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Exploring the Impact of Plasmonic Nanoparticles on Photoluminescence of Er³⁺-Doped Sodium Zinc Tellurite Glass for Solid-State Laser Applications

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ABSTRACT

The present work compares the impact of embedding silver (Ag), gold (Au), titanium (Ti), and titanium nitride (TiN) nanoparticles (NPs) on the absorption, photoluminescence, and Judd Ofelt properties of erbium-doped sodium zinc tellurite glass (TNZE), known as reliable solid-state laser media. Ten absorption bands of Er³⁺ ions in the range of 400–1600 nm are attainable where their bands correspond to their own 4f transitions. Three prominent photoluminescence (PL) bands of Er³⁺ ions were observed at approximately 525 nm, 545 nm, and 630 nm, corresponding to the transitions ²H_{11/2}→⁴I_{15/2}, ⁴S_{3/2}→⁴I_{15/2} and ⁴F_{9/2}→⁴I_{15/2}, respectively. TNZE with 0.15 mol% of TiN NP inclusion showed the highest PL enhancement factor about 35 times, followed by Ti (17 times), Ag (10 times), and Au NPs (5 times), accordingly. This enhanced PL can be attributed to the strong local field induced by the localized surface plasmon resonance (LSPR) of the plasmonic NPs lies within 490–630 nm, which assists the transitions of Er³⁺ ions. The Judd Ofelt parameter was calculated and the TNZE glass with 0.15 mol% of TiN NPs inclusion disclosed the highest spectroscopic quality with a value of 3.57, compared to the TNZE glass with Ti (1.19), Au (0.59), and Ag NPs (0.90) inclusions. This research revealed several potential glass compositions with plasmonic nanoparticles that are attractive for the development of solid-state laser materials.

Keywords: Nanoparticles, Titanium, Tellurite, Photoluminescence.

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Introduction

Plasmonic nanoparticles (NPs) such as gold [1], silver [2], titanium [3] and titanium nitride [[4], [5], [6]] exhibit unique optical properties by enhancing the local field proximity rare earth ions (REI) doped glass whenever their natural frequency matched with excitation frequency. This phenomenon is known as local surface plasmon resonance (LSPR). It may alter the optical properties of the REIs doped glass for various applications, such as fiber optics, passive solar covers, photonic devices, and optical data storage [[1], [2]]. The tunability of glass properties based on composition makes them

versatile as hosts for solid-state lasers. Comparing the effects of different metal NPs on REI luminescence within the same host would offer a systematic approach to navigate the effective plasmonic sensitizer to enhance the photoluminescence (PL) of REIs doped glass.

Sodium zinc tellurite glass doped with erbium (Er³⁺) ions (TNZE) is an attractive candidate as a host for solid-state lasers. TNZE exhibits photoluminescence (PL) that extends from the visible to the mid-infrared (MIR) region (450–3000nm), making it suitable for a wide range of photonic applications [[7], [8]]. It has a high refractive index (>2.3) and a low phonon energy

($\sim 780\text{ cm}^{-1}$). TNZE also shows strong up-conversion (UC) emission intensities due to its distinct energy level spacing and sharp spectral features in the $4f$ electronic transitions [9]. The spectroscopic quality of sodium zinc tellurite glass doped with erbium (Er^{3+}) is calculated using Judd Ofelt simulations. To determine the most suitable plasmonic nanoparticle (NP) as a sensitizer, various types of NPs such as silver (Ag), gold (Au), titanium (Ti), and titanium nitride (TiN) are incorporated into the system. The main objective is to investigate the influence of these NPs on the laser properties of the glass and identify the most effective plasmonic sensitizer.

Sample Preparation and Characterizations

Composition of the glass with formula $68.85\text{-TeO}_2\text{-}20\text{ZnO-}10\text{Na}_2\text{O-}1\text{Er}_2\text{O}_3\text{-}0.15$ MNPs in mol% is prepared using melt quenching technique. The corresponding glass codes for the MNPs are TNZEAg, TNZEAu, TNZETi, and TNZETiN. High purity analytical grade powders ($\approx 99\%$) of TeO_2 , ZnO, Na_2O , Er_2O_3 , Ag, Au, Ti, and TiN NPs from Sigma Aldrich were utilized. Additionally, four MNPs-based glasses without REIs were prepared and coded as Ag_{SPR} , Au_{SPR} , Ti_{SPR} , and TiN_{SPR} , representing glass compositions with Ag, Au, Ti, and TiN NP inclusions, accordingly. These glass is prepared to probe LSPR bands within the host glass. The constituents were

placed in an alumina crucible and melted in an electrical furnace at 1000°C for 30 minutes. The liquid-melt was then poured onto a stainless-steel plate and annealed for three hours at 300°C . After cooling to room temperature, the samples were stored in closed containers to prevent moisture attack. Finally, the samples were polished to obtain a smooth surface for luminescence measurement. The room temperature absorption spectra in the range of 400-1600 nm were recorded using a Shimadzu UV-3600PC scanning spectrophotometer (Kyoto, Japan), while the photoluminescence (PL) was measured using a Hitachi F850 Fluorescence spectrometer (Tokyo, Japan). The Judd-Ofelt analysis was performed where their equations are referring to previous published articles [[7], [8]].

Results and Discussion

The UV-Vis-NIR absorption spectra of prepared sample is displayed in in Figure 1. It shown ten absorption bands centred at 407, 444, 452, 489, 522, 653, 800, 976 and 1532 nm which corresponding to transition from the Er^{3+} ions ground state ($^4\text{I}_{15/2}$) to excited states of $^2\text{G}_{9/2}$, $^4\text{F}_{3/2}$, $^4\text{F}_{5/2}$, $^4\text{F}_{7/2}$, $^4\text{H}_{11/2}$, $^4\text{S}_{3/2}$, $^4\text{F}_{9/2}$, $^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$, accordingly [1]. The absorbance bands disclosed almost similar pattern from previous work [1]. These data were used to perform Judd Ofelt (JO) calculations.

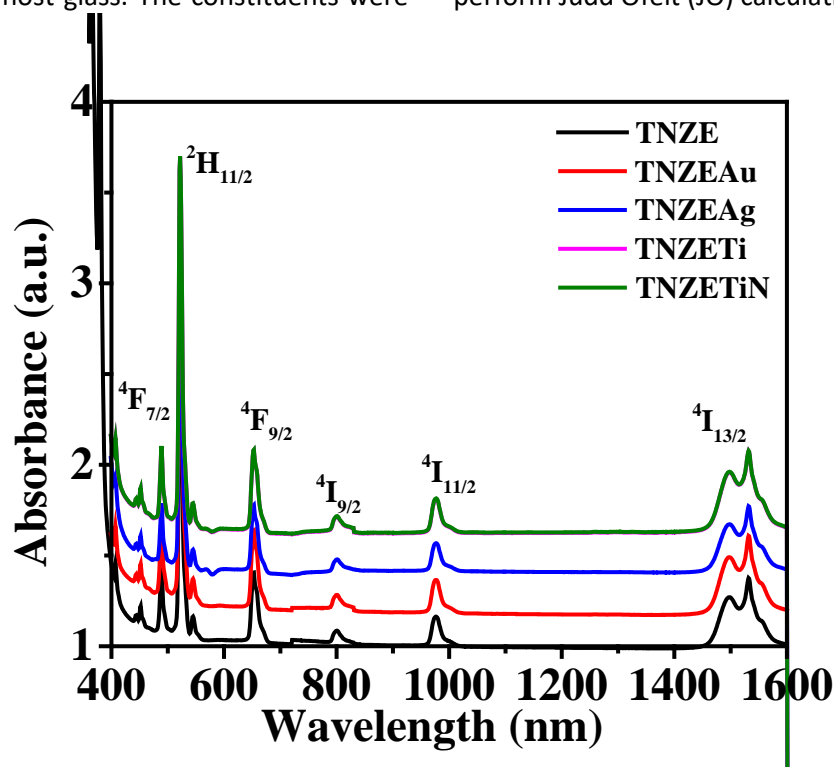
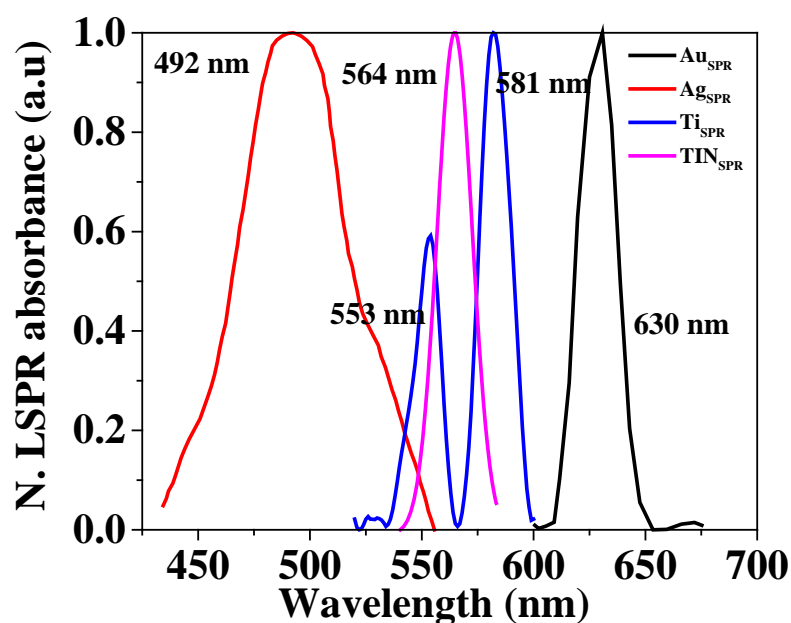


Figure 1 - UV-Vis-NIR absorption spectra of glasses

Table 1 - The JO intensity parameters ($\Omega_2, \Omega_4, \Omega_6$) and spectroscopic quality factors $\chi = (\Omega_4 / \Omega_6)$ of the glasses

Glass code	Metallic NPs used	Contents (mol%)	Ω_2	Ω_4	Ω_6	Trends of Ω_i	χ	LSPR band (nm)	Ref.
TNZE Au	Au	0.15	3.38	1.19	2.02	$\Omega_2 > \Omega_6 > \Omega_4$	0.59	630	Present
TNZE Ag	Ag	0.15	3.74	2.63	2.93	$\Omega_2 > \Omega_6 > \Omega_4$	0.90	492	Present
TNZETi	Ti	0.15	3.11	2.23	1.88	$\Omega_2 > \Omega_4 > \Omega_6$	1.19	553, 581	Present
TNZETiN	TiN	0.15	4.70	2.71	0.77	$\Omega_2 > \Omega_4 > \Omega_6$	3.57	564	Present
TPBFErAu 2	Au	0.2	10.39	2.55	4.98	$\Omega_2 > \Omega_6 > \Omega_4$	0.51	599.652	[12]
TZEAg	Ag	0.5	6.54	2.36	2.82	$\Omega_2 > \Omega_6 > \Omega_4$	0.82	500	[13]
TNZETi	TiO ₂	0.1	3.08	2.15	1.88	$\Omega_2 > \Omega_4 > \Omega_6$	1.14	580	[14]

**Figure 2** - Normalized LSPR band of plasmonic NPs in host glass

The values of JO intensity parameters ($\Omega_2, \Omega_4, \Omega_6$) and spectroscopic quality factors $\chi = (\Omega_4 / \Omega_6)$ of prepared samples are summarized in. Glass with 0.15 mol% of Ti NPs shows lowest value of Ω_2 which indicates high symmetrical around Er³⁺ ion. The low Ω_2 value disclosed ionic characteristic of the glass. Meanwhile its lowest Ω_6 values revealed by glass contains TiN NPs indicate its weakest rigidity. The laser strength of the REIs is access through spectroscopic quality parameter, χ . In present case, χ shows highest in TNZETiN follow by TNZETi, TZEAg and TNZEAu, accordingly.

Figure 2 displayed normalized LSPR bands of Ag, Au and Ti NPs as incorporated into TNZE. The LSPR of Ag, TiN, Ti and Au NPs shows highest peak around 490, 564, 581, and 630 nm, respectively. The Ti NPs exhibit additional LSPR band around 553 due to slight different aspect ratio causes by irregular shape/size [[2], [15]]. This irregular shape tailor different plasma mode and frequency. According to, the localized surface plasmon resonance (LSPR) bands of the plasmonic NPs in present work is comparable with other glass system.

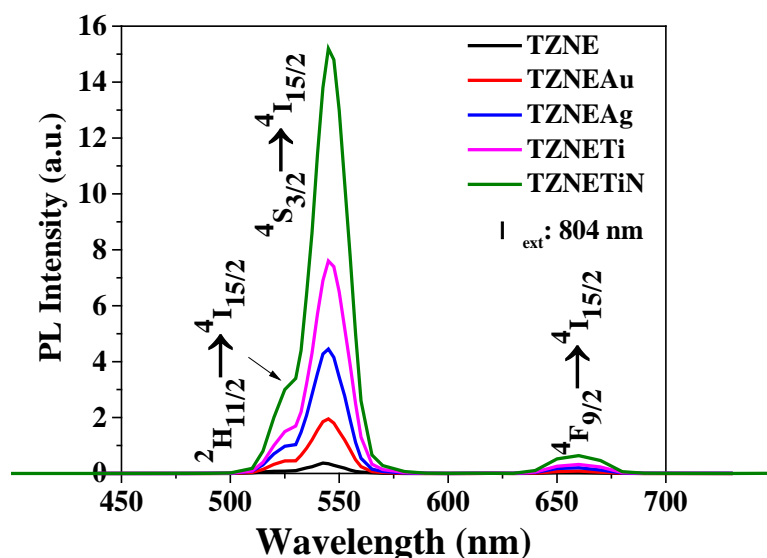


Figure 3 - PL spectra of the glasses with different plasmonic NPs, excited at 804

Figure 3 shows the up-conversion (UC) photoluminescence spectra of Er^{3+} ion as pumped with 804 nm. The photoluminescence (PL) spectra of Er^{3+} ion revealed three prominent bands centred at 525, 545 and 660 nm assigning to ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ transitions, respectively. The PL enhancement factor (η_E) was calculate by dividing the highest PL area of each emission band (525, 545, 660 nm) that incorporated with plasmonic NPs with glass with NPs-free. The highest η_E is revealed by TNZETiN which is about 43, 32, 29 times corresponding to emission band around 525 (${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$), 545 (${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$) and 660 nm (${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$), respectively. Then followed by sample TZNETi (22, 16, 14 times), TNZAg (13, 10, 9 times), and TNZAu (6, 5, 3) tally with transitions ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ accordingly. The enhancement is response to local field enlargement that is proximity Er^{3+} ion. The green band at 525 and 545 nm present highest intensification due to overlap TiN and Ti NPs band LSPR band located around 564 and (553 and 581 nm) with the PL bands [[16], [17], [18], [19], [20]] . Ti and TiN NPs reflect potential as new plasmonic sensitizers replacing Au and Ag NPs.

Conclusion

The impact of Ag, Au, Ti, and TiN NPs on the photoluminescence (PL) of TNZE was examined. The localized surface plasmon resonance (LSPR) of the plasmonic NPs was observed in the range of 490-630 nm. The glass with TiN NPs inclusion exhibited the highest spectroscopic quality among other REI-doped hosts in present work, with a value of 3.57. It also demonstrated the most significant enhancement, averagely 35 times for all observed PL bands. The LSPR bands of Ti and TiNPs about 550-580 nm that is overlapped with the Er^{3+} emission (525-545 nm) could be main cause for the utmost PL enhancements where the energy transfer is possible. Present work revealed that different plasmonic NPs able to modify the luminescence intensity of Er^{3+} ions doped sodium zinc tellurite glass. The prepared glass shown potential as a new gain medium for solid-state laser applications.

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Қатты күйдегі лазерлерде пайдалануға арналған Er^{3+} -легирленген натрий мырыш теллурит әйнегінің фотолюминесценциясына плазмалық нанобөлшектердің әсерін зерттеу

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ТҮЙІНДЕМЕ

Бұл жұмыс күміс (Ag), алтын (Au), титан (Ti) және титан нитриді (TiN) (NPs) нанобөлшектері кірінділерінің эрбиймен легрленген қатты күйдегі лазерлік тасымалдағыш ретінде белгілі шыны (TNZE) натрий мырыш теллуритінің сіңіру, фотолюминесценция және Judd Ofelt қасиеттеріне әсерін салыстырады. Er^{3+} иондарының он жұту жолағы 400-1600 нм диапазонында қол жетімді, мұнда олардың жолақтары өздерінің 4f өтулеріне сәйкес келеді. ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ өтулеріне сәйкес шамамен 525, 545 және 630 нм-де Er^{3+} иондарының үш байқалатын фотолюминесценция (PL) жолағы байқалды. Er^{3+} иондарының үш көрнекті фотолюминесценция (PL) жолағы ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ және ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$, тиісінше, өтулеріне сәйкес шамамен 525 нм, 545 нм және 630 нм аралығында байқалды. TiN NP қосындысының 0,15 моль% TNZE ең жоғары PL күшейту коэффициентін шамамен 35 есе көрсетті, одан кейін тиісінше Ti (17 есе), Ag (10 есе) және Au NPs (5 есе) болады. Бұл күшейтілген PL 490–630 нм диапазонында жатқан плазмоникалық NP-лердің локализацияланған беттік плазмонды резонансы (LSPR) арқылы индукцияланған күшті жергілікті өріске жатқызылуы мүмкін, бұл Er^{3+} иондарының ауысуларына ықпал етеді. Judd Ofelt параметрі есептелді және Ti (1,19), Au (0,59) және Ag (0,90) қосындылары бар TNZE шынысымен салыстырғанда 0,15 моль% TiN NPs қосылған TNZE шынысы 3,57 мәнімен ең жоғары спектроскопиялық сапаны көрсетті. Бұл зерттеу қатты күйдегі лазерлік материалдарды әзірлеу үшін тартымды болып табылатын плазмоникалық нанобөлшектері бар бірнеше әлеуетті шыны формулаларын анықтады.

Түйін сөздер: нанобөлшектер, титан, теллурит, фотолюминесценция.

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Исследование влияния плазмонных наночастиц на фотолюминесценцию натриево-цинкового теллуритного стекла, легированного Er^{3+} , для применения в твердотельных лазерах

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АННОТАЦИЯ

В настоящей работе сравнивается влияние внедрения наночастиц (NPs) серебра (Ag), золота (Au), титана (Ti) и нитрида титана (TiN) на поглощение, фотолюминесценцию и свойства Judd Ofelt легированного эрбием теллурита натрия-цинка стекло (TNZE), известное как надежный твердотельный лазерный носитель. Достижимы десять полос поглощения ионов Er^{3+} в диапазоне 400-1600 нм, где их полосы соответствуют их собственным 4f-переходам. Наблюдались три заметные полосы фотолюминесценции (PL) ионов Er^{3+} примерно при 525, 545 и 630 нм, соответствующие переходам ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$.

соответственно. TZNE с 0,15 mol% включения TiN NP показал самый высокий коэффициент усиления PL примерно в 35 раз, за ним следуют Ti (17 раз), Ag (10 раз) и Au NPs (5 раз) соответственно. Эту усиленную PL можно объяснить сильным локальным полем, индуцированным локализованным поверхностным плазмонным резонансом (LSPR) плазмонных NPs, лежащим в пределах 490-630 nm, что способствует переходам ионов Er³⁺. Был рассчитан параметр Judd Ofelt, и стекло TNZE с включением TiN NPs 0,15 mol% показало самое высокое спектроскопическое качество со значением 3,57 по сравнению со стеклом TNZE с Ti (1,19), Au (0,59) и Ag (0,90) включения. Это исследование выявило несколько потенциальных составов стекла с плазмонными наночастицами, которые привлекательны для разработки твердотельных лазерных материалов.

Ключевые слова: наночастицы, титан, теллурид, фотoluminesценция.

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