Linear and Nonlinear Optical Efficiency of Novel Neodymium Nanoparticles Doped Tellurite Glass for Advanced Laser Glass

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Abstract

The determination of linear and nonlinear optical efficiency of glass materials is crucial in extensive optical applications especially the laser glass. Nanoparticles appear to be an excellent dopant to improve the efficiency of laser glass. In this paper, the novel neodymium nanoparticles (NPs) doped tellurite glass had been fabricated for the first time via melt-quenched technique. The existence of nanoparticles in the glass network was proved by Transmission Electron Microscope (TEM) image with an average size of 20 nm. The structural parameter of TeO$_3$ non-bridging oxygen was determined by FTIR analysis. The optical parameters of neodymium NPs doped tellurite glass were characterized by UV-Vis spectrometer, photoluminescence and Z-scan technique. The optical band gap energy of the glass network was reduced in the range of 3.178 - 3.209. The upconversion emission of the laser glass excited at 800 nm was found in the ultraviolet region. The optical efficiency of neodymium NPs doped tellurite glass exhibited excellent properties for its application in laser glass.

Keywords: neodymium, nanoparticles, tellurite oxide, laser glass

INTRODUCTION

Rare earth doped laser glass had attracted extensive of attentions due to its high optical efficiency. Trivalent rare-earth (RE$^{3+}$) produces an intense luminescence in the region of ultraviolet, visible and infrared. Moreover, the upconversion emission can be produced by RE$^{3+}$ from the excitation of two or more near infrared photons which is highly beneficial to the laser glass [1]. The special characteristic of RE$^{3+}$ is the sharp spectral and emission lines which is due to the 4f-4f orbital interactions surrounded by the crystal field [2]. Hence, the use of RE$^{3+}$ is very important to increase the optical capability of laser glass.
RE$^{3+}$ doped phosphate glass had been produced widely in the industry for the application of fiber laser and laser glass. Phosphate oxide is known to have high solubility, high emission cross section and longer emission lifetime with rare earth oxide [3]. However, the phosphate glass has low Stark splitting effect which leads to thermal disadvantages. As a consequence, RE$^{3+}$ doped phosphate glass has difficulty to produce high laser power at room temperature. Meanwhile, RE$^{3+}$ doped aluminosilicate glass shows good thermal properties and high optical efficiency [4]. However, RE$^{3+}$ doped aluminosilicate glass needs high melting temperature for the glass production and complicated OH$^-$ quenching problems.

Tellurite glass is a promising candidate to be used in laser glass host materials due to its high solubility with RE$^{3+}$, low melting temperature and high Stark splitting effect [5]. The formation of tellurite based glass without any contribution of the modifiers is nearly impossible. Zinc oxide and borate oxide are the best choice of modifiers to stabilize the glass formation and increase the strength of the glass. Zinc oxide offers the reduction of phonon energy and increase the stability of glass materials to achieve high efficiency of laser glass [6]. Furthermore, the introduction of borate oxide in the glass system increase the refractive index and nonlinear optical properties.

Neodymium oxide has extensive of applications such as lasing materials, broadband amplifier and laser glass. The broad emission range from ultraviolet to infrared is one of the unique properties of neodymium oxide [7]. Neodymium doped phosphate laser glass had been used in many commercial applications, however, the phosphate host materials need to be substituted with more suitable host materials. The combination of tellurite oxide and neodymium oxide offers novel and high optical efficiency in laser glass [8]. The size of particles affect greatly to the optical performance of laser glass. The inclusion of nanoparticles in the glass materials enhance the electric field around rare earth and produce quantum effect to increase the optical efficiency of the glass system [9]. Based on this attributes, the neodymium nanoparticles is used to improve the optical properties of the laser glass.

In this paper, the investigations on optical properties of neodymium NPs doped tellurite laser glass are established, for the first time to the best of our knowledge, based on optical absorption, upconversion emission and nonlinear optical properties. To do so, we developed the neodymium NPs doped tellurite laser glass which is stable against crystallization and maintaining the existence of nanoparticles in the glass system to achieve high optical efficiency. The glass system with excellent upconversion emission and high optical nonlinearity has been achieved. In this work, several sharp absorption lines has been realized using UV-Vis spectrometer to determine the possibility of excitation values to be used in luminescence emission. In addition, we introduce the new host materials, tellurite oxide for laser glass to replace the current phosphate laser glass, resulting in improved stability, rare-earth oxide compatibility and optical efficiency. Together our findings point to the potential of high-efficient neodymium NPs doped tellurite glass to be commercialized as advanced laser application.

**METHODOLOGY**

A series of neodumium NPs doped tellurite glass with chemical composition of \(\{(\text{TeO}_2)_{0.7} (\text{B}_2\text{O}_3)_{0.3}\}_{0.7} (\text{ZnO})_{0.3} \times (\text{Nd}_2\text{O}_3 \text{ NPs}) \times \) (where \(x = 0.005, 0.01, 0.02, 0.03, 0.04 \) and 0.05 had been fabricated via melt-quenching method. The chemical reagents for all raw materials are obtained from Alfa Aesar product. The neodymium nanoparticles oxide, Nd$_2$O$_3$ NPs (with size of particles ~15 nm), zinc oxide, ZnO and borate oxide, B$_2$O$_3$ were mixed thoroughly in an alumina crucible. The mixture of the raw materials was pre-heated at 400 °C to remove excessive OH$^-$ in the mixture. The mixture was then
heated at 900 °C for melting process. The molten mixture was poured in a cylindrical stainless steel mould and allowed to cool down at room temperature.

The XRD measurement was performed using X’pert pro pan analytical instrument. Transmission Electron Microscope (TEM) LEO 912AB was used to investigate the nano-size particles in the glass network. The optical absorption analysis was carried out using UV-Vis spectrometer (Shimadzu, model: UV 1650) at room temperature in 190 – 1100 nm of wavelength. The PerkinElmer LS 55 Luminescence spectrometer was used to determine the emission spectra from the glass system at certain excitation value. The optical nonlinearities such as nonlinear refractive index and nonlinear optical absorption were carried out using the Z-scan technique.

RESULTS AND DISCUSSION

Structural analysis: XRD, FTIR and TEM

The structure of the glass system is determined by using X-ray Diffraction spectra analysis. Figure 1 shows the X-ray diffraction spectra of neodymium NPs doped tellurite glass series. It can be seen that the glass series show broad diffusion at lower scattering angles with an obvious broad hump between 2θ = 20° and 40°. This confirmed the existence of structural disorder which in turn correspond to the amorphous structural arrangement of the glass system. The non-existence of sharp peaks in Figure 1 is related to the absence of crystalline structural arrangement in the glass network.

The functional groups and structural parameter of the glass series are determined by using Fourier Transform Infrared (FTIR) analysis. Figure 2 reveals the transmission spectra of neodymium NPs doped tellurite glass in the range 280 – 3000 cm⁻¹. As depicted in Figure 2, several absorption bands are shown corresponding to the local structure of the glass network. The band assignments of neodymium NPs doped tellurite glasses are given in Table 1. The band of TeO₂ structural units are positioned in the region of 600 – 700 cm⁻¹ [10]. After the glass formation, tellurite oxide is established in two structural units which are trigonal pyramidal, TeO₃, and trigonal bipyramidal, TeO₄ [11]. The first functional group of the glass series are located in the range 600 – 650 cm⁻¹ which correlate to trigonal bipyramidal, TeO₄ structural unit [11]. Meanwhile, the second functional group of the glass series are located in the range 650 – 700 cm⁻¹ which correspond to trigonal pyramidal, TeO₃ structural unit [11]. The presence of TeO₃ in the glass system indicates the existence of non-bridging oxygen. The borate oxide structural units can be defined in three clusters. The first functional cluster is located in the range 600 – 800 cm⁻¹ which correspond to bending vibrations of various borate arrangement. The second functional cluster is located in the range 800 – 1200 cm⁻¹ which correspond to B-O stretching of tetrahedral BO₄ units. The third functional cluster is located in the range 1200 – 1800 cm⁻¹ which are due to B-O stretching of trigonal BO₃ units. It can be seen from the transmission spectra that the borate units of the glass series exists in the range of 1225 – 1339 cm⁻¹ which indicate the B-O stretching vibration of BO₃ units in metaborate, pyborate and orthoborate groups [12]. The absence of zinc oxide transmission band shows that the zinc lattice is completely broken down after the glass formation. The transmission spectra of neodymium NPs is not available in the spectra which are due to the low concentration of neodymium NPs.
The transmission electron microscopy of neodymium NPs is depicted in Figure 3 which shows the illustration of nanoparticles in the glass network. The structural characteristics of raw materials of neodymium NPs before the formation of glass system are three-dimensional spherical shapes and the average size is 15 nm. The presence of neodymium NPs after the glass formation is shown in Figure 3. It can be seen that there is no changes on the shape of nanoparticles and the average size is slightly increase to 20 nm. The main contributor to the increasing size of nanopartilces is from the Oswald ripening effect in which the smaller size of particles is diffused to larger size of particles.

Figure 1. XRD spectra of neodymium NPs doped tellurite glasses
Figure 2. FTIR spectra of neodymium NPs doped tellurite glasses

Table 1. Assignments of FTIR spectra of neodymium NPs doped tellurite glasses

<table>
<thead>
<tr>
<th>No</th>
<th>0.005</th>
<th>0.01</th>
<th>0.02</th>
<th>0.03</th>
<th>0.04</th>
<th>0.05</th>
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</tr>
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<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Trigonal B-O bond stretching vibrations in isolated trigonal BO₃ units [12]</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Trigonal B-O bond stretching vibrations of BO₃ units from boroxyl groups [12]</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TeO₃ group are exists in all tellurite containing glass [12]</td>
</tr>
</tbody>
</table>
Figure 3. TEM image of neodymium NPs doped tellurite glasses

Optical absorption spectra

Figure 4 illustrates the optical absorption spectra of neodymium NPs doped tellurite glasses recorded at room temperature in the range 200 – 1000 nm. As shown in Figure 4, the optical absorption edges are not sharply defined which is in accordance with amorphous nature of the glass system. The absorption spectra consist of several in-homogenously broadened bands due to the f-f interaction of Nd$^{3+}$ ions [13]. It can be seen from Figure 4 that the neodymium NPs doped tellurite glass possesses several number of sharp peaks which indicates the excitation of electrons from the ground state $^4I_{9/2}$ to the excited states $^2F_{9/2}$, $^4G_{5/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$ and $^4F_{3/2}$. The absorption spectra revealed that the intensity of the absorption band increases with increasing concentration of neodymium NPs.
Figure 5 shows the Tauc’s plot of $(\alpha h\nu)^{1/2}$ for indirect allowed transitions of the glass series. The values of optical band gap, $E_{\text{opt}}$ of neodymium NPs doped tellurite glasses have been estimated by extrapolating the curves and the obtained results are shown in Figure 6 and listed in Table 2. Figure 6 shows that that the value of optical band gap decreases with an increase of neodymium NPs concentrations. The change in band gap is attributed to the shifts of the valence and conduction band from each other. The decreasing value of optical band gap energy by increasing the neodymium NPs content can be understood in terms of the structural change that are taking place [14].

The increasing concentration of Nd$^{3+}$ ions results in increasing number of non-bridging oxygen. This is supported by the formation of trigonal pyramidal, TeO$_3$ structural units in the glass system as shown in FTIR result. The role of non-bridging oxygen contributes to the increasing number of free electrons which are less tightly bound to the nuclear charge. The free electrons possess high tendency to excite from the valence band to the conduction band. Hence, the existence of non-bridging oxygen leads to the reduction of optical band gap energy. Furthermore, the existence of trivalent electrons of neodymium ions affects the structure of the glass system by increasing number of free electrons which leads to decreasing number of band gap energy [15]. Moreover, the decline in $E_{\text{opt}}$ is caused by the structural change from TeO$_3$ non-bridging oxygen atoms, the high field strength of neodymium ions and high polarizing power of non-bridging oxygen. The information of rigidity in the glass matrix is explained by the value of Urbach energy.

The value of Urbach energy of neodymium NPs doped tellurite glass are tabulated in Table 2. The increasing trend of Urbach energy is found with increasing concentration of neodymium NPs. The increment of Urbach energy indicates that the defect concentration in the glass system increases with
the rise in neodymium NPs. Furthermore, the characterization of the degree of disorderliness is made by using the Urbach energy value. The Urbach energy indicates the extent of the absorption edge smearing due to disordering caused by structural features like lack of long range order as well as those induced by external factors such as density fluctuations, phonon-assisted indirect electron transitions and charged impurities [16]. Hence, the increasing number of Urbach energy indicates that the extension of states of tails into the mobility gap increases with increasing concentration of neodymium NPs.

![Figure 5. $(\alpha \hbar \omega)^{1/2}$ versus photon energy $\hbar \omega$ of neodymium NPs doped tellurite glasses](image)

**Table 2.** Optical band gap ($E_{\text{opt}}$) and Urbach energy ($\Delta E$) of neodymium NPs doped tellurite glass system

<table>
<thead>
<tr>
<th>Mol fraction</th>
<th>$E_{\text{opt}}$ (eV)</th>
<th>Urbach energy, $\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neodymium Nanoparticles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>3.209</td>
<td>0.316</td>
</tr>
<tr>
<td>0.01</td>
<td>3.201</td>
<td>0.312</td>
</tr>
<tr>
<td>0.02</td>
<td>3.198</td>
<td>0.314</td>
</tr>
<tr>
<td>0.03</td>
<td>3.193</td>
<td>0.316</td>
</tr>
<tr>
<td>0.04</td>
<td>3.179</td>
<td>0.318</td>
</tr>
<tr>
<td>0.05</td>
<td>3.178</td>
<td>0.323</td>
</tr>
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</table>
Electronic polarizability and oxide ion polarizability

The trend of electronic polarizability of neodymium NPs doped tellurite glasses calculated in this study are given in Table 3 and plotted in Figure 7. Figure 7 shows the compositional dependence of electronic polarizability. The increasing trend of electronic polarizability is displayed as the concentration of neodymium NPs increases. The deformability of electron cloud is affected by the number of non-bridging oxygen exists in the glass system. Non-bridging oxygen consists of free electrons from the lone pair which are less tightly bound to the nuclear charge. Consequently, the free electrons are easily polarized as the electrical field is penetrated through the medium. The formation of non-bridging oxygen ions is confirmed from the formation of TeO$_3$ and BO$_3$ structural units as shown from FTIR results. The number of non-bridging oxygen ions is increased as the concentration dopant increases. The increment number of non-bridging oxygen leads to the raised number of free electrons in the glass system. Hence, the electronic polarizability is increased as the concentration of dopant increases.

The result of oxide ion polarizability of neodymium NPs doped tellurite glasses is listed in Table 3 and plotted in Figure 7. The non-linear trend of oxide ion polarizability values is found in the glass series. The lowest value of oxide ion polarizability of neodymium NPs doped tellurite glasses is found at 0.03 mol fraction. Zinc oxide possesses dual nature which acts as a modifier or former glass at a certain amount of concentration. Consequently, zinc oxide may acts as former glass at 0.03 mol fraction which leads to the decreasing value of oxide ion polarizability. Dimitrov and Komatsu stated that the strong cationic charge of former glass leads to the high value of unit field strength [17]. The large value of unit field strength affects strongly to the electron charge density of surrounding oxide ions. Hence, the high concentration of former glass with strong cationic charge leads to the decreasing value of oxide ion polarizability. Moreover, zinc oxide, Zn$^{4+}$ possesses high cationic charge with strong unit field strength which leads to the reduction value of oxide ion polarizability. The maximum value
of oxide ion polarizability is found at 0.05 mol fraction of neodymium NPs. The increasing trend of oxide ion polarizability is due to the strong anionic charge of tellurite, Te$^{2-}$ which possesses low unit field strength and high refractive index.

Table 3. Electronic polarizability and oxide ion polarizability of neodymium NPs doped tellurite glasses

<table>
<thead>
<tr>
<th>Mol fraction</th>
<th>Electronic Polarizability, $\alpha_m$(Å)</th>
<th>Oxide ion polarizability, $\alpha_{o^2-}$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neodymium Nanoparticles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>6.091</td>
<td>2.710</td>
</tr>
<tr>
<td>0.01</td>
<td>6.139</td>
<td>2.709</td>
</tr>
<tr>
<td>0.02</td>
<td>6.252</td>
<td>2.717</td>
</tr>
<tr>
<td>0.03</td>
<td>6.272</td>
<td>2.678</td>
</tr>
<tr>
<td>0.04</td>
<td>6.394</td>
<td>2.690</td>
</tr>
<tr>
<td>0.05</td>
<td>6.655</td>
<td>2.774</td>
</tr>
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</table>

Figure 7. Electronic polarizability and oxide ion polarizability versus wavelength of neodymium NPs doped tellurite glasses

Optical basicity and metallization criterion

The obtained data of optical basicity of neodymium NPs doped tellurite glass series are tabulated in Table 4 and plotted in Figure 8. The large value of optical basicity in the glass series revealed that the glass system are more basic. Oxide ions in the glass system act as a Lewis base which donate electrons to the surrounding cations. The high degree of donating ability of oxide ions influence strongly to the acid-base characteristic. Furthermore, Duffy proposed that the optical basicity is related to the polarization state of oxide ions in the glass system [18]. Low polarizing cations in the glass system contributes to the strong donating ability of oxide ions to the surroundings cations. Based on the previous data of oxide ion polarizability, there is a good agreement with optical basicity.
The non-linear trend of optical basicity along with concentration are found in the glass series. The non-linear trend of optical basicity is caused by the structural change in the glass system. Besides that, the optical basicity values are found slightly increases with increasing concentration of neodymium NPs. This trend can be explained by comparing the value of optical basicity of single element in the glass system. In conditions of glass former and modifier, former oxides should less basic compare with modifier oxides. The addition of modifier oxide to former oxide results the modification reaction to be the acid-base reaction in which the acidic region of former oxide is approached by modifier oxide ion in order of decreasing acidities [19].

The values of optical basicity of neodymium NPs doped tellurite glass indicate that the addition of modifier oxide reduces the acidity of former oxide and increase the basicity of the glass system. The values of optical basicity of each oxide are: \( \lambda(\text{Nd}_2\text{O}_3) = 1.014, \lambda(\text{TeO}_2) = 0.93, \lambda(\text{ZnO}) = 0.82, \lambda(\text{B}_2\text{O}_3) = 0.425 \) [20]. As can be seen the optical basicity of borate oxide is small and the value is below 0.75.

The mixture of former and modifier oxides results in the optical basicity of borate oxide to increase. This is due to the higher number of optical basicity in neodymium NPs oxide (1.014), tellurium oxide (0.93) and zinc oxide (0.82). Tellurite as the glass former is the primary role of the acid-base property of the glasses has a significant effect. The increasing number of optical basicity means that the ability of oxide ions to donate electrons to surrounding cations is increased.

The obtained values of metallization criterion of neodymium NPs doped tellurite glasses are tabulated in Table 4 and plotted in Figure 8. The results show that the values of metallization criterion are decreased along with concentration. The reduction in metallization criterion shows the metallizing of the glass samples which leads to tailing and shrinking of the band gap [21]. Metallization criterion depends on the band gap of the glass system. The decrement value of optical band gap indicates that the valence and conduction band are broadened. This effect will lead to the metallization of the glass system.

The direct relationship between metallization criterion and the optical band gap is found by comparing their values. The increasing number of optical band gap leads to the reduction of metallization criterion. The result is in accordance with metallization criterion calculated by Dimitrov and Sakka [22]. The glass samples with a small value of metallization criterion indicate that the chemical bonds with large ionic contribution are formed in the glass system. The large ionicity of the glass samples is proved from the previous data of high optical basicity and high oxide ion polarizability of neodymium NPs doped tellurite glass.
Linear and Nonlinear Optical Efficiency of Novel Neodymium Nanoparticles Doped Tellurite Glass for Advanced Laser Glass

**Figure 8.** Optical basicity and metallization criterion versus concentrations of neodymium NPs doped tellurite glasses

**Table 4.** Optical basicity and metallization criterion of neodymium NPs doped tellurite glasses

<table>
<thead>
<tr>
<th>Mol fraction</th>
<th>Optical basicity, ( \lambda )</th>
<th>Metallization criterion</th>
</tr>
</thead>
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<tr>
<td>Neodymium Nanoparticles</td>
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<td></td>
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<tr>
<td>0.005</td>
<td>1.191</td>
<td>0.518</td>
</tr>
<tr>
<td>0.01</td>
<td>1.190</td>
<td>0.517</td>
</tr>
<tr>
<td>0.02</td>
<td>1.190</td>
<td>0.514</td>
</tr>
<tr>
<td>0.03</td>
<td>1.175</td>
<td>0.506</td>
</tr>
<tr>
<td>0.04</td>
<td>1.173</td>
<td>0.501</td>
</tr>
<tr>
<td>0.05</td>
<td>1.170</td>
<td>0.485</td>
</tr>
</tbody>
</table>

**Upconversion emission spectra**

The upconversion emission spectra excited at 800 nm of wavelength for neodymium NPs doped tellurite glass series are depicted in Figure 9. The ultraviolet emission peaks have been observed for all the glass samples under excitation wavelength in the range 380 – 390 nm. These emission peaks are attributed to \( ^2D_{3/2} \rightarrow ^4I_{9/2} \) transition. It is observed from the emission peaks that there are a shift and emission broadening along with neodymium NPs concentrations. The occurrence of the shift in emission peaks is due to several processes which are: a. band gap renormalization, b. changes in donor-acceptor pair, c. impurity band formation and d. surface states and/or the potential distribution in the crystal [23]. The emission peaks of neodymium NPs show to have blue shifts at 0.01 and 0.03 mol fraction and a red shift at 0.02 mol fraction. The blue shift observed from the spectra is usually related to the quantum confinement effect in nanoparticles. The strong effect of quantum confinement leads to the increasing number of free charge carriers and oscillator strength of the glass system. Consequently, the emission peaks tend to shift to the shorter wavelength (blue shift). Another possibility is that, the blue shift is due
to the coulomb interactions which is related to donor-acceptor pair [23]. The red shift at 0.02 mol fraction of neodymium NPs dopant is due to the potential fluctuations that leads to the formation of vacancies, impurities, dangling bonds and structural defects. The influence of nanoparticles induces the structural defects and as a consequence, the red shift is obviously observed on the emission peak. The quenched in emission peaks for neodymium NPs is related to the energy transfer and cross-relaxation process.

The combinations of mechanisms such as energy transfer, cross-relaxation process, excited state absorption process and nonradiative relaxation in upconversion of neodymium NPs are explained in detail by using the schematic diagram as illustrated in Figure 10. The 800 nm of energy excites Nd$^{3+}$ ions from the ground state, $^4$I$_{9/2}$ level to the excited states, $^2$H$_{9/2}$ level. The ions at $^2$H$_{9/2}$ level undergo fast nonradiative relaxation and reach to $^4$F$_{3/2}$ level which has a greater lifetime (stability) [24]. The Nd$^{3+}$ ions at $^4$F$_{3/2}$ level are then excited to populate $^4$D$_{3/2}$ level through excitation state absorption (ESA) process

$$^4F_{3/2} + \text{a photon} \rightarrow ^4D_{3/2}.$$ 

The population of Nd$^{3+}$ ions at $^4$D$_{3/2}$ transition level are decay nonradiatively to populate $^2$D$_{3/2}$ level. The upconversion of ultraviolet emission peaks is produced by the radiative relaxations process from $^2$D$_{3/2}$ level to $^4$I$_{11/2}$ level. The strong upconversion emission of Nd$^{3+}$ is highly related to the low phonon energy of the host matrix. The intense emission peaks of neodymium NPs doped tellurite glass is located at 0.02 mol fraction. The increasing intensity of emission peaks can be explained by energy transfer process. The energy transfer process is strong in a high concentration of active Nd$^{3+}$ ions. Moreover, the efficiency of energy transfer is influence by the distance ($r_1$) or polaron radius ($r_p$) between identical Nd$^{3+}$ - Nd$^{3+}$ ions. The Nd$^{3+}$ ions in the excited states of $^4$F$_{3/2}$ transfer the energy to the adjacent Nd$^{3+}$ ions at the same level through the following mechanism:

$$^4F_{3/2} + ^4F_{3/2} \rightarrow ^2D_{3/2} + ^4I_{9/2}$$

The first Nd$^{3+}$ ion transit to the ground state and the second Nd$^{3+}$ ion excite to $^2$D$_{3/2}$ transition level. This energy transfer process is enhanced by the low phonon energy of the host glass and leads to the high population at $^2$D$_{3/2}$. The quenched of emission peaks of neodymium NPs is due to cross-relaxation process. The cross-relaxation process occurs through resonant quasi pathway of:

$$^2D_{3/2} + ^4I_{9/2} \rightarrow ^4G_{7/2} + ^4I_{15/2}$$

The above mechanisms are similar to the previous reports [25]. The energy lost while the cross-relaxation process is formed as lattice vibrations.
Figure 9. Upconversion spectra of neodymium NPs doped tellurite glasses
Factors that affect nonlinearity of refractive index are electronic polarizability, electrostriction, molecular orientation, photorefractive effect, and thermal effect [26]. Moreover, the nonlinear refractive index consists of third or higher order nonlinearity. The close aperture curves indicating the nonlinear refractive index of neodymium NPs are depicted in Figure 11. The nonlinear refraction coefficient, $\eta_0$ (cm$^2$/W) of neodymium NPs doped tellurite glass obtained in the present work are listed in Table 5. It can be seen that the Z-scan curves exhibit peak-and-valley ration which corresponds to positive nonlinear refraction ($\eta_2 > 0$) and self-focusing behavior.

The negative or positive sign of nonlinear refractive index correlate to self-defocusing and self-focusing are depended on sample properties. In the case of self-focusing, as the sample glass move closer to the focal area, the incident laser is diverged and leads to an increase in irradiance before it arrives at the focal point. As the sample arrives at the focal point, the incident laser is collimated and caused a decrease in irradiance [27]. It is observed that the distance of peak-to-valley is approximately
1.7 times of Rayleigh length from the laser source. Hence, it is confirmed that the nonlinear refractive index is caused by the third-order response.

It can be seen from the Table 5 that the nonlinear refractive index coefficient for neodymium NPs is in nonlinear variation along with dopant concentration. This variation might be due to the effect of dopant concentration. Moreover, the nonlinear refractive index for neodymium NPs are in high value. The nonlinear refractive index is related to the value of the linear refractive index. Chen et al., stated that a glass materials which has a high refractive index possess high nonlinear refractive index [28].

The maximum point of nonlinear refractive index of neodymium NPs is at 0.01 mol fraction. The increasing number of the nonlinear refractive index is highly related to the formation of [TeO\(_3\)]\(^2-\) clusters in the glass matrix. The formation of TeO\(_3\) clusters is proved from the previous FTIR spectra. The presence of lone pair in TeO\(_3\) structural units leads to an increase in polarizability. Consequently, the increment of polarizability caused an increase in the nonlinear refractive index. The reduction in the nonlinear refractive index at a certain amount of neodymium NPs is due to the effect of structural defects in the glass matrix.

**Non-linear optical absorption**

The nonlinear optical absorption is measured by using the open aperture mode from the Z-scan technique (S=1). Moreover, the nonlinear absorption can be divided into two conditions: a. saturation absorption, b. reverse saturation absorption. The existence of valley curves at focus point (Z=0) corresponds to saturation absorption, meanwhile the presence of a peak at focus point (Z=0) is ascribed to reverse saturation absorption. The valley curves indicating nonlinear absorption of neodymium NPs is shown in Figure 12. It is confirmed that the nonlinear absorption of neodymium NPs doped tellurite glass is in saturation absorption. It is observed that the optical transmission is decreased towards the laser focus (z = 0) which ascribed to the occurrence of nonlinear absorption as the laser density decreased. The presence of valley curves proved the existence of two-photon absorption (2PA) at a fix visible laser wavelength.

The obtained value of nonlinear absorption coefficient is tabulated in Table 5. It can be seen that the nonlinear absorption coefficient exhibits nonlinear variations which are due to the effect of dopant concentration. The highest value of nonlinear absorption coefficient is at 0.04 mol fraction. The increment of nonlinear absorption coefficient can be attributed to the increasing number of non-bridging oxygen in the glass matrix. Shanmugavelu et al., stated that the valence electrons in non-bridging oxygen are less stable and weakly bound to the host materials [29]. Consequently, the valence electrons are easy to deform by the laser electromagnetic field which leads to an increase in nonlinear absorption coefficient. The FTIR studies also reported that the non-bridging oxygen is increased with increasing content of neodymium NPs. Slightly decreases of nonlinear absorption coefficient are found in the glass series. This trend is attributed to the loss of a few fractions of photocarriers from the ground state [30]. Hence, when the incident laser intensity is greater than saturation intensity, the nonlinear absorption coefficient is decreased. The small value of nonlinear absorption coefficient indicates that the present glass sample is suitable for optical limiting devices.

The third order susceptibility of neodymium NPs is calculated by applying \(\eta_2\) and \(\beta\) values. Moreover, the third order susceptibility consists of real parts, \(\text{Re}(\chi)\) and imaginary parts, \(\text{Im}(\chi)\) which are obtained by using the nonlinear refractive index, \(\eta_2\) and nonlinear absorption coefficient, \(\beta\). The obtained data of third order susceptibility of neodymium NPs doped tellurite glass are tabulated in Table
5. It is observed that the third order susceptibility of neodymium NPs doped tellurite glasses exhibit nonlinear variations. The third order nonlinearity is highly related to the structural properties of the glass network.

Table 5 revealed that the highest susceptibility of neodymium NPs is at 0.04 and 0.05 mol fraction. The dependence of $\chi$ on the structure of the glass network indicates that the high intensity of $[\text{TeO}_3]$ pyramidal in the glass network enhance the value of third order susceptibility. The formation of $[\text{TeO}_3]$ pyramidal is proved from the previous data of FTIR. Moreover, Eroni et al., stated that the increase in nonlinearity of the glass system is associated with the higher ratio of oxygen-to-cation which consequently increase the polarizability of the glass system [31]. A slight decrease of third order susceptibilities for neodymium NPs doped tellurite glasses is due to the effect of dopant compositions. Moreover, the decreasing variations of third order susceptibility can be due to the substitutions of higher polarizable compounds with lower polarizable compounds in the glass network.

![Figure 11. Z-scan closed aperture curves of neodymium NPs doped tellurite glasses](image-url)
Linear and Nonlinear Optical Efficiency of Novel Neodymium Nanoparticles Doped Tellurite Glass for Advanced Laser Glass

Table 5. Nonlinear refractive index, $\eta$ of neodymium NPs doped tellurite glasses

<table>
<thead>
<tr>
<th>Mol fraction</th>
<th>Phase change, $\Delta\phi$</th>
<th>Linear absorption coefficient, $\alpha$ (x 10$^{-12}$)</th>
<th>Non-linear refractive index, $\eta$ (x 10$^{-12}$)</th>
<th>Nonlinear absorption, $\beta$ (x 10$^{-3}$)</th>
<th>Third order susceptibilities, $\chi$ (x 10$^{-6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neodymium nanoparticles</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>0.03</td>
<td>18.87</td>
<td>0.734</td>
<td>3.60</td>
<td>14.6</td>
</tr>
<tr>
<td>0.01</td>
<td>0.14</td>
<td>11.33</td>
<td>3.14</td>
<td>2.45</td>
<td>10.0</td>
</tr>
<tr>
<td>0.02</td>
<td>0.07</td>
<td>16.86</td>
<td>1.63</td>
<td>2.08</td>
<td>8.56</td>
</tr>
<tr>
<td>0.03</td>
<td>0.08</td>
<td>10.13</td>
<td>1.78</td>
<td>2.02</td>
<td>8.53</td>
</tr>
<tr>
<td>0.04</td>
<td>0.13</td>
<td>7.68</td>
<td>2.98</td>
<td>7.92</td>
<td>33.8</td>
</tr>
<tr>
<td>0.05</td>
<td>0.08</td>
<td>7.80</td>
<td>1.91</td>
<td>7.65</td>
<td>34.3</td>
</tr>
</tbody>
</table>

Figure 12. Z-scan open aperture of neodymium NPs doped tellurite glasses

CONCLUSION

In summary, the novel neodymium NPs doped tellurite glass had been successfully fabricated and characterized its optical efficiency. Based on the experimental results of UV-Vis, upconversion luminescence and Z-Scan technique, the glass series possesses sharp spectral lines in UV-Vis region, reduction trend of optical band gap, upconversion emission in ultraviolet region and high degree of optical nonlinearity. The 4f-4f orbital in neodymium NPs is the main contributor to the sharp spectral lines in UV-Vis spectra. The small size of nanoparticles reduce the value of optical band gap and leads to the increasing value of electronic polarizability. The results of optical basicity show that the glass series is tend to be more basic rather than acidic. The reduction in metallization criterion indicates the
metallizing of glass materials which is beneficial to the semiconductor materials. Double electron excitation can be found in the upconversion emission mechanism which leads to the emission at ultraviolet region. Based on these results, the novel neodymium NPs doped tellurite glass is a suitable materials for high optical efficiency of laser glass and having outstanding performance over the current commercial laser glass.

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