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RESEARCH PAPER

Optical Properties of Neodymium Doped Magnesium Zinc Sulfo-Phopshate Glass: Impact of Gold Nanoparticles Inclusion

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Abstract

Gold (Au) nanoparticles (NPs) incorporated in magnesium zinc sulfo-phosphate glass with the molar composition of ($58.5P_2O_5$–20MgO–$20ZnSO_4$–$1.5Nd_2O_3$–*x*Au NPs (where *x* = 0.0, 0.1, 0.2, 0.3, and 0.4 mol%) were prepared via melt quench technique. The effect of Au NPs as incorporated in Nd^{3+} doped glasses were studied using X–ray diffraction (XRD), High Resolution-Transmission Electron Microscope (HR–TEM), UV–Visible-NIR absorption spectrometer and photoluminescence spectrometer. The amorphous nature of glass is confirmed via XRD measurements and existence of Au NPs inside the glass is reveal by HR-TEM. The typical absorption bands of Nd^{3+} are attained which positioned around 352, 430, 459, 474, 512, 525, 581, 626, 682, 744, 801and 875 nm. Up-conversion (UC) photoluminescence (PL) demonstrated six prominent emission bands located around 420, 445, 460, 484, 515 and 545 nm corresponding transition $^2P_{1/2}\rightarrow{}^4I_{9/2}$, $^2D_{5/2}\rightarrow{}^4I_{11/2}$, $^2P_{1/2}\rightarrow{}^4I_{11/2}$, $^2D_{5/2}\rightarrow{}^4I_{13/2}$, $^2K_{15/2}$,$^4G_{7/2}\rightarrow{}^4I_{11/2}$,$^4I_{9/2}$ and $^2D_{5/2}\rightarrow{}^4I_{15/2}$ respectively. Glass containing 0.1 mol% of Au NPs shows utmost PL enhancement and the emission decrease beyond 0.1 mol% of Au NPs depicts re-absorption of SPR and increase of non-radiative channel. The improvement of PL intensity attributed to local field effect of Au NPs that altered the environment in proximity Nd^{3+} ions. The proposed glass could be potential for improvement of solid state laser design.

Keywords: Gold Nanoparticles, Surface plasmon resonance, Neodymium ion, Up-conversion, photoluminescence, Sulfophosphate glass

Abstrak

Emas (Au) nanopartikel (NPS) yang dimasukkan di dalam kaca magnesium zink sulfo-fosfat dengan komposisi molar ($58.5P_2O_5$–20MgO–$20ZnSO_4$–$1.5Nd_2O_3$–*x*Au NPs (di mana x = 0.0, 0.1, 0.2, 0.3, dan 0.4% mol) telah disediakan melalui teknik sepuh lindap. Kesan Au NPS seperti yang dimasukkan di dalam kaca terdop Nd^{3+} telah dikaji menggunakan belauan sinar-X (XRD), Resolulsi tinggi- mikroskop pengaliran Electron (HR-TEM), UV-tampak-NIR spektrometer dan fotokilauan spektrometer. Sifat amorfus kaca disahkan melalui ukuran XRD dan kewujudan Au NPS dalam kaca telah ditunjukkan oleh HR-TEM. Jalur penyerapan Nd^{3+} yang telah dicapai diletakkan pada 352, 430, 459, 474, 512 , 525, 581, 626, 682, 744, 801 dan 875 nm. Penukaran-atas (UC) fotokilauan (PL) menunjukkan enam jalur pancaran yang terletak pada $^2P_{1/2}\rightarrow{}^4I_{9/2}$, $^2D_{5/2}\rightarrow{}^4I_{11/2}$, $^2P_{1/2}\rightarrow{}^4I_{11/2}$, $^2D_{5/2}\rightarrow{}^4I_{13/2}$, $^2K_{15/2}$,$^4G_{7/2}\rightarrow{}^4I_{11/2}$,$^4I_{9/2}$ dan $^2D_{5/2}\rightarrow{}^4I_{15/2}$. Kaca yang mengandungi 0.1 mol% Au NPS menunjukkan peningkatan PL dan pengurangan pancaran melebihi 0.1 mol% Au NPS menggambarkan penyerapan SPR dan peningkatan saluran bukan radiasi. Peningkatan ketumpatan PL dikaitkan dengan kesan medan setempat Au NPS yang mengubah persekitaran yang berdekatan dengan Nd^{3+} ion. Kaca yang dicadangkan berpotensi untuk menambah reka bentuk laser pepejal.

Kata kunci: Emas nanozarah, Permukaan resonan plasmon, Ion neodymium, Penukaran-atas, fotokilauan, kaca sulfofosfat

INTRODUCTION

The uniqueness of metal nanoparticles that exhibit surface plasmon resonance (SPR) properties has gain interest in the field of photonic and optic where these metal NPs intensive used to alter optical behaviour of glass containing rare earth (RE) ions for solid-state laser application (Mawlud, 2019; Ahmadi et al., 2018). The SPR may assist RE's luminescence by modifying electromagnetic field surrounding RE ions via its electron cloud (Jianbei et al., 2016). Metal nanoparticles such as Ag NPs were proven to enhance luminescence of Dy^{3+} ion doped magnesium zinc sulfophosphateglass by 1.5 times for transition $^4F_{9/2} \rightarrow {}^6H_{9/2}$ (Ahmadi et al., 2018). Meanwhile in subsequent year, Au NPs is also evidenced to enhance the emission of Pr^{3+} ion in B_2O_3-PbO-Bi_2O_3-GeO_2 glass (Herrera and Balzaretti, 2017). However role of Au NPs in modifying optical properties of RE-doped glass are less exploit compare to Ag NPs even it exhibit prominent SPR in visible region (520-600 nm), more stable and less toxic NPs compare to Ag NPs (Alaqad & Saleh, 2016).

Generally, phosphate glass exhibit many merits such as high transparency, high RE solibility, low refractive index and able govern large emission cross section (Ratnakaram et al., 2016). However large phonon energy of phosphate has limited the usage of phosphate glass in most application. Yet, the problem is overcome by adding suitable modifier, which in present case using MgO and $ZnSO_4$ (Ahmadi et al., 2016). Meanwhile Nd^{3+} ion is used luminescence centre as it is known as most efficient RE ion due to its wide-range absorption level from UV to NIR that made them useful in the field of telecommunication and ultrafast laser medium (Ratnakaram et al., 2016). In present studies, we presented the effect of Au NPs on optical properties of magnesium zinc sulfophophate glass containing Nd^{3+} ion to oversee its potential as improved optical material.

MATERIALS AND METHODS

The glass sample were prepared via melt-quenching technique by following composition $58.5P_2O_5$–$20MgO$–$20ZnSO_4$–$1.5Nd_2O_3$–xAu NPs (where x = 0.0, 0.1, 0.2, 0.3, and 0.4 mol% in excess) and labelled as PMZ1.5Nd, PMZ1.5Nd0.1Au, PMZ1.5Nd0.2Au, PMZ1.5Nd0.3Au and PMZ1.5Nd0.4Au respectively. All the high purity raw material≈ 99.9% were purchased from Sigma Aldrich. Each batch (22 g) mixed in the alumina crucible and undergo preheat process at 300 °C for 30 minute before melt in the electric furnace at 1100 °C for 1.5 hours. The melt is immediately poured on preheated stainless steel mould and goes annealing at 300 °C for 3 hours. The annealing process is required to ensure that the glass less impacted from thermal and mechanical stress. The solidify sample is kept in a desiccator to avoid moisture attack. The glass were polished using appropriate grade of sand paper and diamond paste to attain transparent and shiny surface for better optical measurement.

The amorphous nature of the glass is determine using X-ray diffraction (XRD) measurements were performed using PANalytical X'Pert PRO MRD PW3040 with Cu Kα radiations (λ = 1.54 Å) in scanning angle of 2θ ranging between 20^o and 80^o operated at 40kV and 35 mA. In addition, lattice-spacing of Au NPs are determine via High resolution transmission electron microscope (HRTEM, JEOL 2100F) operated at an acceleration voltage of 200 kV. The absorption spectra of the prepared glasses were recorded using Shimadzu UV-3600 spectrophotometer. The emission spectra are recorded by a Perkin Elmer LS-55 photoluminescence (PL) spectro-meter (UK).

RESULTS AND DISCUSSION

XRD

Figure 1 present XRD pattern for samples contains Au NPs (PMZ1.5Nd0.4Au) and without (PMZ1.5Nd) where both samples displayed a broad hump between 20–30° which confirmed the amorphous nature of prepared glass. No crystalline peak correspond to Au NPs is observed for glass containing Au NPs due to its low concentration (Jagannath et al., 2018) and small size (Herrera et al., 2016). Previous studies disclosed the same pattern where crystalline peak is undetectable for glass incorporated with metal NPs (Herrera & Balzaretti, 2017).

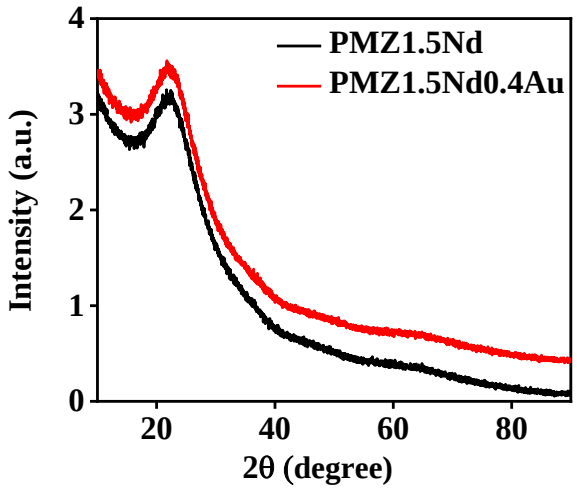

Figure 1. XRD of selected prepared samples (with and without Au NPs)

TEM

TEM measurement reveals direct morphology image inside the glass structure which used to probe the existence of Au NPs inside the glass. Figure 2 shows the TEM image of sample PMZ1.5Nd0.4Au where nucleation of Au NPs is evidenced with fringe spacing of 0.22 nm (insert in Figure 2), matched with its crystalline plane (1 1 1) corresponding to face centred cubic (FCC) structure as listed in JCPDS card no. 4–784 (Jagannath et al. 2018; Mawlud et al., 2017).

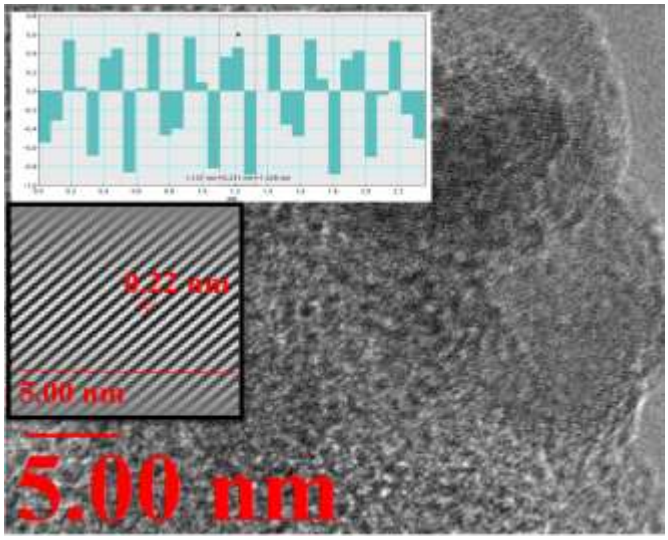

Figure 2. HRTEM of sample PMZ1.5Nd0.4Au (insert: profile spacing of Au NPs lattice)

Absorption spectrum

UV-Vis-NIR absorption spectra of prepared sample containing different concentration of Au NPs is shown in Figure . Based on 4f-4f transition of the Nd^{3+} ions by Carnal et al., twelve prominent absorption band are evidenced positioned around 352, 430, 459, 474, 512, 525, 581, 626, 682,744, 801and 875 nm which assigned to transition state $^2D_{1/2}+^4D_{3/2}+^4D_{5/2}$, $^2P_{1/2}$, $^4G_{11/2}$, $^2D_{3/2}+^2P_{3/2}+^2G_{9/2}$, $^4G_{9/2}+^2K_{13/2}$, $^4G_{7/2}$, $^4G_{5/2}+^2G_{7/2}$, $^4H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}+^4S_{3/2}$, $^4F_{5/2}+^2H_{9/2}$ and $^4F_{3/2}$ from ground sate $^4I_{9/2}$, respectively (Carnall et al., 1968). These absorption transition are expected broadened due to short-range order of glassy material (Suresh Kumar et al., 2018). Nevertheless, the position of Nd^{3+} absorption band inside the glass are in agreement with previous studies (Azlan & Halimah, 2018; Zamratul et al., 2016). Generally, no significant absorbance change is perceived with increasing Au NPs contents. However some intensities of the transition are slightly affected with addition of Au NPs which signifies the modification of local environment in proximity of Nd^{3+} ion (Rao, 2018). It was reported that excitation rate of Nd^{3+} ion increase due to stimulated local electromagnetic field mediated by SPR effect from Au NPs (Ma et al., 2018). However, SPR band of Au NPs is probably overshadow by Nd^{3+} ion absorption band therefore is not observe in present case (Mawlud, 2019). According to Jagannath et al., the SPR band of Au NPs could be located around 565–597 nm (for a glass with refractive index 1.6) where the peak of SPR band are hardly distinguished due overlapping of interband resonance band with the plasmon band (Jagannath et al. 2018; Sasai & Hirao, 2001).

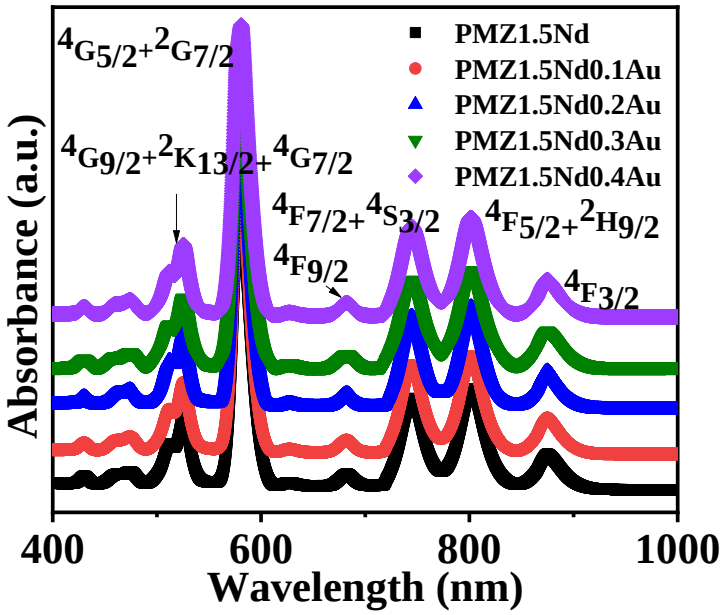

Figure 3. Absorption spectra of prepared sample

PL spectrum

Up-conversion (UC) photoluminescence, excited at 580 nm ($^4G_{7/2}\rightarrow{}^4I_{9/2}$) is manifest in Figure 3. The excitation wavelength (580 nm) is selected based on excitation spectra that depicts highest intensity for UC process. Six prominent emission bands are observed located around 420, 445, 460, 484, 515 and 545 nm corresponding to transition $^2P_{1/2}\rightarrow{}^4I_{9/2}$, $^2D_{5/2}\rightarrow{}^4I_{11/2}$, $^2P_{1/2}\rightarrow{}^4I_{11/2}$, $^2D_{5/2}\rightarrow{}^4I_{13/2}$,$^2K_{15/2}$,$^4G_{7/2}\rightarrow{}^4I_{11/2}$,$^4I_{9/2}$ and $^2D_{5/2}\rightarrow{}^4I_{15/2}$ respectively. Emission band of present data matched with previous studies (Bolundut et al., 2017; Som & Karmakar, 2009; Stanley et al., 1993). Glass incorporated with 0.1 mol% of Au NPs shows the optimum enhancement, ascribed to local field effect of Au NPs in the vicinity of Nd^{3+} ions (Ghoshal et al., 2015). Even frequently mention as possible mechanism in assisting UC PL improvement, energy transfer process from Au→ Nd is less likely to occur due to short plasmon lifetime of Au NPs compare to Nd^{3+} ion (Dousti et al., 2014). Emission band near expected plasmon band of Au NPs (565–597nm) may promote more inverse population responsible for PL action, thus green emission (545 nm) enhanced better than blue emission (420 nm) (Ghoshal et al., 2015). Meanwhile the appearance of luminescence quenching for sample contains over 0.1 mol% of Au NPs is thought associated with re-absorption of SPR which extend plasmon band over the Nd^{3+} ion emission band (Ghoshal et al., 2015). Random distribution of Au NPs generate random polarized distribution or plasmon mode (transverse and longitudinal mode) which may cancel each other by superimposed and shifted the plasmon band away from the emission band of Nd^{3+} ions [23]. Present results discern that Au NPs at different concentration inside the glass play a dynamic role in modifying the fluorescence behaviour of Nd^{3+} ions which the information accumulated may assist developing better optical material.

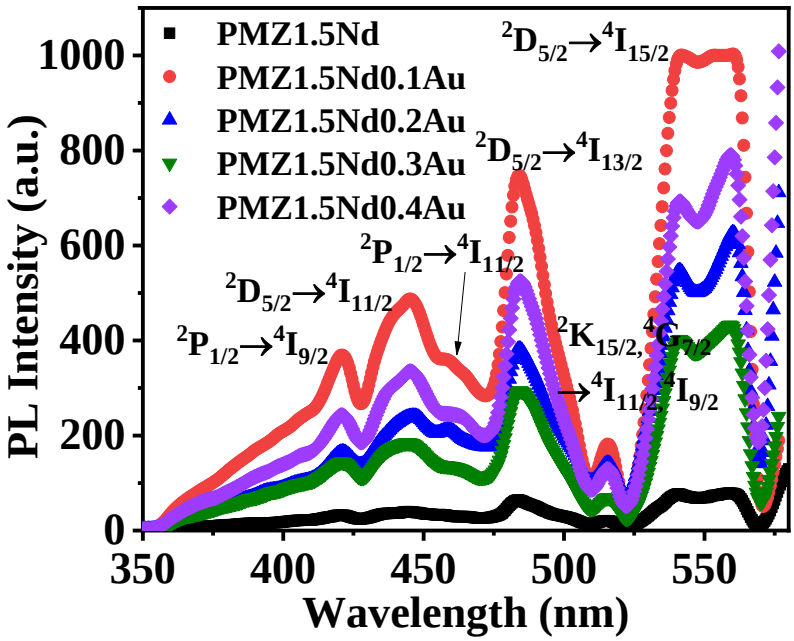

Figure 3. UC PL of prepared samples

CONCLUSION

Impact of Au NPs inclusion on optical properties of magnesium zinc sulfo-phosphate glasses were scrutinized. The glasses were prepared via melt-quenching technique and characterized. Crystalline plane of Au NPs inside the glass is undetectable via XRD and presence of Au NPs embedded inside the glass is confirmed via HRTEM imaging. The position of Nd^{3+} absorption bands remain unchanged with addition Au NPs, however slight change of absorbance probably due modification of local area surrounded Nd^{3+} ions. Glass contains 0.1 mol% of Au NPs revealed highest PL enhancement due local field effects induces by SPR that promote excitation rate of Nd^{3+} ions. Results suggest that new composition of glass could be useful in determine appropriate configuration to develop better optical and solid state laser materials.

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