38][40][41]} The structural evolution of the glass network
310 caused by the addition of various lanthanide ions in the *titanium tellurite glass* (in mol%,
311 $90\text{TeO}_2-10\text{TiO}_2$) network has been studied here by Raman spectroscopic technique, under 785
312 nm laser excitation. The measured and baseline corrected Raman spectra of *titanium tellurite*
313 *glass* have been presented in Supplementary Information (S-VI (a) and (b)). The Raman
314 spectrum of *titanium tellurite glass* reveals the strongest peak at 630 and 660 cm^{-1} (S-VI (b)).
315 However, in the earlier effort authors have observed the gradual enhancement of the relative
316 intensity of peaks at 730 and 780 cm^{-1} with the systematic inclusion of La_2O_3 in the *titanium*
317 *tellurite glass* (TTL) network by the formation of TeO_3 and TeO_{3+1} units, over TeO_4 .^[9] To
318 formulate TTLG glass, La_2O_3 has partially been substituted by Gd_2O_3 in the TTL10 (i.e.
319 $80\text{TeO}_2-10\text{TiO}_2-10\text{La}_2\text{O}_3$) network. The partial substitution of La_2O_3 by Ho_2O_3 in the TTLG
320 network has been causing an increase of intensity of peak at 790 cm^{-1} . The increase of the
321 intensity at 790 cm^{-1} has been attributing to the steady formation of TeO_3 units over TeO_4 units.
322 The area of decomposed Gaussian line profiles of the modified Raman spectra for glass samples
323 has been utilized to estimate the average Te–O coordination number (n_{TeO}) and presented in
324 Supplementary Information (S-VII). The *titanium tellurite glass* has n_{TeO} -value as 3.65.
325 Nevertheless, the average coordination number (n_{TeO}) of TTLG, TTLGH1, and TTLGH2 has

326 been estimated to be 3.49, 3.45, and 3.46, respectively. For the pure amorphous TeO_2 sample, ^[38]
327 the n_{TeO} has been reported to be 3.64, which is almost identical to the estimated value for
328 *titanium tellurite glass* in the present study. The similarity of the n_{TeO} values for pure amorphous
329 TeO_2 and *titanium tellurite glass* is not ambiguous; because of the Te^{4+} (network former) ions
330 have successfully been substituted by the Ti^{4+} (network modifier) ions. The progressive inclusion
331 of Holmium oxide in the TTLG network has confirmed the larger formation of terminal oxygen
332 (i.e. $\text{Te}=\text{O}$) containing TeO_{3+1} (polyhedron) and TeO_3 (*tp*) structural units, which has reduced
333 their respective average coordination number. Furthermore, the corrected Raman spectra of
334 glass-ceramic samples have been showing elevated baseline (Figure 7 (b)). The coexistence of
335 nano-crystalline and residual amorphous phases in the glass-ceramics has contributed notably in
336 the scattering, which is responsible for the elevated baseline. As a result, Gaussian line profiles
337 are not aptly fitting for the Raman spectra of glass-ceramic samples. However, the tendency to
338 progressively form TeO_3 and TeO_{3+1} unit over TeO_4 has been clear from the corrected Raman
339 spectra of glass-ceramic samples. The peak at 470 cm^{-1} has assigned to the stretching and
340 bending vibration of TeO_3 *tp* having a weak interaction.^[39] For the GCs of TTLG, the phase-
341 separated domains have size of 150 – 200 nm. But, with Holmium oxide addition in the network,
342 domain size and domain connectivity have reduced considerably. As a result, propagation of
343 phonon has reduced significantly in Ho_2O_3 doped GCs. Consequently, with the addition of
344 Ho_2O_3 , Raman profile of respective GCs has resembled to amorphous profile.

345 The concentration of Ho_2O_3 in the TTLG network has influenced the domain size of the
346 *spherulites* ^[42] and resulting nanostructures. Moreover, the Raman spectra of glass-ceramics have
347 shown the amorphous profiles while, XRD patterns exhibit intense and discrete Bragg-maxima;
348 which confirmed that the formed crystalline phases are *anti-glass* type. The changes in the

349 nanostructure of glass-ceramics with the addition of Holmium oxide have been typical
350 consequence of free energy of the system at ceramization temperature. Therefore, it can be
351 concluded that controlled heat treatment schedule and free energy of the system are the basis for
352 tuning the size of the domains which have converted into the nano-sized crystalline phases. The
353 change in nanostructure of the glass-ceramics can be explained on the basis of free energy of the
354 system. The XRD pattern for TTLG-3h-GC and TTLG-24h-GC (Figure 4(b)) further reveal that
355 interpenetrated crystalline phases decomposed into multiple phases. BF-TEM image (Figure
356 5(a)) and the significant Z-contrast (atomic number based intensity contrast) image (Figure 5(d))
357 are also confirming the presence of interpenetrated phases in TTLG-24h-GC. Therefore, XRD,
358 bright field and HAADF studies establish that the thermodynamic instability of the TTLG
359 composition causes diffusion-controlled compositional fluctuation in the phase-separated
360 domains that generates interpenetrated phase, upon ceramization. Nevertheless, during prolong
361 heat treatment for 24 h, spinodal decomposition plays a crucial role and decompose the observed
362 interpenetrated phase into highly interconnected multiple crystalline phases. On the other hand,
363 TEM nanostructure of Ho_2O_3 doped TTLG glass network reveal non-obvious formation of
364 phase-separated domains (Figure 1(d) and (e)). Upon crystallization, the formation of spherical
365 phase separated domains that are randomly dispersed in the matrix has been observed in glass-
366 ceramics of Ho_2O_3 doped TTLG network. This implies that with Ho_2O_3 addition in the TTLG
367 network, binodal decomposition might occur in glass-ceramics.^[44] Moreover, the elemental maps
368 presented in figures S-II (b) and (c) could not reveal the compositional fluctuation in the phase-
369 separated domains of Ho_2O_3 substituted glass-ceramics; which confirms that the event of phase
370 separation for relevant samples are governed by density fluctuation only. Further, density
371 fluctuation driven phase separation lead to the controlled crystallization via binodal

372 decomposition. This implies that with Ho_2O_3 addition in the TTLG network, the decomposition
373 process is limited to the binodal decomposition for the selected heat treatment schedule. This
374 resulted into the small domains of nanostructured crystalline phases. In case of the *anti-glass*
375 phase, a metal sub-lattice of the large cationic radius (e.g. Sr^{2+} , Pb^{2+} , Ln^{3+}) along with Te^{4+} ions
376 have formed an ordered array of cations.^{[25][44]} The ordered cationic array has been the reason for
377 the Bragg-diffraction maxima in X-ray diffraction experiments. But, an anion-deficient lattice of
378 the anti-glass structure is incapable of the propagation of phonons; therefore, an amorphous
379 profile has been exhibited for Raman and IR experiments of glass-ceramics. In the present study,
380 the melt-quenched TTLG series of glass (annealed at 350 °C) has not shown any phase-separated
381 domains in the nanoscale (Figure 1 (c-e)). However, heat treatment of the glasses at 450 °C and
382 successive slow rate of cooling have resulted in the liquid-liquid phase transition (LLPT) and
383 simultaneous crystallization.

384 It is assumed that the identified *anti-glass* crystalline phases are decomposed because of
385 the formation of the *spherulitic* microstructure in the glass. It is well known that fluorite-type
386 crystalline formation in AX_2 type compounds demands the cation (A) to anion (X) radius ratio in
387 the range of 0.73 – 1.00. Though, $R(\text{Te}^{4+})/R(\text{O}^{2-}) = 0.51$ ratio stand far away from the required
388 value, owing to the suitable $R(\text{Ln}^{3+})/R(\text{O}^{2-})$ values of 0.86, 0.81 and 0.72 for Ln^{3+} : Gd^{3+} , La^{3+} ,
389 and Ho^{3+} , respectively and the possibilities to have irregular Te^{4+} coordination sites fluorite-type
390 Lanthanide tellurite crystalline phases generally forms in TeO_2 glass system.^[22] Nevertheless,
391 when the sizes of crystallites are larger than the wavelength of incident light the scattering loss
392 also increases significantly. In accordance to the proposed theories, the retention of transparency
393 in the glass-ceramics can be achieved if the size of crystallites are less than 30 – 40 nm.^{[45]–[47]}
394 BF-TEM analysis (Figure 5(a)) for TTLG-24h-GC clearly revealed that highly interconnected

395 and phase-separated domains are very large in size, nearly 150 – 200 nm. Because of such large
396 domains, the opacity has been induced in TTLG glass-ceramics. The TTLG-3h-GC and TTLG-
397 24h-GC are appeared to be opaque in the whole transmission spectrum (Figure 3(a) and 3(b)).
398 Remarkable retention in transparency has been observed with the addition of Ho₂O₃ in the TTLG
399 glass network due to reduction in domain size of crystallites. The size of phase-separated
400 domains lies in the range of 20 – 25 nm in TTLGH1-24h-GC (Figure 5(b)) and 9 – 12 nm in
401 TTLGH2-24h-GC (Figure 5(c)). This resulted in the retention of the transparency of Holmium
402 doped glass-ceramics. TTLGH1-3h-GC and TTLGH1-24h-GC samples have partially retained
403 their transparency, while, TTLGH2-3h-GC and TTLGH2-24h-GC have retained even more
404 transparency.

405 Selected area electron diffraction (SAED) pattern of glass-ceramics confirms that the
406 observed droplets are primarily responsible for the formation of nanostructured *anti*-glass phases.
407 The SAED patterns, depicted in Figure 6 (a-c), are resembling the superstructure of FCC lattice
408 of (1-x) ZrO₂ – x Ln₂O₃ (Ln: Ho, Dy, Tb, and Gd) oxide system.^[48] Therefore, in analogy to
409 ZrO₂-Ln₂O₃ system, the presently reported SAED patterns might have appeared due to the
410 partitioning of lattice structures of δ-TeO₂ (fluorite-type, space group *Fm3m* and $a_F \sim 5.691 \text{ \AA}$)^[49]
411 and Ln₂O₃ (C-type sesquioxide-type, space group *Ia3* and $a = 2a_F$). The δ-TeO₂ and C-type
412 sesquioxide structures have almost identical cation arrays, while the anions (i.e. O²⁻) have
413 occupied the tetrahedral sites in both the cases. In analogy to ZrO₂-Ln₂O₃ system, for the δ-TeO₂
414 structure, the anions have occupied all the tetrahedral sites while for C-type sesquioxide
415 structure, only three-quarters of tetrahedral (i.e. 48(e)) sites have filled in an ordered array.
416 Furthermore, depending upon the composition, the remaining one-quarter of tetrahedral sites (i.e.
417 16(c) sites) have filled partially.^[50] Ordering of oxygen vacancy for such lattice have been

418 proposed by Withers *et. al.* [48][51] as well as, Suzuki *et. al.*, [52] via the modulation wave approach.
419 According to which, the local symmetry of lattice depends on the number of locally excited
420 primary $\frac{1}{4}\{220\}_F^*$ -type modulation waves and their phase relationships. Whereas, structural
421 relaxations are associated with second harmonic $\{001\}_F^*$ -type modulations with metal atom
422 ordering. The significant difference has been observed in the SAED patterns depicted in
423 Supplementary Information (S-III (a)) where the satellite diffraction maxima are absent for
424 TTLG-24h-GC. Nevertheless, the non-obvious formation of satellite maxima for TTLGH2-24h-
425 GC sample (Supplementary Information S-III (b)) might be owing to the small phase-separated
426 domains. The difference in ionic radius of Ho^{3+} compared to those of Gd^{3+} and La^{3+} ions,
427 possibly helps to introduce higher oxygen vacancy concentration of the structure hence, satellite
428 reflections might have appeared in the SAED patterns of TTLGH1-24h-GC sample. The absence
429 of $\frac{1}{4}\{220\}_F^*$ -type satellite reflections along $[001]^*_F$ zone axis (Figure 6(a)), has been explained
430 based on the superposition of primary $\frac{1}{4}\{220\}_F^*$ -type and second harmonic $\{001\}_F^*$ -type
431 modulation waves. For TTLG-24h-GC sample, La^{3+} and Gd^{3+} ions are present in an equal
432 concentration, with the small difference of ionic radius. Therefore, upon crystallization, lattice
433 structure accommodates La^{3+} or Gd^{3+} in more of random fashion. This prevents the respective
434 structure to orderly distribute their oxygen deficiency which has been the plausible reason for the
435 absence of satellite diffraction maxima in TTLG-GC-24h.

436 The luminescence intensity of TTLGH1 based glass and glass-ceramics have been
437 superior compared to TTLGH2, implying that for TTLGH2 sample Ho^{3+} ion-ion interactions are
438 affecting its emission properties. The deconvolution of luminescence band of Ho^{3+} : $^5I_7 \rightarrow ^5I_8$
439 transition has resolved into 3 Gaussian profiles with peak wavelengths at 1965, 2022 and 2065
440 nm, respectively. The relative ratio of Gaussian profiles of emission band has altered from glass

441 to glass-ceramics and causing the change in shape function of the emission band. In effect, the
442 emission bandwidth has enhanced in glass-ceramic samples, as shown in Figure 8 (c). For
443 transparent glass-ceramics the coexistence of glass and crystalline phases are prevalent, therefore
444 the possibility of diverse local environments of active (Ho^{3+}) ions is obvious; which effectively
445 enhance the FWHM of Ho^{3+} related NIR luminescence (~ 2050 nm), band. For glass-ceramics,
446 Ho^{3+} ions are positioned into the lattice of $\text{Ho}_2\text{Te}_6\text{O}_{15}$ phase which has attributed in a
447 considerable variation of the ligand and/or crystal field effect around the chromophore (i.e. Ho^{3+})
448 ion in the glass-ceramics compare to its glass counterpart. Furthermore, the enhanced
449 luminescence intensity in transparent glass-ceramics has been realized compare to its glass
450 counterpart; the presence crystal field effect for the glass-ceramics is the basis of such
451 enhancement. The enhanced FWHM of ~ 2050 nm luminescence band is of considerable
452 technological importance, as the ultra-short laser pulse generation necessarily requires enhanced
453 luminescence bandwidth. The luminescence decay dynamics of 550 and 1200 nm emission
454 bands have been studied for present glass and glass-ceramic samples which are depicted in
455 Supplementary Information (S-VIII). Compared to TTLGH1 specimen, the fluorescence lifetime
456 for TTLGH2 has been decreased. The possible reason for this decrease of fluorescence lifetime
457 is concentration quenching due to ion-ion interaction. However, the fluorescence lifetime of
458 glass-ceramics has been superior compared to their glass counterpart; which is attributing to the
459 low phonon crystal-field effect of transparent glass-ceramics. Furthermore, the authors have
460 fabricated the series of transparent glass-ceramics doped with various species of lanthanide ions
461 in the TTLG network but, will be discussed in the upcoming studies.

462 **Conclusions:**

463 A new series of TeO₂ based transparent glass-ceramics by the growth of nanostructured
464 Ln₂Te₆O₁₅ *anti*-glass phase have been synthesized and their potential applications have been
465 explored as MIR photonic material. XRD and electron microscopic analysis revealed that
466 crystallization of TTLG glass leads to interpenetrating phase formation with domain size is 150 –
467 200 nm via spinodal decomposition upon crystallization. This exhibits the formation of opaque
468 glass-ceramic (TTLG-3h-GC and TTLG-24h-GC). Translucent glass-ceramic has been
469 accomplished via crystallization of TTLGH1 glass, where phase-separated domain size is 20 –
470 25 nm (TTLGH1-24h-GC). Further inclusion of Ho₂O₃ in the network (TTLGH2) has reduced
471 the phase-separated domain size to 9 – 12 nm (TTLGH2-24h-GC) and enhanced the
472 transparency of the glass-ceramics. The rigorous modification in the nanostructure of glass-
473 ceramics with Ho₂O₃ substitution has been attributed to the density-driven LLPT induced binodal
474 decomposition dependent crystallization. The electron diffraction patterns of TTLGH1-24h-GC
475 reveal the satellite diffraction peak formation, which confirms the partitioning of δ-TeO₂ and C-
476 type Ln₂O₃ sesquioxide structure-dependent ordering of oxygen vacancy. The XRD of glass-
477 ceramics reveal intense Bragg reflection peaks but, Raman spectra have been depicting the
478 amorphous profile that confirms the formed phases are *anti*-glass type. The optimized Ho₂O₃
479 concentration in the glass-ceramics leads to considerable enhancement in the NIR as well as MIR
480 luminescence, which signify the promising performance of transparent glass-ceramics for optical
481 amplification, MIR lasers, and many more NIR and MIR photonic applications.

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487 **References:**

488 **References:**

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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.

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| 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 |