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Intense Upconverted White Light Emission from Tm^{3+} - Er^{3+} - Yb^{3+} Doped Zinc Tungsten Tellurite Glasses

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Tellurite glasses,
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Abstract: The different amount of rare earth ions doped zinc tungsten tellurite glasses with the compositions (70-x-y-z)TeO_2 – 20ZnO – 10WO_3 – xEr_2O_3 – yTm_2O_3 – zYb_2O_3 (x = 0.3, 0.5; y = 0.3, 0.5; z = 3) have been synthesized using melt quenching technique. Blue, green, red and infrared luminescence via energy transfer and frequency upconversion mechanisms in $Tm^{3+}/Er^{3+}/Yb^{3+}$ triply-doped zinc tungsten tellurite glasses were investigated under single 975 nm diode laser excitation. Intense blue (Tm^{3+}: $^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_6$; 477 nm), green ($^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$; 525 nm and 549 nm), red (Er^{3+}: $^4F_{9/2} \rightarrow {}^4I_{15/2}$, Tm^{3+}: $^1G_4 \rightarrow {}^3F_4$; 659 nm) and infrared ($Tm^{3+}$: $^1G_4 \rightarrow {}^3H_5$, $^3H_4 \rightarrow {}^3H_6$; 807 nm) emissions were observed simultaneously at room temperature. Intense white light emission from all samples was observed with CCT values higher than 6500 K and CRI values lower than 80. The CIE coordinates of the emitted white light were found to shift to yellowish-greenish region with increasing pumping power. The possible energy transfer and upconversion mechanisms are discussed and plausible explanations are made.

Tm^{3+} - Er^{3+} - Yb^{3+} Katkılı Çinko Tungsten Tellürit Camlarından Üst Enerji Dönüşümü Yoluyla Şiddetli Beyaz Işık Emisyonu

Anahtar Kelimeler
Tellürit camları,
Beyaz ışık,
Nadir toprak iyonları,
Üst enerji dönüşümü

Özet: (70-x-y-z)TeO_2 – 20ZnO – 10WO_3 – xEr_2O_3 – yTm_2O_3 – zYb_2O_3 (x = 0.3, 0.5; y = 0.3, 0.5; z = 3) bileşimine sahip farklı miktarlarda nadir toprak iyonları katkılandırılmış çinko tungsten tellurit camları ergitme döküm tekniği kullanılarak sentezlenmiştir. $Tm^{3+}/Er^{3+}/Yb^{3+}$ üçlü nadir toprak iyonu katkılı çinko tungsten tellürit camlarında üst enerji dönüşümü ve enerji transfer süreçleri yoluyla elde edilen mavi, yeşil, kırmızı ve kızılötesi lüminesansları 975 nm diyot lazer uyarımı altında araştırılmıştır. Buna göre, şiddetli mavi (Tm^{3+}: $^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_6$; 477 nm), yeşil ($^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$; 525 nm and 549 nm), kırmızı (Er^{3+}: $^4F_{9/2} \rightarrow {}^4I_{15/2}$, Tm^{3+}: $^1G_4 \rightarrow {}^3F_4$; 659 nm) ve kızılötesi (Tm^{3+}: $^1G_4 \rightarrow {}^3H_5$, $^3H_4 \rightarrow {}^3H_6$; 807 nm) emisyonları eş zamanlı olarak oda sıcaklığında gözlenmiştir. Bütün numunelerden CCT değerleri 6500 K'den büyük ve CRI değerleri 80'den küçük şiddetli beyaz ışık emisyonu gözlenmiştir. Yayılan beyaz ışığın CIE koordinatlarının, artan pompalama gücü ile sarımsı-yeşilimsi bölgeye kaydığı bulunmuştur. Olası enerji transfer süreçleri ve üst enerji dönüşüm mekanizmaları tartışılmış ve gerekli açıklamalar yapılmıştır.

1. Introduction

In recent years there is a great and growing interest in generation of white light sources for wide range of applications like 3D displays, light emitting diodes, lighting, etc. One of the best way for producing white light is the frequency upconversion (UC) of rare earth ions (REI) doped materials. UC is a nonlinear optical process in which incident low energy photons converted into high energy photons via sequential absorption of two or more photons. The emission and the control of the relative intensities of the three primary colors (red, green and blue) are required to obtain application specific white light emission. This can be achieved by controlling the type and the amount of REIs. Hence there is a requirement for novel phosphor materials doped with different type and amount of REIs [1-7].

Among optical gain media, glasses are attractive because of the long lifetime of REIs in glasses and their capability of incorporating large amount of REIs

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without inducing crystallization. Tellurite glasses are promising host materials for REI upconversion purposes because of having some excellent properties, such as good corrosion resistance, low melting point (~750 °C), high dielectric constant, chemical and thermal stability, low phonon energy, transparency in a wide spectral region (0.3–7 μm), and high index of refraction (2.1 to 2.3) [7-11].

Tellurium oxide, TeO_2, is the most stable form of tellurium and does not able to form glass easily by itself. A network modifier should be added into the system in order to obtain tellurite-based glasses. The optical properties of tellurite glasses are strongly affected by the type and the amount of the modifier in the glass composition [12-14]. Hence, it is important to study the glass forming of tellurium oxide with different metal oxides, fluorides, or chlorides. Since the local structure and the distribution of the REIs in the host matrix have a strong effect on the spectroscopic parameters, the search for the best host-ion combination is also crucial [15]. Because of this reason, studying the frequency UC in alternative glass hosts and identifying the processes leading to visible emission is important for designing new glasses for photonic applications. At this point, WO_3 and ZnO are known as good glass modifiers and adding them to the tellurite glass system can enhance the thermal stability and as a result improve the resistance for crystallization. Furthermore, both these modifiers provide relatively wide glass forming region and they also provide glasses with good optical quality. There are also many publications on upconversion emission and white light emission properties of tellurite glasses with different modifiers that can be found in literature. Intense red, green and blue UC emission has simultaneously been observed in $Tm^{3+}/Er^{3+}/Yb^{3+}$ codoped oxyhalide tellurite glasses under 980 nm excitation [1]. Desirena et al, have obtained multicolors and white light emission with CIE coordinates (0.32; 0.33) from $Yb^{3+}/Tm^{3+}/Ho^{3+}$ doped tellurite glasses modified by ZnO and Na_2O under 970 nm excitation [16]. Dwidedi et al, also demonstrated the single colors UC and white light emission from tellurite glasses doubly and triply doped with Pr/Er/Yb ions [17].

In present study, zinc tungsten tellurite glasses co-doped with different amount of Tm^{3+}, Er^{3+}, Yb^{3+} ions were synthesized using melt quenching technique to obtain white light emission and obtained visible UC emission was characterized by measuring UC emission spectra and color quality parameters.

2. Material and Method

Zinc tungsten tellurite glasses were prepared from the powders of TeO_2, ZnO, WO_3, Tm_2O_3, Er_2O_3 and Yb_2O_3 as starting materials by using the melt quenching technique. The synthesized glass compositions are tabulated in Table 1. The oxide powders were of analytical grade (99.99%) and purchased from Sigma-Aldrich and Alfa Aesar. A high precision scale was used to weigh appropriate amounts of powders in calculated molar ratio. Then, powders were mixed using an agate mortar and pestle. The batches of 7g of the powders were then melted in a platinum crucible in a Carbolite Elf 11/6 model muffle furnace under ambient air conditions at 800°C for 1 h and quenched on a preheated stainless steel mold. The as-cast glasses were then kept at 200°C below their glass transition temperature for 2 h to relieve internal stresses formed in the glasses.

Table 1. Glass Compositions

Glass ID	Glass Compositions (mole %)					
	TeO_2	ZnO	WO_3	Er_2O_3	Tm_2O_3	Yb_2O_3
TZW-1	66.4	20	10	0.3	0.3	3
TZW-2	66.2	20	10	0.5	0.3	3
TZW-3	66.2	20	10	0.3	0.5	3

The UC emission of materials under 975 nm laser diode (CNI-MDL-H-975 Model) excitation were recorded using a Princeton Instruments SP2500i model monochromator and an Acton series SI440 model Silicon detector.

An AsenseTek Lighting Passport illuminance meter was used to determine color quality parameters of obtained visible UC emissions such as The Commission International De I'Eclairage (CIE) 1931 coordinates, correlated color temperature (CCT), and color rendering ındex (CRI). All above measurements were carried out at room temperature.

3. Results and Discussions

Three glass samples with different Tm^{3+}, Er^{3+}, and Yb^{3+} concentrations were successfully synthesized. The UC emission spectra of all samples were recorded upon 975 nm laser diode excitation at room temperature. The UC spectra of all samples are given in Figure 1 with corresponding transitions as a function of pumping excitation power. As seen from the figure, intense UC emission in the blue, green, red and infrared spectral regions were observed for the samples which are localized at around 477 nm, 525 nm, 549 nm, 659 nm and 807 nm respectively. The UC spectra of the three samples are very similar. The obtained UC emission bands can easily be assigned to the transitions between energy levels of Er^{3+} and Tm^{3+} ions. The observed blue, green, red and infrared UC emission bands are assigned to the $^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_6$ transitions of Tm^{3+}, the $^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_6$ transitions of Tm^{3+}, $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+}, $^4F_{9/2} \rightarrow {}^4I_{15/2}$, $^1G_4 \rightarrow {}^3F_4$ transitions of Er^{3+} and Tm^{3+} and $^1G_4 \rightarrow {}^3H_5$, $^3H_4 \rightarrow {}^3H_6$ transitions of Tm^{3+}, respectively.

The possible mechanisms responsible for blue, green, red and infrared UC emissions are discussed based on the energy level diagrams of Er^{3+}, Tm^{3+} and Yb^{3+} ions given in Figure 2. Since Yb^{3+} concentration is high and it offers the advantage of high absorption cross section, the responsible mechanism for obtained UC emission is the Energy Transfer (ET) from highly doped Yb^{3+} ions to the Er^{3+} and Tm^{3+} ions. Once the sample is excited by 980 nm laser light Yb^{3+} ions absorb the incident photons and transfer its energy to the other ions. The excitation process of the blue emission process of ${}^1D_2\rightarrow{}^3F_4$, ${}^1G_4\rightarrow{}^3H_6$ transitions of Tm^{3+} can be explained as follows: an ET process between Yb^{3+} and Tm^{3+} resulted in the excitation of Tm^{3+} ion from ${}^3H_6$ ground state to the ${}^3H_5$ level. Then it relaxes non-radiatively to the ${}^3F_4$ level. Another ET process between Yb^{3+} and Tm^{3+} ions populates the ${}^3F_2$ level and then it decays to the ${}^3H_4$ level non-radiatively. Finally, Tm^{3+} in the ${}^3H_4$ level is excited to the ${}^1G_4$ level via another ET from Yb^{3+}. Tm^{3+} ions decay radiatively to the lower energy levels from the ${}^1G_4$ level which is giving rise to the visible (477 and 659 nm) and infrared (807 nm) emissions. Radiative decay from ${}^1D_2$, which is populated via ${}^1G_4\rightarrow{}^1D_2$ process induced by Yb^{3+} to Tm^{3+} ET process is also contribute to the 477 nm blue emission. It can be easily seen from above discussions that three-photon absorption is responsible for 477 nm blue emission. It is worth noting here that the cooperative upconversion process of Yb^{3+} could also be responsible for the blue emission but its efficiency is lower than that of ET process [6].

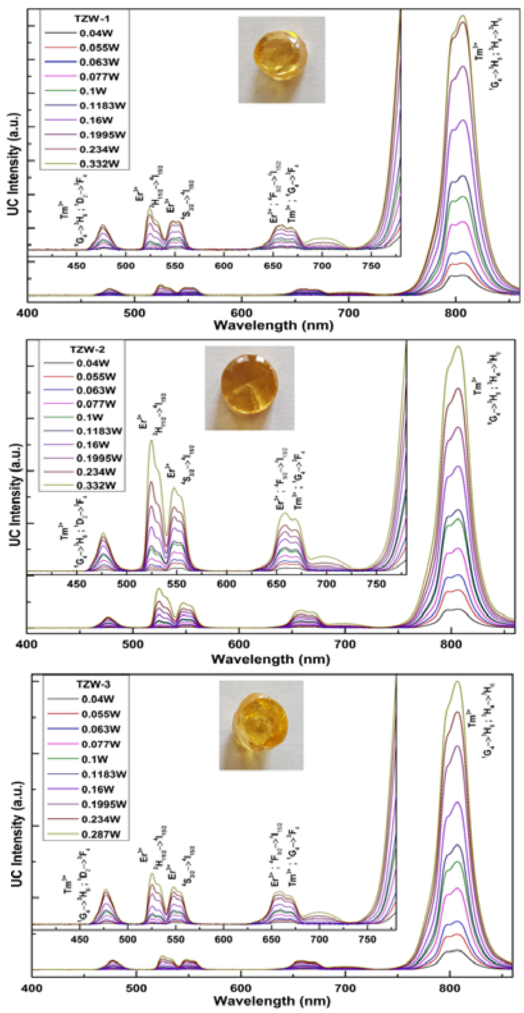

Figure 1. The UC spectra of all samples with corresponding transitions.

The responsible mechanism for the green (525 and 549 nm) and red (659) emissions is the ET process from Yb^{3+} to Er^{3+}. First, the Er^{3+} ion is excited to the ${}^4I_{11/2}$ level from the ground state and subsequently to the ${}^4F_{7/2}$ level of Er^{3+}. Then this level populates lower ${}^2H_{11/2}$ and ${}^4S_{3/2}$ levels which are giving rise to green emissions at 525 and 549 nm, respectively. The ${}^4F_{7/2}$ level also populates the ${}^4G_{9/2}$ level via non-radiative relaxation which is resulted in 659 nm red emission. The ${}^4F_{7/2}$ level is also populated from ${}^4I_{13/2}$ level via ET process.

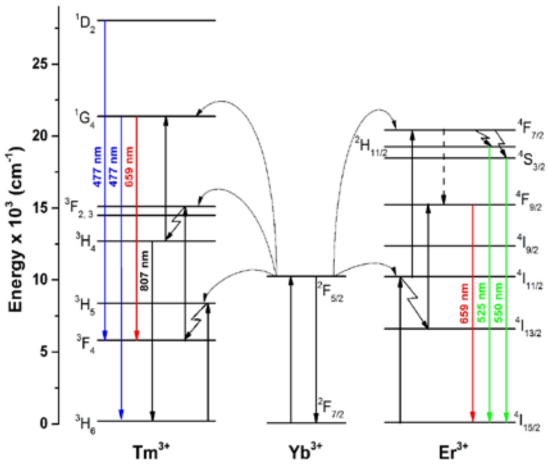

Figure 2. Simplified energy level diagram with proposed UC mechanisms of Er^{3+}, Tm^{3+} and Yb^{3+} ions in zinc tungsten tellurite glass.

To better understand the UC mechanisms, the pumping laser power dependencies of the UC emissions were measured and the representative pump power dependence of the UC intensity of the TZW-2 sample is given in Figure 3. The power law is expressed as $I \propto P^n$ where I is the intensity of the emission, P is the pumping laser power, and n is the number of the laser photons included in the process. The n values determined from the slope of the curve ln(I) versus ln(P) are given in Table 2 for all samples. The experimental n values indicate that more than one photon is involved in the UC processes even if expected n values are higher than the obtained values using power law. Since two photons are required for green and red and three photons for blue UC emissions, as discussed in energy level diagram, the n values given in Table 2 are smaller than those expected values. Since the UC intensity values starts to deviate from the power law at higher power density values, the lower values of n than expected could be explained by saturation of the UC process.

The color quality parameters like CIE coordinates, CCT and CRI were measured using an illuminance meter. The pumping power dependence of the CIE coordinates of obtained visible UC emission is given in Figure 4. The UC emission from TZW-2 sample found to lie in white region (x = 0.3103; y = 0.3493) of CIE diagram at low pumping power values and then started to shift to greenish region with increasing pumping power values. Even if CIE coordinates of UC emissions from TZW-1 and TZW-3 samples at low pumping power values seem greenish to the naked eye they still lie within the white region of the CIE diagram. All UC emissions from all samples were found to shift to greenish region with increasing pumping power. Therefore, small variations in the molar ratios of the dopant ions do not make much sense and white emission is still available. Since UC spectra of all samples are not continuous (includes peaks and valleys), unlike the black body emission, the CCT and CRI values of obtained upconverted white light emission were found as > 6500 K and <80 for all samples, which means obtained white emissions are cool in appearance [18-20].

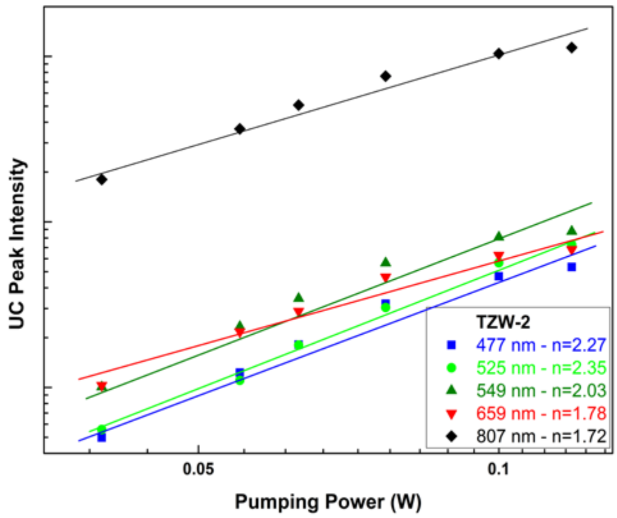

Figure 3. Pump power dependence of the UC luminescence intensity in TZW-2 sample.

Table 2. The *n* values for all glass samples.

Glass ID	***n* Values**				
	477 nm	525 nm	549 nm	659 nm	807 nm
TZW-1	2.02	1.72	1.58	1.48	1.40
TZW-2	2.27	2.35	2.03	1.78	1.72
TZW-3	2.05	1.90	1.65	1.80	1.60

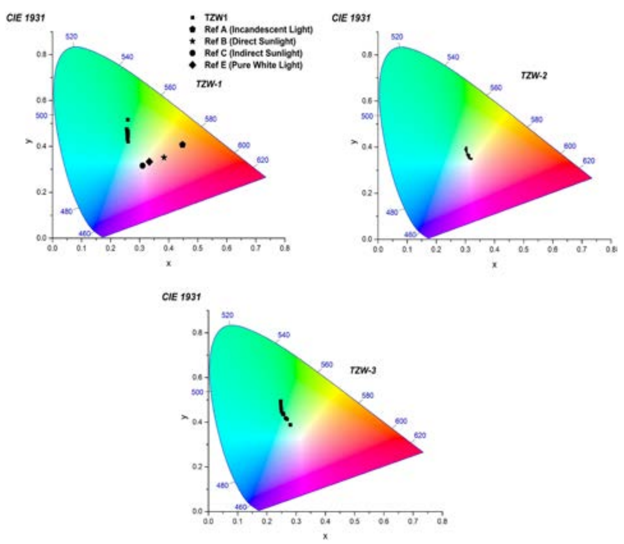

Figure 4. CIE coordinates of obtained UC luminescence in all samples.

4. Discussion and Conclusion

Zinc tungsten tellurite glasses triply doped with different amounts of Tm^{3+}, Er^{3+}, and Yb^{3+} ions were successfully synthesized. Bright white light emission as a result of energy upconversion were obtained by using proper molar ratio combination of Tm^{3+}, Er^{3+}, and Yb^{3+} ions. It is found that upconverted white light emissions from all samples lie in the white region of the CIE diagram. Hence these materials can be used in white light applications in the photonic applications and the color of the emitted UC light for specific application can be tuned by controlling the amount of dopant ions.

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