Tuning Surface Plasmon Resonance Peak of Glass Containing Metallic Nanoparticles

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Abstract. Recent development in various host glasses has a beneficial feature for its application in optical devices. This present work is done by incorporating TiO₂ metallic nanoparticles (NPs) in glass matrix due to their surface roughness and plasmonic properties as well as to overcome the limitation of rare earth ions in stimulating emission. A series of tellurite glass is prepared with composition of (70−x−y)TeO₂−20ZnO−9Na₂O−1Er₂O₃−(x)TiO₂, where x= 0, 0.1, 0.2 and 0.3 mol% via melt-quenching method. In addition, glass batch without erbium content is prepared in order to identify the presence of surface plasmon resonance (SPR) peak of metallic nanoparticles. Glass samples are characterized by using X-ray diffraction (XRD), Ultraviolet-Visible spectroscopy (UV-Vis) and Transmission electron microscopy (TEM). XRD pattern confirms the amorphous structure of glass. UV-VIS spectra of glass with erbium content shows the appearance of seven absorbance peaks represent the transitions of erbium ion from ground state to excited state. Glass sample without erbium content shows the appearance of plasmon peak in range of 554 nm to 555 nm due to contribution of titanium nanoparticles. TEM image confirmed the presence of titanium NPs with Gaussian distribution having mean aspect ratio of 1.5.

1. Introduction

Rare earth doped glasses are exponentially growing due to their potency of enhancing optical and structural properties of glasses [1-2]. This study is focusing on the incorporation of metallic NPs in rare earth doped glasses as it can overcome the limitation of the Er³⁺ small absorption and emission cross section [3]. Tellurite based-glass is used as the host glass for its promising feature such as wide transmission range, high transparency, high earth ion solubility, good thermal stability and chemical durability [4].

Titanium is introduced apart from silver and gold as these elements are excellent in chemical stability as well as mediated strong surface SPR effect. This metallic NPs acquired the properties to exhibit SPR effect due to its surface roughness and plasmonic properties [5], and is attractive for plasmonic and photonic application. In this work, we report the effect and improvements of TiO₂ NPs embedded erbium-doped tellurite glasses in its absorption properties. The variations in physical and spectroscopic properties of glass are observed and analysed.
2. Materials and method

Table 1 shows a series of glass with erbium content of composition \((70 - x - y)\) \(\text{TeO}_2 - 20\text{ZnO} - 9\text{NaO}_2 - 1\text{Er}_2\text{O}_3 - (x)\) \(\text{TiO}_2\) where \(x = 0.0, 0.1, 0.2\) and \(0.3\) in mol%. Table 2 shows a series of glass without erbium content of composition \((70 - x - y)\) \(\text{TeO}_2 - 20\text{ZnO} - 9\text{NaO}_2 - (x)\) \(\text{TiO}_2\) where \(x = 0.0, 0.1, 0.2\) and \(0.3\). All glass samples are synthesized via melt-quenching method. The doping levels of \(\text{Er}^{3+}\) in the first series of glasses are kept low in order to avoid dipolar interaction. Analytical grade starting materials of tellurium dioxide (\(\text{TeO}_2\), purity 99%) from Acros, zinc oxide (\(\text{ZnO}\), purity \(\geq 99\%\)), sodium oxide (\(\text{Na}_2\text{O}\), purity 80%), erbium III oxide (\(\text{Er}_2\text{O}_3\), purity \(\geq 99.99\%\)) and titanium IV oxide (\(\text{TiO}_2\), purity \(\geq 99.5\%\)) from Sigma Aldrich are milled for 30 minutes to obtain a homogeneous powder. A platinum crucible containing all constituent powder is placed inside the electrical furnace at 950°C for 20 minutes. Upon the complete molten state is achieved, the melt is poured into a mould and transferred to another furnace and cooled down at room temperature for two days. The glass is then cut for optical measurements. The amorphous nature of glass is verified by using PANalytical X’Pert 3 MRD using Cu radiations (\(\lambda = 1.54\) Å) operated at 40kV and 30mA with scanning angle of \(2\theta\) ranging between 5° and 80°. Transmission electron microscope (TEM) Tecnai G² F20 is used to investigate the nucleation of titanium nanoparticles. Room temperature optical absorption spectra are recorded by using Agilent Cary 60 spectrophotometer for a wavelength in range of 190 – 1100 nm.

### Table 1. Composition of synthesized glass samples with erbium content (mol%).

| Glass code | \(\text{TeO}_2\) | \(\text{ZnO}\) | \(\text{Na}_2\text{O}\) | \(\text{Er}_2\text{O}_3\) | \(\text{TiO}_2\) |
|------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| TZNE       | 70              | 20              | 9               | 1               | 0               |
| TZNETi0.1  | 69.9            | 20              | 9               | 1               | 0.1             |
| TZNETi0.2  | 69.8            | 20              | 9               | 1               | 0.2             |
| TZNETi0.3  | 69.7            | 20              | 9               | 1               | 0.3             |

### Table 2. Composition of synthesized glass without erbium content (mol%).

| Glass code | \(\text{TeO}_2\) | \(\text{ZnO}\) | \(\text{Na}_2\text{O}\) | \(\text{Er}_2\text{O}_3\) | \(\text{TiO}_2\) |
|------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| TZN        | 70              | 20              | 9               | -               | 0               |
| TZNTi0.1   | 69.9            | 20              | 9               | -               | 0.1             |
| TZNTi0.2   | 69.8            | 20              | 9               | -               | 0.2             |
| TZNTi0.3   | 69.7            | 20              | 9               | -               | 0.3             |

3. Results and discussion

Figure 1 shows the XRD pattern for glass containing erbium content (TZNE, TZNETi0.1, TZNETi0.2 and TZNETi0.3 glass). The typical broad hump is observed between 25° to 33° confirms the amorphous nature of glass without any appearance of sharp crystallization peak.
The UV-Vis absorption spectra of all glass samples are shown in Figure 2(a) comprised of seven prominent absorption bands centered at 450, 491, 523, 544, 653, 799 and 975 nm corresponding to the transitions of erbium from ground state to excited state which represent by \( ^{4}I_{15/2} \rightarrow ^{4}F_{9/2}, \) \( ^{4}I_{15/2} \rightarrow ^{4}F_{7/2}, \) \( ^{4}I_{15/2} \rightarrow ^{2}H_{11/2}, \) \( ^{4}I_{15/2} \rightarrow ^{4}S_{3/2}, \) \( ^{4}I_{15/2} \rightarrow ^{4}F_{5/2}, \) \( ^{4}I_{15/2} \rightarrow ^{2}I_{9/2}, \) \( ^{4}I_{15/2} \rightarrow ^{2}I_{7/2} \) and \( ^{4}I_{15/2} \rightarrow ^{4}I_{9/2} \), respectively. The UV-Vis absorption is dependent on the size of the added NPs [6]. From the figure, an addition of titanium NPs in glass matrix causes a red shift at the absorption edge due to the generation of non-bridging oxygen (NBOs) [7-8]. However, there is no appearance of plasmon band in the samples containing both titanium NPs and erbium ions (Figure 2(a)) due to the overlapping of the plasmon band with erbium peaks. The absorption spectra of Er\(^{3+}\) ions exhibiting several bands in the visible region overshadow the plasmon band of titanium NPs [19].

To precisely locate the plasmon band, four glass samples with same amount of titanium and without erbium content are prepared. Figure 2(b) shows the appearance of weak plasmon peak of titanium NPs for glass without erbium content. A weak plasmon band is observed in the range between 554 nm to 555 nm. The presence of plasmon band confirms the existence of titanium NPs which stimulating the SPR effect [9-10]. The resonance between coherent oscillation of surface conduction electron of titanium NPs and incident electromagnetic radiation manifested the occurrence of plasmon absorption band [11-12]. The SPR band can be tuned by varying the concentration of NPs [13]. Refer to Figure 2(b), increasing the concentration of TiO\(_2\) led to the red shift of plasmon peak due to the increasing mean particle diameter [14-15].
Figure 2. (a) UV-Vis absorption spectra of glass samples in the range of 380-1100 nm and (b) SPR band positions of TiO$_2$ nanoparticles.

Figure 3 shows the transmission electron microscopy (TEM) image of TZNETi0.3 glass sample. The appearance of non-spherical black spots as shown by the arrows represents the distribution of titanium NPs in glass matrix. Figure 4(a) and 4(b) shows the round up size distribution of titanium NPs exhibit diameter of longitudinal and transverse axis of 8 – 21 nm and 6 – 11 nm, respectively. Table 4 shows the aspect ratio, $R$ which can be defined as (longitudinal, $L$/ transverse axis, $D$).

Aspect ratio is defined as $R = L/D$, where $L$ is the major axis and $D$ is the minor axis [16-17]. Meanwhile, Figure 5 shows the corresponding histogram for the aspect ratio of TZNETi0.3 glass sample. The mean aspect ratio (major axis/ minor axis) of NPs in TZNETi0.3 glass sample is lies in between of 1.00 to 2.250. Generally, the anisotropic shaped-like NPs with sharp edges in the form of ellipsoids, nanorods and triangles exhibits more potential for optical coupling to achieve nanometal enhanced optical interaction as reported by Som and Karmakar [18]. However, in present study the NPs distribute in glass matrix are found in form of non-spherical shape with different aspect ratio.

Figure 3. TEM image of TZNETi0.3 glass sample.
Figure 4. Round up size distribution of titanium NPs in TZNETi0.3 glass for (a) longitudinal axis and (b) transverse axis.

Table 3. Aspect ratio of TZNETi0.3 glass.

| No. of particles | Longitudinal axis, $L$ (nm) | Transverse axis, $D$ (nm) | Aspect ratio | No. of particles | Longitudinal axis, $L$ (nm) | Transverse axis, $D$ (nm) | Aspect ratio |
|------------------|----------------------------|---------------------------|--------------|------------------|----------------------------|---------------------------|--------------|
| 1                | 17.059                     | 9.412                     | 1.812        | 16               | 9.412                     | 7.059                     | 1.333        |
| 2                | 12.941                     | 8.823                     | 1.467        | 17               | 10.000                    | 7.059                     | 1.417        |
| 3                | 10.588                     | 10.000                    | 1.059        | 18               | 15.882                    | 7.059                     | 2.250        |
| 4                | 9.412                      | 6.471                     | 1.454        | 19               | 12.353                    | 7.647                     | 1.615        |
| 5                | 7.647                      | 6.471                     | 1.154        | 20               | 9.412                     | 5.882                     | 1.600        |
| 6                | 11.765                     | 8.235                     | 1.429        | 21               | 12.941                    | 7.647                     | 1.692        |
| 7                | 7.647                      | 7.647                     | 1.000        | 22               | 10.588                    | 7.059                     | 1.500        |
| 8                | 15.294                     | 8.235                     | 1.857        | 23               | 12.353                    | 8.235                     | 1.500        |
| 9                | 15.882                     | 7.059                     | 2.250        | 24               | 11.176                    | 8.235                     | 1.357        |
| 10               | 14.706                     | 9.412                     | 1.562        | 25               | 14.706                    | 11.176                    | 1.316        |
| 11               | 21.176                     | 9.412                     | 2.250        | 26               | 14.706                    | 10.588                    | 1.389        |
| 12               | 11.176                     | 6.471                     | 1.727        | 27               | 17.059                    | 8.823                     | 1.933        |
| 13               | 12.941                     | 10.000                    | 1.294        | 28               | 12.353                    | 9.412                     | 1.312        |
| 14               | 14.706                     | 7.059                     | 2.083        | 29               | 11.176                    | 10.000                    | 1.118        |
| 15               | 12.941                     | 6.471                     | 2.000        | 30               | 13.529                    | 8.235                     | 1.643        |
4. Conclusion
We established the variations in spectroscopic properties of TiO$_2$ NPs embedded in erbium-doped tellurite glasses by varying the concentration of TiO$_2$. XRD pattern confirms the amorphous structure of the glass. The absorption bands of all glass containing erbium content are found to be discerned at 450, 491, 523, 544, 653, 799 and 975 nm. The SPR band of titanium NPs for glass without erbium content is probed between 545 nm to 555 nm. This is due to the localised surface plasmon resonance is mediated by the contribution of TiO$_2$ nanoparticles in glass matrix. The TEM image confirms the presence of titanium NPs with aspect ratio ranges from 1.00 to 2.250.

5. References
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