Nd$^{3+}$ Doped In Zinc Barium Tellurite Oxyfluoride Glasses For Laser Application

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Abstract: The tellurite glasses doped with Nd$^{3+}$ ion were prepared with the compositions $(55-x)$TeO$_2\cdot10$ZnF$_2\cdot35$BaO-xNd$_2$O$_3$ (where x = 0.00, 0.05, 0.10, 0.50 1.00 and 1.50 mol%) by the normal melt quenching technique and characterized the spectroscopic properties. The spectroscopic properties of tellurite glasses measured from the absorption and emission measurements with Judd-Ofelt analysis. The X-ray diffraction (XRD) pattern confirms the amorphous nature. UV-Vis-NIR absorption spectra of tellurite glasses divulged nine significant peaks. The absorption peaks slightly increase with increasing of Nd$^{3+}$ concentration. The NIR emission spectra at 913, 1,069 and 1,341 nm have been registered for Nd$^{3+}$ in tellurite glasses, which corresponds to the transitions originating from $^4F_{3/2}$ level to the $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ levels of Nd$^{3+}$ ion, respectively, under the excitation of 523 nm. The results indicate that the prepared glass system could be a suitable candidate for using it as laser gain media around 1,069 nm.

Keywords: tellurite glasses, Nd$^{3+}$ ion, Judd-Ofelt analysis

1. Introduction

Nowadays, glass materials have received attention. Tremendously for the development of new materials as a host for the world's rare optical and fluorescent (RE) devices and laser medium. Similarity with other glasses, tellurite glasses are very interesting due to its, low phonon energy, high reflective index high transparency, good rare earth solubility nature and low melting point. [1]

Tellurium oxide based glasses is known as the heavy metal oxide glasses, with phonon energies around 700-880 cm$^{-1}$. Unique combinations of optical and spectroscopic properties, along with their attractive environmental resistance and mechanical properties are observed for these. The most important features of the glasses are low phonon energy, low melting temperature, high solubility of rare-earth oxides, high dielectric constant, wide infrared transmittance, high linear and nonlinear refractive indices [2-4]. Accordingly, a large variety of laser glasses doped with Nd$^{3+}$ ion have been investigated with the purpose of generating efficient broadband laser emission around 1060 nm with many technological applications, which are well documented in the open literature. [5-12]

In the present work have been investigation the physical, optical and luminescence propertied of
tellurite glasses doped with varied concentrations of Nd\(^{3+}\) ion to be used as a laser application.

2. Experimental work

2.1 Glass preparation

The glasses samples were prepared using the composition (55-x)TeO\(_2\)-10ZnF\(_2\)-35BaO-xNd\(_2\)O\(_3\) (where x = 0.00, 0.05, 0.10, 0.50, 1.00 and 1.50 mol%). The chemicals are TeO\(_2\), ZnF\(_2\), BaCO\(_3\) and Nd\(_2\)O\(_3\) all of high purity (99.9%) using a normal melt quenching technique. The raw materials were mixed into 6 batches each of 15 g. The mixtures were homogeneous by grounding in an agate mortar for 1 hr. The mixed powder were melted by electrical furnace at 950°C in a alumina crucible for 1 hr. After that, take out from the furnace and poured into the preheated graphite plate. They were annealed in an oven temperature at 350°C for 3 hrs. The glass samples then were cut and polished to the dimension of 1.0×1.5×0.3 cm\(^3\) for measurements.

2.2 Measurements

Tellurite glasses were evaluated for characterization for confirm the structural by X-ray diffraction pattern, density to measure from Archimedes method using the densitometer HR-200 weighing balance. The refractive index of these samples were measured at room temperature by using Reflectivity Meter (PRM). The density, molar volume and refractive index of the samples with various concentration of Nd\(^{3+}\) ion are summarized in Table 1. The absorption spectra of tellurite glasses in the range of 400–1,000 nm were investigated in the UV-Vis-NIR regain to using a UV–3600 Shimadzu UV–VIS–NIR spectrophotometer. Photoluminescence Spectrometer (PTI, Quantum Master-300) was used to investigate the excitation and emission spectra of the samples. The J-O intensity parameters which provide significant information regarding local structure and bonding in the vicinity of Nd\(^{3+}\) ion have been calculated and reported here.

3. Results and discussion

3.1 XRD spectral analysis

Figure 1. Shown the XRD spectrum of an un-doped Nd\(^{3+}\) in glasses. The spectra do not have any continuous or discrete sharp peaks in the diffraction pattern is the spectral range 10°≤θ≤80° Only a hump about 30° demonstrated. The absence of sharp peaks authenticates the amorphous nature of present glasses.[13]
3.2 Physical properties

Table 1. Physical properties of the Nd$^{3+}$ ion doped tellurite glasses.

| Sample No. | Physical properties | Nd$_2$O$_3$ concentration (mol%) |
|------------|---------------------|---------------------------------|
|            |                     | 0.00 | 0.05 | 0.10 | 0.50 | 1.00 | 1.50 |
| 1          | Density (g/cm$^3$)   | 5.279±0.002 | 5.240±0.006 | 5.251±0.004 | 5.236±0.002 | 5.243±0.006 | 5.238±0.002 |
| 2          | Molar Volume (cm$^3$/mol) | 28.751 | 30.542 | 30.522 | 31.044 | 31.537 | 32.108 |
| 3          | Refractive index     | 1.60 | 1.75 | 1.78 | 1.82 | 1.85 | 1.86 |

Figure 2. present the variation in density ($\rho$), molar volume ($V_M$) and refractive index as a function of mol% of Nd$_2$O$_3$. The fluctuating density of glasses. The values of density are in the range of 5.236±0.002 to 5.279±0.002 g/cm$^3$, while their molar volumes ($V_M$) are in the range of 28.751 to 30.108 cm$^3$/mol. The molar volumes of glasses were increased with increasing of Nd$_2$O$_3$ concentration. The increased value of the molar volume was on account of the higher ionic radius of the Nd$^{3+}$ ion [14,15], reflecting that more non-bridging oxygen has been increased, cause the glass structure was expanded with higher concentration of Nd$_2$O$_3$. In parts of refractive index were increased with increasing of Nd$_2$O$_3$ concentration.

3.3 Optical properties

The absorption spectra of tellurite glasses doped with Nd$^{3+}$ ion at the room temperature in the range of 400-1,000 nm is shown in Figure 3. The spectrum has 9 absorption peaks which observed in UV-VIS-NIR region. Several absorption bands are observed depending on the doping concentrations of Nd$^{3+}$. All the absorption bands have been occurred from the ground state $^4I_{9/2}$ to various excited states $^2D_{3/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4S_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$ and $^4F_{3/2}$ at wavelengths 473, 513, 527, 582, 626, 683, 748, 806 and 880 nm respectively. The hypersensitive transition of 3+ ion is $^4I_{9/2} \rightarrow^4G_{5/2}$ centered at 582 nm and found to be more intense than the other transitions. These absorption spectra were assigned by comparing the band positions in the absorption spectra with those reported in the literature [16, 17].
3.4 Judd–Ofelt intensity parameters

Measure the potential of rare earth doped materials for laser applications, the radiative properties of the luminescent ions in the host matrix must be determined. These properties can be predicted from the optical absorption spectra using the Judd–Ofelt (J–O) theory [18-21]. By using the area under the absorption curve it is possible to calculate the experimental oscillator strength \( f_{\text{exp}} \) given by:

\[
 f_{\text{exp}} = 4.318 \times 10^{-9} \int \alpha(\nu) d\nu
\]  

(1)

where \( \alpha \) is the absorption coefficient (\( \text{cm}^{-1} \)), \( N \) is the number of active ions (\( \text{mol} \cdot \text{L}^{-1} \)). The calculated oscillator strength \( f_{\text{cal}} \) of electric dipole absorption transition from the ground state, to the excited state, that depended on the J–O intensity parameters yields:

\[
 f_{\text{cal}} = \frac{8\pi^2 mc\nu}{3\hbar(2J + 1)} \left[ \frac{(n^2 + 2)^2}{9n} \right] \times \sum_{\lambda=2,4,6} \Omega_\lambda \left( \psi_J \| U^J \| \psi_J' \right)^2
\]  

(2)

where \( m \) is the electron mass, \( e \) is the electronic charge, \( c \) is the light velocity, \( n \) is the refractive index and \( \lambda \) is the wavelength.

Where \( (\nu) \) is the molar extinction coefficient of the absorption band at an average energy in \( \text{cm}^{-1} \) obtained from Beer–Lambert's law. The \( f_{\text{exp}} \) and \( f_{\text{cal}} \) values of the Nd\(^{3+} \) doped tellurite glasses. The tabulated results show that the oscillator strength value does not vary remarkably with the increasing concentration of Nd\(^{3+} \) ion. The equation use to calculate the root mean square deviation (rms), \( \sigma_{\text{rms}} \), of the sample glasses follow as

\[
 \sigma_{\text{rms}} = \left[ \frac{\sum (f_{\text{exp}} - f_{\text{cal}})^2}{N} \right]^{1/2}
\]  

(3)
Where $N$ is number of levels included in the fit. The total emission cross-sections of Sm$^{3+}$ doped tellurite glasses are shown in Table 2. The J-O intensity comparison between another works and tellurite glasses are shown in Table 3.

**Table 2.** Experimental and calculated oscillator strengths ($x10^{-6}$) for 0.5 mol% and the total emission cross-section of Nd$^{3+}$ ion doped tellurite glasses.

| Transition          | $\lambda_p$ (nm) | $\sigma_{ms}$ ($x10^{-22}$ cm$^2$) | $\beta(R)$ | Exp | Cal |
|---------------------|-------------------|-----------------------------------|-------------|-----|-----|
| $^4F_{3/2}\rightarrow^4I_{9/2}$ | 913               | 0.784                             | 0.016       | 0.487 |
| $^4F_{3/2}\rightarrow^4I_{11/2}$ | 1069              | 0.316                             | 0.697       | 0.435 |
| $^4F_{3/2}\rightarrow^4I_{13/2}$ | 1341              | 0.322                             | 0.285       | 0.073 |

**Table 3.** J–O intensity parameters of the Nd$^{3+}$ ion doped tellurite glasses and other reported Nd$^{3+}$ doped glasses.

| Glass sample         | J–O intensity parameters($x10^{-20}$ cm$^2$) | Tends | References |
|----------------------|----------------------------------------------|-------|------------|
|                      | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | Present work | [22] |
| 0.5mol%Nd$_2$O$_3$   | 4.6       | 4.8       | 3.1       | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | Present work | [22] |
| TeO$_2$–WO$_3$–Nd$_2$O$_3$ | 4.71     | 4.06     | 3.89     | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | [22] |
| TWNd                 | 4.6       | 3.3       | 3.5       | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | [22] |
| BZBNd                | 2.67      | 3.31      | 3.98      | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | [22] |
| 68TeO$_2$–31ZnO–1Nd$_2$O$_3$ | 3.62     | 4.63     | 4.26     | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | [24] |
| TZNLN                | 2.13      | 3.29      | 3.83      | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | [25] |

### 3.5 Luminescence properties

The excitation spectra of the Nd$^{3+}$ doped tellurite glasses as representative displays in Figure 4. The excitation spectra has eight peaks. The highest peak of excitation spectra is observed at 523 nm. This wavelength can be excited tellurite glasses for the best luminescence. The spectra show different excited peaks from the ground state to various excited states of the Nd$^{3+}$ that obtained at the emission wavelength of 1069 nm. The peaks observed at $^4I_{9/2}\rightarrow^2F_{1/2}$ (428 nm), $^4I_{9/2}\rightarrow^2D_{3/2}$ (476 nm), $^4I_{9/2}\rightarrow^2G_{7/2}$ (523 nm), $^4I_{9/2}\rightarrow^4S_{3/2}$ (745 nm), $^4I_{9/2}\rightarrow^2H_{9/2}$ (745 nm), $^4I_{9/2}\rightarrow^4S_{3/2}$ (800 nm) and $^4I_{9/2}\rightarrow^4F_{5/2}\rightarrow^2H_{9/2}$ (879 nm).

Figure 5 shows the emission spectra of the different concentration prepared glasses at an excitation wavelength of 404 nm. The spectra show four significant peaks together with the nominal peak at the longer wavelength. The observed emission peaks are centered at 913 nm, 1,069 nm, and 1,341 nm. These peaks are coincident to $^4F_{3/2}\rightarrow^4I_{9/2}$, $^4F_{3/2}\rightarrow^4I_{11/2}$, and $^4F_{3/2}\rightarrow^4I_{13/2}$, the transitions of the Nd$^{3+}$ ion. The highest peak of emission spectra is observed at 1,069 nm.
4. Conclusion

The amorphous nature present in the prepared glasses have been studied by XRD. The density of glasses sample are fluctuated but molar volumes and refractive index of glasses were increased with increasing of Nd$_2$O$_3$ concentration. The spectrum has 9 absorption peaks which observed in UV-VIS-NIR region. The observed trend in the difference of the J-O parameter was $\Omega_4 > \Omega_2 > \Omega_6$. Three emission lines at 913 nm, 1,069 nm, and 1,341 nm. These peaks are corresponding to $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{9/2} \rightarrow ^4I_{11/2}$ and $^4I_{9/2} \rightarrow ^4I_{13/2}$, the transitions of the Nd$^{3+}$ ion. Systematic analysis of the results suggested...
that the glass doped with Nd$_2$O$_3$ concentration near 0.5 mol% is suitable for laser material and optical device applications.

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