Effect of the Addition of Pb$_3$O$_4$ and TiO$_2$ on the Optical Properties of Er$^{3+}$/Yb$^{3+}$:TeO$_2$–WO$_3$ Glasses

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ABSTRACT: Heavy metal oxide tungstate-based tellurite glasses TeO$_2$–WO$_3$ (TW) containing Er$^{3+}$/Yb$^{3+}$ ions have been prepared by the melting and quenching method. The optical absorption and upconversion (UC) emission studies for the doped/codoped glasses have been performed. The effect of the addition of Pb$_3$O$_4$ and TiO$_2$ to the Er$^{3+}$/Yb$^{3+}$:TW glass on its physical properties, optical absorption, and UC emission spectra under 980 nm/808 nm excitations has been studied. A significant enhancement in the UC emission intensity lying in the green and red region has been observed on introducing Pb$_3$O$_4$ and TiO$_2$ into the Er$^{3+}$/Yb$^{3+}$:TW glass. The improvement in the UC emission intensity and full width at half maximum of the bands have been explained on the basis of energy transfer, local field correction factor, and Urbach energy. The non-color tunability in the color emitted from the prepared Er$^{3+}$/Yb$^{3+}$:TWPTi glass upon near-infrared (NIR) excitation at different pump power has been reported. Also, the color-correlated temperature and color purity have been measured under both NIR excitations.

1. INTRODUCTION

The tellurite-based glasses doped with rare earth (RE) ions are the main subject of research because of their special optical and physical properties such as high thermal stability, low phonon energy (∼800 cm$^{-1}$), low melting point, non-hygrosopic nature, and high nonlinear refractive indices.1,2 The hosts used to prepare the glasses should have high radiative emission rates and low absorption coefficients within the wavelength range of interest. In the tellurite glasses, tellurium dioxide (TeO$_2$) is the main component as the glass itself, but it cannot produce the glass itself. Therefore, to prepare the glasses, other supporting metal oxides like WO$_3$, Pb$_3$O$_4$, TiO$_2$, etc. are used as the glass modifiers. The heavy metal oxide-based tellurite (HMT) glasses have low phonon energy, low melting point, high refractive index, and high infrared transmittance when compared to the borate, silicate, and phosphate glasses.3–6 Because of their low phonon energy, the RE ion-doped glassy/crystalline materials exhibit low non-radiative relaxations (NRRs) as well as high probability of radiative transitions upon near-infrared (NIR) excitation. Researchers all over the world are trying to investigate such RE ion-doped crystalline powder or glassy hosts that show efficient frequency upconversion (UC). The HMT glasses and various crystalline nanomaterials doped with RE ions have great potential applications in the field of photonics, biomedical and home appliances, etc.5,6–10

The absorption spectra of RE ion-doped/codoped glasses play a vital role in determining the Judd–Ofelt intensity parameters, experimental and calculated oscillator strengths, transition probabilities, radiative and NRR rates, absorption cross-sections, etc.6,11,12 Among all the lanthanide elements, the doping of erbium oxide (Er$_2$O$_3$) is more sensitive than other elements for the development of fluorescent materials. The erbium (Er$^{3+}$) ions in heavy metal oxide (HMO) glassy materials are more interesting to produce UC emissions upon 808 and 980 nm excitation. The $^4I_{15/2}$ and $^4I_{11/2}$ energy levels of the Er$^{3+}$ ion have energy around $\sim$12 376 cm$^{-1}$ (808 nm) and $\sim$10 204 cm$^{-1}$ (980 nm); therefore, the Er$^{3+}$ ions easily absorb 808 and 980 nm laser photons to produce green and red UC emission bands corresponding to $^4I_{15/2} \rightarrow ^4I_{13/2}$ and $^4I_{9/2} \rightarrow ^4I_{15/2}$ transitions.6,13,14 Infrared to visible UC emission spectra in the Er$^{3+}$-doped TeO$_2$–WO$_3$–Bi$_2$O$_3$ glasses with silver nanoparticles have been studied by de Campos et al.15 The Yb$^{3+}$ ions directly absorb the 980 nm laser photons, because it has the energy levels $^2F_{7/2}$ (ground level) and $^2F_{5/2}$ (excited level) with an energy gap $\approx$ 10 204 cm$^{-1}$. They have a very high absorption cross-section corresponding to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ absorption transition when compared to the $^4I_{15/2} \rightarrow ^4I_{11/2}$ absorption transition of the Er$^{3+}$ ion.12,14,16 Li et al. studied the frequency UC emission upon 808 and 980 nm laser excitations in the 32Nb$_2$O$_5$–10La$_2$O$_3$–16ZrO$_2$ glass activated with Er$^{3+}$/Yb$^{3+}$.13 Ragin et al. reported the Er$^{3+}$/Yb$^{3+}$-doped/codoped low hydroxide bismuth-germanate glass to enhance the mid-infrared 2.7 μm luminescence corresponding to $^4I_{11/2} \rightarrow ^4I_{15/2}$ under 980 nm pump radiation and concluded that the developed glass can be used in mid-infrared applications.16 Because of their special physical and chemical properties, the RE ion-doped HMO glasses have potential applications in three dimensional color displays, fluorescent biolabels, solid-state lasers, solar cells, NIR to visible upconverters, temperature sensors, intrinsic optical bistability for optical switching,

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etc.\textsuperscript{12–20} Oliveira et al.\textsuperscript{21} reported the frequency UC of CW infrared radiation at 1.06 \textmu m into the visible in the Er\textsuperscript{3+}/Yb\textsuperscript{3+}:Ga\textsubscript{2}S\textsubscript{3}:La\textsubscript{2}O\textsubscript{3} glasses followed by the energy transfer and non-radiative phonon-assisted processes. The thermally induced three-fold infrared to visible UC emission enhancement in the Er\textsuperscript{3+}/Yb\textsuperscript{3+}:Ga\textsubscript{2}S\textsubscript{3}:La\textsubscript{2}O\textsubscript{3} glasses upon excitation at 1.064 \textmu m is reported by dos Santos et al.\textsuperscript{22} An enhancement observed in the Er\textsuperscript{3+}/Yb\textsuperscript{3+}:PbO–GeO\textsubscript{2} glass containing silver nanoparticles under 980 nm excitation has been reported. This has been explained on the basis of the energy transfer process from the Yb\textsuperscript{3+} to Er\textsuperscript{3+} and the local field due to silver nanoparticles.\textsuperscript{23} An enhanced frequency UC emission in the Er\textsuperscript{3+}/Yb\textsuperscript{3+}-codoped HMO-based glasses upon 980 nm excitation has been reported.\textsuperscript{20} Even after so many studies, research in this area for different applications in different fields is still going on. For practical applications, the concentration of the dopants should not be very small. However, the problem of concentration quenching, “which occurs at a high concentration of the dopants,” limits their applications. Therefore, to reduce the problem of concentration quenching at a high dopant concentration and to improve the spectroscopic properties for practical applications, researchers are in the process of finding a suitable host.

In view of the above discussion, the present article reports the frequency UC of 980 nm/808 nm radiations into visible and its related processes in the Er\textsuperscript{3+}/Yb\textsuperscript{3+}-codoped TeO\textsubscript{2} nanoparticles.\textsuperscript{23} An enhanced frequency UC emission in the Er\textsuperscript{3+}/Yb\textsuperscript{3+}-codoped HMO-based glasses upon 980 nm excitation has been reported.\textsuperscript{20} Even after so many studies, research in this area for different applications in different fields is still going on. For practical applications, the concentration of the dopants should not be very small. However, the problem of concentration quenching, “which occurs at a high concentration of the dopants,” limits their applications. Therefore, to reduce the problem of concentration quenching at a high dopant concentration and to improve the spectroscopic properties for practical applications, researchers are in the process of finding a suitable host.

2. RESULTS AND DISCUSSION

2.1. Study of Absorption Spectra. UV–vis–NIR absorption spectra of the Er\textsuperscript{3+}/Er\textsuperscript{3+}/Yb\textsuperscript{3+}-doped/codoped glasses in the 400–2000 nm region are shown in Figure 1. Seven absorption bands centered at ~490, ~522, ~545, ~800, ~982, and ~1506 nm are observed. These observed absorption bands are due to the absorption transitions of the Er\textsuperscript{3+} ions from its ground state (4I\textsubscript{15/2}) to different excited states such as F\textsubscript{2} (7/2), H\textsubscript{11/2}, S\textsubscript{1/2}, F\textsubscript{5/2}, F\textsubscript{7/2}, I\textsubscript{11/2}, and I\textsubscript{13/2}, respectively.\textsuperscript{21,24} The positions of absorption bands are not altered significantly because of the shielding effect generated by the 5s\textsuperscript{2} and 5p\textsuperscript{6} completely filled atomic orbitals of the RE ion. However, because of the variation in crystal field strengths, the observed absorption bands are inhomogeneously broadened in all the synthesized glasses. In the codoped glasses, the absorption band around ~982 nm appears broader because of the superposition of the 4F\textsubscript{7/2} \rightarrow 2H\textsubscript{11/2} and 3F\textsubscript{7/2} \rightarrow 2F\textsubscript{5/2} absorption transitions of Er\textsuperscript{3+} and Yb\textsuperscript{3+} ions, respectively. The Yb\textsuperscript{3+} ions have a large absorption cross-section corresponding to the 2F\textsubscript{2} \rightarrow 2F\textsubscript{5/2} transition when compared to the absorption cross-section of the Er\textsuperscript{3+} ions corresponding to the 4I\textsubscript{15/2} \rightarrow 4I\textsubscript{11/2} transition in the developed HMT glasses.\textsuperscript{15,18} The absorption cross-section (~14.87 × 10\textsuperscript{18} cm\textsuperscript{2}) corresponding to the 2F\textsubscript{2} \rightarrow 2F\textsubscript{5/2} (Yb\textsuperscript{3+}) transition is about seven times larger than that of the Er\textsuperscript{3+} ion corresponding to the 4I\textsubscript{15/2} \rightarrow 4I\textsubscript{11/2} transition (~2.21 × 10\textsuperscript{18} cm\textsuperscript{2}) in the TW glass. The observed absorption band corresponding to the 4I\textsubscript{15/2} \rightarrow 2H\textsubscript{11/2} transition centered at ~522 nm is observed the highest among all other absorption bands because of its hypersensitive nature, and because it follows the selection rule as ΔJ\textsubscript{J} ≤ 2 and ΔJ\textsubscript{L} ≤ 2. In many cases, hypersensitive transitions follow the selection rule ΔJ\textsubscript{J} ≤ 2, ΔJ\textsubscript{L} ≤ 2, and Δ|S| ≤ 0.6.\textsuperscript{25}

2.2. Optical Band Gap and Urbach Energy Analysis. The absorption spectrum plays the key role in finding out the optically induced transitions and calculating the optical band gap in the glass materials. It also helps in finding out the absorption coefficient (α) by using the Beer–Lambert law (or Beer’s law).\textsuperscript{20} The direct optical band gap has been investigated (Figure 2) for all the Er–TW, Er–Yb–TW, Er–Yb–TWP, and Er–Yb–TWPTi glasses by using their respective absorption spectra (Figure 1). In the amorphous materials, the absorption edge is not well defined and found to be less sharp when compared to that of crystalline materials.\textsuperscript{27} The absorption coefficient (α), optical band gap (E\textsubscript{g}), and incident photon energy (hv) are correlated by a relation and are given by Tauc and Mott,\textsuperscript{28,29}

\begin{equation}
αhv = A(hv - E_g)^{r}
\end{equation}

where, “A” represents the proportionality constant and “r” is used for a particular real number, such as, r = 1/2 and 3/2 for direct allowed and direct forbidden transitions, whereas r = 2 and 3 are used for indirect allowed and indirect forbidden transitions, respectively.\textsuperscript{12} Therefore, to calculate the direct optical band gap in all the RE ion-doped/codoped glasses, r = 1/2 has been considered in eq 1. The curves between (αhv)\textsuperscript{2} versus incident radiation energy “hv (eV)” for all the doped/codoped glasses are shown in Figure 2. The optical band gap values have been examined by extrapolating the linear portion of the plotted curves up to (αhv)\textsuperscript{2} = 0. For all the prepared Er–TW, Er–Yb–TW, Er–Yb–TWP, and Er–Yb–TWPTi glasses, the optical band gap values are found to be 2.94, 2.92, 2.76, and 2.14 eV, respectively. In both the Er\textsuperscript{3+}-doped and Er\textsuperscript{3+}/Yb\textsuperscript{3+}-codoped TW glasses, the band gap value is found to be approximately the same, but it decreases up to 2.14 eV on introducing the Pb\textsubscript{3}O\textsubscript{4} and TiO\textsubscript{2} into the Er\textsuperscript{3+}/Yb\textsuperscript{3+}-codoped TW glass. This reduction in the optical band gap is basically due to the modification in the local field around the RE ions, and hence, the structure of the Er\textsuperscript{3+}-doped TW glass remains the same on codoping the Yb\textsuperscript{3+} ions but changes on introducing the Pb\textsubscript{3}O\textsubscript{4} and TiO\textsubscript{2}.

In the amorphous solid materials, there is a forbidden energy gap which is called the Urbach energy of the material. The disorderness in the structure of the amorphous material is measured on the basis of Urbach energy. According to Urbach,
in an amorphous material, the relation between the absorption coefficient and incident photon energy can be expressed as\textsuperscript{30}

\[
\alpha = B \exp\left(\frac{\hbar \nu}{E_U}\right)
\]

(2)

where, "\(B\)" is another proportional constant. The exponential behaviour given in eq 2 has been demonstrated and the curves are plotted between logarithmic values of the absorption coefficient versus incident photon energy for all the prepared RE ion-doped/codoped Er\textsuperscript{3+}–TW, Er\textsuperscript{3+}–Yb\textsuperscript{3+}–TWP, and Er\textsuperscript{3+}–Yb\textsuperscript{3+}–TWPTi glasses, respectively (Figure 3). The reciprocal of the slope of the linear portion of the curve between ln(\(\alpha\)) versus \(\hbar \nu\) (shown in Figure 3) provides the value of Urbach energy.\textsuperscript{31} The values of Urbach energy are found to be 0.31, 0.22, 0.48, and 1.23 eV for all the Er\textsuperscript{3+}–TW, Er\textsuperscript{3+}–Yb\textsuperscript{3+}–TW, Er\textsuperscript{3+}–Yb\textsuperscript{3+}–TWP, and Er\textsuperscript{3+}–Yb\textsuperscript{3+}–TWPTi glasses, respectively. Therefore, on the basis of Urbach energy, it could be concluded that the disorder in the structure of the codoped TW glass increases on introducing the Pb\textsubscript{3}O\textsubscript{4} and TiO\textsubscript{2} HMOs, respectively. The numerical values of the direct optical band gap and Urbach energy of all the prepared glasses are listed in Table 1.

2.3. Study of Different Optical and Physical Parameters. 2.3.1. Refractive Index. The refractive indices of all the Er\textsuperscript{3+}–TW, Er\textsuperscript{3+}–Yb\textsuperscript{3+}–TW, Er\textsuperscript{3+}–Yb\textsuperscript{3+}–TWP, and Er\textsuperscript{3+}–Yb\textsuperscript{3+}–TWPTi glasses have been determined by using Brewster’s angle polarization method. For this measurement, a He–Ne laser of wavelength 6328 Å and output power of 5 mW was used as an optical source. In this experiment, the samples are placed on
The calculated values of local field correction factors and the reflection loss in different glasses are reported in Table 1.

2.3.2. Density Measurement. The density ($\rho$) is an important factor to determine various parameters such as molar volume ($V_m$), RE ion concentration ($N_{REE}$), molar refraction ($R_m$), etc. The density of all the prepared glass samples has been determined by using an experimental setup based on the Archimedes principle in which xylene was used as the immersion liquid\textsuperscript{6,14,18,33}

$$\rho (g/cm^3) = \frac{W \times \text{density of xylene}}{W_x - W_b} \quad (5)$$

where, “$W_x$” and “$W_b$” represent the weight of the glass sample in air and xylene, respectively. The density of xylene is 0.86 g (cm$^{-3}$). The density of the Er$^{3+}$/Yb$^{3+}$-doped/codoped TW glass was found to be ~5.23 g/cm$^3$. The density of glass samples increases up to 5.48 and 5.86 g/cm$^3$ on incorporating the Pb$_2$O$_4$ and TiO$_2$ materials, respectively. It means that the degree of structural compactness of the geometrical configuration of the glass matrix enhances on introducing the Pb$_2$O$_4$ and TiO$_2$ HMO materials.\textsuperscript{18} The RE ion concentration ($N_{REE}$) and inter-ionic separation between RE ions ($R_{EE}$) in all the prepared glasses have been calculated by using the following relations\textsuperscript{12,18,33}

$$N_{REE} (ions/cm^3) = \frac{N_A \times \text{glass density \times mol \% of rare earth ions}}{\text{average molecular weight}}$$

and

$$R_{EE} = \left[ \frac{1}{N_{REE}} \right]^{1/3} \quad (6)$$

where, “$N_A$” is the Avogadro number ($6.022 \times 10^{23}$). In the present case, the RE ion concentration and the inter-ionic separation almost remain the same. The molar volume ($V_m$) and corresponding molar refraction ($R_m$) of each glass sample have been calculated with the help of their respective densities by using the following equations\textsuperscript{34,35}

$$V_m (cm^3/mol) = M / \rho$$

and

$$R_m = \frac{\mu - 1}{\mu + 1} V_m \quad (7)$$

where, “$M$” represents the molecular weight of the corresponding glass sample and other parameters have their usual meaning as explained above. According to eq 7, the molar volume depends on the molecular weight and density of the glass; however, the molar refraction is directly proportional to its molar volume. Because of this, some discrepancy is observed in the molar volume and molar refraction for all the prepared glasses. The molar electronic polarizability ($\alpha_m$) and metallization criterion parameter ($M_c$) of the glass samples can be determined\textsuperscript{6,11} as

$$\alpha_m = \frac{3}{4\pi N_A} \times R_m \quad \text{and} \quad M_c = \left( 1 - \frac{R_m}{V_m} \right) \quad (8)$$

According to the theory of metallization of the condensed matter, the value of $M_c$ becomes zero when $R_m/V_m$ becomes unity (i.e. $R_m/V_m = 1$).\textsuperscript{11,35} Under this condition, the electron in the material behaves like a mobile charge particle and the
system of material shows metallic properties. Therefore, for the solid material with non-metallic nature, the ratio of molar refraction to the molar volume should be less than unity (i.e. $R_m/V_m < 1$). In both the Er$^{3+}$/Yb$^{3+}$-doped/codoped TW glasses, the “$M$” remains the same (0.73), but it slightly decreases up to 0.71 on introducing the PbO$_4$ and TiO$_2$ materials into the Er$^{3+}$/Yb$^{3+}$-codoped TW glass. This means that the tendency of metallization of Er–Yb–TW glass increases on incorporating the PbO$_4$ and TiO$_2$ HMOs. The numerical values of densities, RE ion concentrations, interionic separation of RE ions, molar volumes, molar refraction, molar electronic polarizability, and metallization criterion parameter for all the Er–TW, Er–Yb–TW, Er–Yb–TWP, and Er–Yb–TWPTi glasses are listed in Table 1.

### 2.4. UC Study

#### 2.4.1. UC by Using 980 nm Laser Excitation

Figure 4 displays the recorded frequency UC emission spectra of the optimized 1.0 mol % Er$^{3+}$/1.0 mol % Er$^{3+} + 3.0$ mol % Yb$^{3+}$-ion-doped/codoped (a) Er–TW, (b) Er–Yb–TW, (c) Er–Yb–TWP, and (d) Er–Yb–TWPTi glasses upon 980 nm laser excitation. Insets of this figure show photographs of the emitted light from the glasses and the UC emission spectrum of singly Er$^{3+}$-ion-doped TW glass.

![UC emission spectra](image)

**Table 2. fwhm and Intensity Enhancement in Green and Red Bands Corresponding to the $^2$H$_{11/2}$ $→$ $^4$I$_{15/2}$ and $^4$S$_{3/2}$ $→$ $^4$I$_{15/2}$ Transitions of All the Prepared Samples upon 980 nm Excitation**

| glass samples     | enhancement (times) | green (nm)   | red (nm)   |
|-------------------|---------------------|--------------|------------|
| Er–TW             | (green, red)        | 16.60 ± 0.06 | 16.70 ± 0.06 |
| Er–Yb–TW          | (~9, ~19)           | 16.65 ± 0.07 | 16.75 ± 0.07 |
| Er–Yb–TWP         | (~13, ~39)          | 17.30 ± 0.05 | 17.75 ± 0.05 |
| Er–Yb–TWPTi       | (~33, ~87)          | 20.35 ± 0.04 | 21.45 ± 0.09 |

bands of Er–Yb–TWP and Er–Yb–TWPTi glasses could be because of the increase in the local field correction factor and, hence, the local field modifications around the RE ions (Table 1). This leads to the increase in the radiative transition probabilities and branching ratios corresponding to the $^2$H$_{11/2}/^4$S$_{3/2}$ $→$ $^4$I$_{15/2}$ and $^2$F$_{9/2}$ $→$ $^4$I$_{15/2}$ transition and one broad red UC emission band centered at ~669 nm corresponding to the $^2$F$_{9/2}$ $→$ $^4$I$_{13/2}$ transition.

The discrepancy in the UC emission intensity of the observed bands is due to their different radiative transition probabilities, local field correction factors, and oscillator strengths in all the Er–TW, Er–Yb–TW, Er–Yb–TWP, and Er–Yb–TWPTi glasses. On introducing the Yb$^{3+}$ ions into the Er$^{3+}$-doped TW glass, the green and red UC emission bands corresponding to the $^2$H$_{11/2}/^4$S$_{3/2}$ $→$ $^4$I$_{15/2}$ and $^2$F$_{9/2}$ $→$ $^4$I$_{15/2}$ transitions are enhanced ~9 and ~19 times under 980 nm laser diode excitation. This enhancement in the UC emission bands of the Er$^{3+}$/Yb$^{3+}$-doped TW glass is basically due to the efficient energy transfer (ET1 and ET2) from the Yb$^{3+}$ ions to the Er$^{3+}$ ions, because, in the present case, the absorption cross-section corresponding to the $^2$F$_{9/2}$ $→$ $^2$F$_{5/2}$ absorption transition is ~7 times larger when compared to the $^4$I$_{15/2}$ $→$ $^4$I$_{11/2}$ absorption transition of Er$^{3+}$ ions. The large variation in the red UC emission intensity corresponding to the $^2$F$_{9/2}$ $→$ $^4$I$_{15/2}$ transition is because of energy transfer and cross relaxation (CR) processes ($^2$I$_{13/2}$ + $^2$F$_{5/2}$ $→$ $^2$F$_{7/2}$ + $^2$F$_{5/2}$). The intensity ratio of the green to red UC emission band (i.e. $I_{green}/I_{red}$) is found to be ~10.36 and ~4.75 in the Er$^{3+}$/TW and Er$^{3+}$/Yb$^{3+}$/TW glasses, respectively. Because of the combination of these green and red UC emission bands, the color emitted from the samples appears yellowish green to the naked eyes. The photographs of the actual color emitted from the Er$^{3+}$/Yb$^{3+}$-doped/codoped TW glasses are displayed in the inset of Figure 4a,b.

After the incorporation of PbO$_4$ and TiO$_2$ HMOs into the Er$^{3+}$/Yb$^{3+}$-doped TW glass, the UC emission bands corresponding to the $^2$H$_{11/2}/^4$S$_{3/2}$ $→$ $^4$I$_{15/2}$ (green) and $^2$F$_{9/2}$ $→$ $^4$I$_{15/2}$ (red) transitions are found at the same positions but the intensity of the UC emission bands is enhanced many folds when compared to the Er$^{3+}$/Yb$^{3+}$ codoped TW glass. An intensity enhancement of about ~13/33 and ~39/87 times corresponding to the green and red bands in the Er$^{3+}$/Yb$^{3+}$/TW/Er$^{3+}$/Yb$^{3+}$/TWPTi glasses when compared to the Er$^{3+}$/TW glass has been observed. The enhancement observed corresponding to different UC emission bands along with full width at half maximum (fwhm) values in the prepared glasses is given in Table 2. This enhancement in the UC emission...
around the RE ions due to the incorporation of the Pb3O4 and TiO2 HMOs.6,14,18 The UC emission intensity of all the observed bands increases on increasing the pump power density of the incident photons.18,36 The UC emission spectra of Er−TW and Er−Yb−TWPTi glasses have been recorded at 13.19, 23.66, 34.90, 45.11, 55.89, 66.94, and 81.24 W/cm² pump power density of incident photons under 980 nm laser diode excitation {Figure 5a,b}. The associated bar curves between the integrated UC emission intensity versus pump power density of the Er−TW/Er−Yb−TWPTi glasses have been recorded at 6.8, 101, 306, 421, 523, 711, and 945 mW pump power upon 808 nm laser diode excitation {Figure 6a,b}. The UC emission intensity at different pump power densities of (a) 1.0 mol % Er³⁺-doped TW and (b) 1.0 mol % Er³⁺ + 3.0 mol % Yb³⁺-codoped TWPTi glasses upon 980 nm laser diode excitation. The inset bar curves of (a,b) show the integrated UC emission intensity vs pump power density for green and red bands in both the glasses.

2.4.2. UC by Using 808 nm Laser Excitation. Figure 6 shows the frequency UC emission spectra recorded at room temperature in the visible range between 400 and 700 nm for all the Er−TW, Er−Yb−TW, Er−Yb−TWP, and Er−Yb−TWPTi glasses upon 808 nm laser excitation at 600 mW pump power. Insets in the figure show the photographs of the emitted color from the glass samples, respectively.

The singly Er³⁺-doped TW glass intensity of the observed UC emission band corresponding to the $^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$ transition is found to be ~4 times large when compared to that of the Er³⁺/Yb³⁺-codoped TW glass under 808 nm laser diode excitation [Figure 6a,b]. The decrement in the intensity of the green UC emission band of the Er³⁺/Yb³⁺-codoped TW glass is due to the back energy transfer (BET) process from the Er³⁺ to the Yb³⁺ ions. Because of this BET, the intensity of the observed NIR band centered around ~940 nm increases on increasing the pump power density of the incident photons.14 The color emitted from both doped and codoped TW glasses upon 808 nm excitation is found effectively green because of the large green to red UC emission band intensity ratio ($I_{\text{green}}/I_{\text{red}}$) when compared to that observed under 980 nm excitation. The photographs of the actual color emitted from the Er−TW and Er−Yb−TW samples are displayed in the insets of Figure 6a,b, respectively.

On introducing the Pb3O4 and TiO2 materials, respectively, into the Er³⁺/Yb³⁺-codoped TW glass, the UC emission intensity as well as the fwhm of the bands increase gradually because of the inhomogeneous local field generation (Table 1) around the RE ions {Figure 6c,d}. The $I_{\text{green}}/I_{\text{red}}$ ratio for both the Er−Yb−TWP and Er−Yb−TWPTi glasses at ~600 mW pump power is ~9.28 and ~15.16, respectively. Because of the large green to red band intensity ratio, the color emitted from the samples is observed to be intense green by the naked eyes. The photographs of the actual color emitted from both the Er−Yb−TWP and Er−Yb−TWPTi samples are displayed in the insets of Figure 6c,d, respectively.

A pump power-dependent study has been performed for Er−Yb−TWPTi and the Er−TW glasses. The UC emission spectra of the Er³⁺-doped TW and Er³⁺/Yb³⁺-codoped TWPTi glasses have been recorded at 6.8, 101, 306, 421, 523, 711, and 945 mW pump power upon 808 nm excitation {Figure 7a,b}. It is noted that the UC emission intensity of the green and red bands corresponding to the $^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^2F_{9/2} \rightarrow ^4I_{15/2}$ transitions increases with the pump power in both the glasses. The bar curves for the pump power versus integrated UC emission intensity of both the green and red bands of the Er−TW and Er−Yb−TWPTi glasses are also shown in the insets of Figure 7a,b. No significant change in the intensity ($I_{\text{green}}/I_{\text{red}}$) ratio on increasing the pump power in Er−TW and Er−Yb−TWPTi glasses is reported, whereas the green to red band intensity ratio (i.e. $I_{\text{green}}/I_{\text{red}}$) in both the glasses increases on increasing the pump power (Table 3). It is found to be ~58.60 and...
Increasing the Pump Power upon 808 nm Laser Excitation of Er$^{3+}$/Yb$^{3+}$-Doped/Codoped TW and TWPTi Glass Samples

I green and red bands gives the slope value ($P_{\text{log}}$) of pump powers {ln($I_{\text{UP}}$)} corresponding integrated UC emission intensity {ln($I_{\text{UP}}$)} of pump photons involved in the UC process. The plot between the logarithmic values of pump powers {ln($I_{\text{UP}}$)} versus thr UC emission intensity vs pump power for green and red bands.

Table 3. Variation of the Intensity Ratios of $^2H_{11/2} \rightarrow ^4I_{15/2}$ to $^4S_{3/2} \rightarrow ^4I_{15/2}$ (i.e. $I_{\text{UP}}/I_k$) Transitions and Green to Red Bands on Increasing the Pump Power upon 808 nm Laser Excitation of Er$^{3+}$/Yb$^{3+}$-Doped/Codoped TW and TWPTi Glass Samples

| Pump Power (mW) upon $\lambda_{\text{ex}} = 808$ nm | Er–TW | Er–Yb–TWPTi |
|-----------------------------------------------|-------|-------------|
| $I_{\text{UP}}/I_k$ ratio | $I_{\text{green}}/I_{\text{red}}$ ratio | Enhancement (times) | $I_{\text{UP}}/I_k$ ratio | Green/Red ratio | Enhancement (times) |
| 6.8 | 0.14 | ~11.61 | (green, red) | 0.14 | ~18.67 | (green, red) |
| 101 | 0.13 | 12.90 | (~2, ~1) | 0.15 | ~27.33 | (~3, ~2) |
| 306 | 0.12 | 13.03 | (~3, ~2) | 0.15 | ~53.25 | (~8, ~3) |
| 421 | 0.12 | 13.06 | (~3, ~3) | 0.16 | ~54.26 | (~10, ~3) |
| 523 | 0.12 | 13.06 | (~4, ~4) | 0.17 | ~54.32 | (~12, ~4) |
| 711 | 0.12 | 14.14 | (~6, ~5) | 0.18 | ~54.41 | (~17, ~6) |
| 945 | 0.13 | 18.27 | (~15, ~9) | 0.18 | ~58.60 | (~24, ~8) |

~18.27 in the Er–Yb–TWPTi and Er–TW glasses, respectively, at 945 mW pump power.

The pump power-dependent UC emission spectra (Figures 5 and 7) of the Er$^{3+}$-doped TW and Er$^{3+}$/Yb$^{3+}$-codoped TWPTi glasses upon 980 nm 808 nm laser diode excitations are helpful to obtain the information on the number of pump photons involved in the UC process. The plot between logarithmic values of pump powers {ln($I_{\text{UP}}/I_k$)} versus corresponding integrated UC emission intensity {ln($I_{\text{UP}}/I_k$)} of green and red bands gives the slope value ($n$) by using the relation $I_{\text{UP}}/I_k = k(P_{\text{PUMP}})^n$, where, “$k$” is the constant and “$n$” represents the number of photons participating in the UC process. The slope values for the green UC band corresponding to the $^2H_{11/2} \rightarrow ^4S_{3/2}$ transition are ~1.71 ± 0.05 and ~1.75 ± 0.06, whereas for the red band corresponding to the $^4I_{15/2} \rightarrow ^4S_{3/2}$ transition they are ~1.51 ± 0.12 and ~1.65 ± 0.10. Therefore, from these slope values, it is concluded that two photons are involved in radiation of the green and red emissions from Er–TW and Er–Yb–TWPTi glasses.

2.4.3. UC Emission Mechanism Explained Through the Energy Level Diagram. The processes involved in the UC emission transitions under the 980 and 808 nm laser diode excitations could be easily explained using the energy level diagram (Figure 9). The energy of the 980 nm (i.e. ~10 204 cm$^{-1}$) photon is just equivalent to the integer multiple of energy of the $^4I_{15/2} \rightarrow ^4I_{11/2}$ and $^4I_{11/2} \rightarrow ^4F_{7/2}$ absorption transitions of the Er$^{3+}$ ion. Therefore, in the singly Er$^{3+}$-doped glass the $^4F_{7/2}$ level is populated through the ground state absorption (GSA) and excited state absorption (ESA) processes, and after that it relaxes non-radiatively to the $^2H_{11/2}$ and $^4S_{3/2}$ levels. The radiative transitions from these levels to the ground state emit green and red lights corresponding to the $^2H_{11/2} \rightarrow ^4S_{3/2}$ ($\sim$532 nm/550 nm) transitions. The $^4F_{9/2}$ level is populated because of the ESA process from the $^1I_{3/2}$ level. A radiative transition from the $^4F_{9/2}$ level to the $^4I_{15/2}$ level emits red photons corresponding to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition. In the Er$^{3+}$/Yb$^{3+}$-codoped TW glass, apart from the Er$^{3+}$ ions, the Yb$^{3+}$ ions also have the ground state ($^2F_{7/2}$) and one excited state ($^2F_{5/2}$).
The excited state $^2F_{5/2}$ has the energy just equivalent to that of the 980 nm (≈10 204 cm$^{-1}$) laser photon. Therefore, the 980 nm laser photons are easily absorbed by the Yb$^{3+}$ ions corresponding to the $^2F_{7/2} \rightarrow ^2F_{5/2}$ absorption transition in the Er$^{3+}$/Yb$^{3+}$-codoped glasses. Because the absorption cross-section corresponding to the $^2F_{7/2} \rightarrow ^2F_{5/2}$ absorption transition (≈14.87 × 10$^{-18}$ cm$^2$) of Yb$^{3+}$ ions is about 7 times larger than the absorption cross-section (≈2.21 × 10$^{-18}$ cm$^2$) corresponding to the $^4I_{15/2} \rightarrow ^4I_{11/2}$ transition of Er$^{3+}$ ions, the intensity of all the observed UC emission bands in the Er$^{3+}$/Yb$^{3+}$-codoped TW glass enhances because of the efficient energy transfer (ET) from the Yb$^{3+}$ ions to the Er$^{3+}$ ions in the form of ET1 and ET2 processes simultaneously. In the Er$^{3+}$/Yb$^{3+}$-codoped TW glass, comparatively more enhancement is observed in the red UC emission band corresponding to the $^2F_{9/2} \rightarrow ^4I_{11/2}$ transition. This is because of the enhanced population of Er$^{3+}$ ions in the $^2F_{9/2}$ level through the energy transfer from the Yb$^{3+}$ to Er$^{3+}$ ions as well as CR $^2F_{4/2}$ (Yb$^{3+}$) + $^4I_{13/2}$ (Er$^{3+}$) → $^2F_{7/2}$ (Yb$^{3+}$) + $^4F_{9/2}$ (Er$^{3+}$) processes. On introducing the PbO$_4$ and TiO$_2$ HMOs into the Er$^{3+}$/Yb$^{3+}$-codoped TW glass, the UC emission intensity of the green and red bands is further enhanced by several folds (as discussed earlier) because of the energy transfer from Yb$^{3+}$ ions to the Er$^{3+}$ ions and the inhomogeneous local field generation around the RE ions.

However, for the UC emission under 808 nm excitation, it is found that the energy gap between the levels corresponding to the $^4I_{15/2} \rightarrow ^4I_{9/2}$, $^4I_{13/2} \rightarrow ^2H_{11/2}$, and $^4I_{11/2} \rightarrow ^4F_{5/2}$ absorption transitions of Er$^{3+}$ ions in singly doped glasses synchronizes with the energy of the 808 nm photon (i.e. ≈12 376 cm$^{-1}$) (Figure 9). Upon 808 nm (i.e. ≈12 376 cm$^{-1}$) excitation, the higher lying excited levels ($^4F_{7/2}$, $^4F_{5/2}$, $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{3/2}$) of Er$^{3+}$ ions in the Er–TW glass are populated through GSA, ESA, and NRR processes (Figure 9). The population of Er$^{3+}$ ions in the $^2H_{11/2}$ and $^4S_{3/2}$ levels partially transits downward radiatively to the ground state by emitting the green UC emission band centered at ≈532 and 550 nm corresponding to the $^2H_{11/2}$/$^4S_{3/2} \rightarrow ^4I_{15/2}$ transition. The remaining population in the $^2H_{11/2}$ and $^4S_{3/2}$ levels decay non-radiatively to the $^4F_{2/2}$ level, which again relaxes radiatively to the ground state by emitting a weak red emission band peaking at ≈696 nm corresponding to the $^4F_{2/2} \rightarrow ^4I_{15/2}$ transition. In the Er$^{3+}$/Yb$^{3+}$-codoped TW glass, the UC emission intensity of the observed bands decreases because of the BET from the Er$^{3+}$ ions to Yb$^{3+}$ ions. On introducing the PbO$_4$ and TiO$_2$ HMOs into the Er$^{3+}$/Yb$^{3+}$-codoped TW glass, the UC emission intensity under 808 nm excitation is enhanced further due to the modification in the local field around the RE ions.

### 2.5. Nature of Bonding between RE Ions and Surrounding Oxygen Atoms.

The nature of bonding between the RE ions and their surrounding oxygen atoms in all the prepared Er–TW, Er–Yb–TW, Er–Yb–TWP, and Er–Yb–TWPTi glasses has been studied from the recorded absorption spectra (Figure 1). These slight variations in the peak positions of absorption bands in all the prepared glasses occur because of the modification in the environment around the RE ions on complexion, which is called the “nephelauxetic effect.”

Also, variation in the positions of absorption bands arises because of the expansion of the partially filled 4f-shell, because in the different glass compositions the charge is transferred from the ligand to the core of central RE ions. The energy of the absorption bands corresponding to the $^4I_{13/2}$ → $^4I_{11/2}$, $^4I_{15/2}$ → $^4I_{11/2}$, $^4I_{15/2} → ^4I_{9/2}$, $^4I_{15/2} → ^4I_{7/2}$, $^4I_{15/2} → ^2H_{11/2}$, and $^1I_{15/2} → ^2F_{7/2}$ absorption transitions for all the prepared Er–TW, Er–Yb–TW, Er–Yb–TWP, and Er–Yb–TWPTi glasses are listed in Table 4. The average value of the nephelauxetic ratio “β” is calculated by using the following expression

$$\beta = \frac{1}{N} \sum_{\nu_{\text{free ions}}} \frac{K_{\text{comp}}}{N}$$  \hspace{1cm} (9)

where, “N” represents the number of observed absorption bands in the respective glass matrix. The energies (in cm$^{-1}$) corresponding to these bands in each glass are represented by “$\nu_{\text{comp}}$” and “$\nu_{\text{free ions}}$” is the energy of free ions.

### Table 4. Band Positions (in cm$^{-1}$), Average Nephelauxetic Ratio ($\beta$), Covalency ($\delta$), Bonding Parameters ($k^{1/2}$), and the Nature of Bonding between RE Ions and the Oxygen Atoms in Er$^{3+}$/Yb$^{3+}$-Doped/Codoped Different Glass Matrices

| Transitions | Er–TW (present) | Er–Yb–TW (present) | Er–Yb–TWP (present) | Er–Yb–TWPTi (present) | SPME$^{[1]}$ | SPMEA0.1$^{[1]}$ |
|-------------|----------------|----------------|----------------|----------------|----------|----------|
| $^4I_{13/2}$ → | 6639.9 | 6607.7 | 6618.4 | 6613.2 | 6515.0 | 6514.5 |
| $^4I_{11/2}$ → | 10 178.5 | 10 155.5 | 10 211.4 | 10 162.5 | 10 252.0 | 10 245.9 |
| $^4I_{9/2}$ → | 12 503.6 | 12 565.4 | 12 456.3 | 12 524.6 | 12 512.0 | 12 554.0 |
| $^4I_{7/2}$ → | 15 250.2 | 15 302.5 | 15 302.6 | 15 283.2 | 15 350.0 | 15 337.3 |
| $^4I_{5/2}$ → | 14 202.9 | 14 200.9 | 14 360.2 | 14 435.2 | 14 216.0 | 14 284.8 |
| $^4I_{3/2}$ → | 19 146.5 | 19 098.9 | 19 149.2 | 19 047.6 | 19 239.0 | 19 174.4 |
| $^4I_{1/2}$ → | 20 416.5 | 20 473.5 | 20 450.9 | 20 430.5 | 20 555.0 | 20 576.1 |
| $\beta$ | 1.0077 | 1.0081 | 1.0078 | 1.0073 | 1.0007 | 1.0006 |
| $\delta$ | -0.0076 | -0.0080 | -0.0077 | -0.0072 | -0.0714 | -0.0692 |
| $k^{1/2}$ | 0.0620i | 0.0636i | 0.0624i | 0.0604i | |
| Nature | ionic | ionic | ionic | ionic | ionic | ionic |
The covalency ($\delta$) and bonding parameters ($b^{1/2}$) have been evaluated by using the following expressions:

$$\delta = \left[ 1 - \frac{\bar{\beta}}{\beta} \right] \quad \text{and} \quad b^{1/2} = \left[ 1 - \frac{\bar{\beta}}{2} \right]^{1/2}$$

The calculated values of $\bar{\beta}$, $\delta$, and $b^{1/2}$ for all the Er−TW, Er−Yb−TW, Er−Yb−TWP, and Er−Yb−TWPTi glasses are listed in Table 4 and compared with those of the other reported Er$^{3+}$/Yb$^{3+}$-doped/codoped SPME and SPMEA0.1 glasses. The positive or negative value of $\delta$ justifies the covalent or ionic nature of bonding between the RE ions and their surrounding oxygen atoms. In the present work, the negative value of the covalency parameter confirms the ionic character of bonding between the RE ions and their surrounding oxygen atoms.

### Table 5. CIE Color Coordinates, Correlated Color Temperature (K), and Color Purity (CP %) of Different Glasses at Different Pump Powers upon 980 and 808 nm Diode Laser Excitations

| glass sample codes | 980 nm excitation | 808 nm excitation |
|-------------------|-------------------|-------------------|
|                   | $P$ (mW) | $X_s$ | $Y_s$ | CCT (K) | CP | $P$ (mW) | $X_s$ | $Y_s$ | CCT (K) | CP |
| Er−TW             | 944     | 0.30 | 0.67 | 5984   | 89.6 | 600     | 0.29 | 0.69 | 6111   | 97.4 |
| Er−Yb−TW          | 944     | 0.30 | 0.68 | 5974   | 92.1 | 600     | 0.31 | 0.68 | 5826   | 94.7 |
| Er−Yb−TWP         | 944     | 0.31 | 0.68 | 5826   | 92.1 | 600     | 0.31 | 0.68 | 5826   | 94.7 |
| Er−Yb−TWPTi       | 203     | 0.32 | 0.64 | 5697   | 82.0 | 6.8     | 0.31 | 0.68 | 5964   | 97.3 |
| Er−Yb−TWPTi       | 364     | 0.32 | 0.66 | 5690   | 87.1 | 101     | 0.30 | 0.68 | 5974   | 94.7 |
| Er−Yb−TWP         | 537     | 0.31 | 0.67 | 5833   | 89.6 | 306     | 0.30 | 0.70 | 5955   | 99.8 |
| Er−Yb−TWPTi       | 694     | 0.31 | 0.68 | 5826   | 92.1 | 523     | 0.30 | 0.70 | 5955   | 99.8 |
| Er−Yb−TWPTi       | 860     | 0.30 | 0.68 | 5974   | 92.1 | 711     | 0.29 | 0.70 | 6111   | 100.0|
| Er−Yb−TWP         | 1030    | 0.30 | 0.68 | 5974   | 92.1 | 945     | 0.29 | 0.70 | 6099   | 100.0|
| Er−Yb−TWPTi       | 1170    | 0.30 | 0.68 | 5974   | 92.1 | 1110    | 0.29 | 0.70 | 6099   | 100.0|

2.6. Study of the CIE Diagram through UC Emission Data. The position of color coordinates in the CIE diagram of the color emitted in the UC emission spectra from Er−TW, Er−Yb−TW, Er−Yb−TWP, and Er−Yb−TWPTi glasses upon 980 and 808 nm excitations at fixed pump power (944 and 600 mW upon 980 and 808 nm excitations, respectively) is shown in Figure 10a,b. As the Er$^{3+}$/Yb$^{3+}$-codoped TWPTi glass produces intense UC emissions, the position of color coordinates of the color emitted from the Er$^{3+}$/Yb$^{3+}$-codoped TWPTi glass at different pump powers upon 980 and 808 nm excitations has been determined (Figure 10c,d). All the observed color coordinates under both the excitations are listed in Table 5. No significant variation in the position of color coordinates lying in the green region at different pump powers has been marked. Therefore, the Er$^{3+}$/Yb$^{3+}$-codoped TWPTi glass material can be used in colorless tunable pure...
green optical display devices under 980 and 808 nm laser excitations.\textsuperscript{14,37}

The color-correlated temperature (CCT) has been calculated for all the samples at fixed and different pump powers upon 980 and 808 nm laser excitations by using the following mathematical McCamy empirical formula

\[ \text{CCT} = -437p^3 + 3601p^2 - 6861p + 5514.31 \]

where, the sample color coordinate \((X_i, Y_i)\) is listed in Table \ref{tab:5} and the coordinates of the epicenter \((X_e, Y_e)\) are \((0.3320, 0.1858)\),\textsuperscript{6,18} which helps in determining the parameter “p” \(p = \left\{ (X_e - X_i)/(Y_e - Y_i) \right\}\). The CCT values of all the codoped samples vary from 5690 to 5974 K under 980 nm laser excitation, whereas they vary from 5826 to 6111 K under 808 nm laser diode excitation. The light sources available commercially have CCT values in the range from 2700 to 6500 K.\textsuperscript{6,42} In the lighting industry, the lamps have a CCT value in the range from 2700 to 4000 K which provides warm light; however, the lamps having a higher CCT value, in the range from 4000 to 6500 K provide cool light.\textsuperscript{18,43} On the basis of above investigations, it has been concluded that the Er\textsuperscript{3+}/Yb\textsuperscript{3+}-codoped TWPTi glass having CCT values 5974 and 6099 K, respectively, under 980 and 808 nm laser excitations can be applicable in fabricating home appliances.\textsuperscript{18}

To determine the color purity (CP) of the emitted color from the samples under the 980 and 808 nm laser diode excitations, the following relation has been used\textsuperscript{6,18}

\[ \text{CP} = \sqrt{\frac{(X_e - X_i)^2 + (Y_e - Y_i)^2}{(X_d - X_i)^2 + (Y_d - Y_i)^2}} \times 100\% \]

where, \((X_e, Y_e)\) represent the coordinates of the illuminant point \((0.3101, 0.3162)\),\textsuperscript{6,18} \((X_i, Y_i)\) and \((X_d, Y_d)\) are the sample color coordinates (listed in Table \ref{tab:5}) and the coordinates corresponding to the dominant wavelength (i.e. 550 nm), respectively. In the present work, the coordinates corresponding to the dominant wavelength are found to be \((0.28, 0.71)\) and \((0.29, 0.70)\) upon 980 and 808 nm laser diode excitations, respectively. The values of CP from the corresponding glass samples and corresponding pump powers are given in Table \ref{tab:5}. From Table \ref{tab:5}, it is concluded that the CP of the emitted color from the Er–Yb–TWPTi glass increases on increasing the pump powers upon both the laser excitations. The Er–Yb–TWPTi glass shows the maximum CP, that is, 92.1 and 100% upon 980 and 808 nm laser diode excitations, respectively. Therefore, the Er\textsuperscript{3+}/Yb\textsuperscript{3+}-codoped TWPTi glass indicate the promising applications to develop the yellowish green as well as pure green optical devices and solid state lighting.

4. EXPERIMENTAL TECHNIQUES AND CHARACTERIZATION

All the Er\textsuperscript{3+}/Yb\textsuperscript{3+} ion-doped/codoped glasses synthesized by the melting and quenching technique\textsuperscript{18} are listed in Table \ref{tab:6}. High purity raw materials have been used to prepare the glasses.

To prepare the Er\textsuperscript{3+}/Yb\textsuperscript{3+}-doped/codoped TW, TWP, and TWPTi glass samples, proper amounts (in grams according to the concentration) of the starting reagents are taken in the powdered form. The raw materials corresponding to each composition (Table \ref{tab:6}) are ground in an agate mortar for up to 2.0 h to obtain a fine homogeneous mixture. These homogeneously mixed compositions of each sample \((3.0 \text{ g})\) were poured in an alumina crucible one by one for melting purposes and placed in a high-temperature electric furnace at 850 °C until the liquid sample changed into the transparent form. The transparent form of each sample was cooled quickly in the preheated brass mould kept at 500 °C and covered by another hot thick brass plate. After cooling, these glass samples were cut into a particular shape of thickness 2.0 mm and polished carefully to find a smooth surface for better optical characterization.

The refractive indices of all the transparent glasses were determined by using the Brewster’s angle polarization method in which a He–Ne laser of wavelength 6328 Å \((5 \text{ mW output power})\) was used as an optical source. For density measurements, the Archimedes principle experiment was used with xylene as an immersion liquid. The absorption spectra have been recorded in the 400–2000 nm wavelength range using a double beam UV–vis–NIR spectrophotometer with a spectral resolution of 0.5 nm. The frequency UC spectra have been recorded through a monochromator attached with a photomultiplier tube under the 980 and 808 nm laser diode excitations. Photometric characterization has been performed for all the prepared glasses. All the measurements have been

**Table 6. Glass Compositions and Their Respective Codes**\textsuperscript{44}

| glass code       | glass composition                                      |
|------------------|--------------------------------------------------------|
| Er–TW            | \((85 - x)\text{TeO}_2 + 15\text{WO}_3 + x\text{Er}_2\text{O}_3\) |
| Er–Yb–TW         | \((85 - x - y)\text{TeO}_2 + 15\text{WO}_3 + x\text{Er}_2\text{O}_3 + y\text{Yb}_2\text{O}_3\) |
| Er–Yb–TWP        | \((80 - x - y)\text{TeO}_2 + 15\text{WO}_3 + 5\text{Pb}_2\text{O}_4 + x\text{Er}_2\text{O}_3 + y\text{Yb}_2\text{O}_3\) |
| Er–Yb–TWPTi      | \((-65 - x - y)\text{TeO}_2 + 15\text{WO}_3 + 5\text{Pb}_2\text{O}_4 + 15\text{TiO}_2 + x\text{Er}_2\text{O}_3 + y\text{Yb}_2\text{O}_3\) |

\textsuperscript{44}Optimized value of \(x = 1.0 \text{ mol }\%\) and \(y = 3.0 \text{ mol }\%\).
carried out at room temperature (27 °C). The CCT and CP were determined through the GoCIE software.

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**Notes**

The authors declare no competing financial interest.

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