

Thermal and Photoluminescence Properties of Nd³⁺ doped Tellurite Nanoglass

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Abstract. Series of glasses based on (75-x)TeO₂-15MgO-10Na₂O-xNd₂O₃, where x=0, 1.0, 2.0 and 3.0, are synthesized by conventional melt-quenching technique. The nanoglass particles are derived from heat treatment of this glass near crystallisation temperature for 3 hours. The existence of nanocrystalline nature of this glass is confirmed by x-ray diffraction (XRD) technique followed by calculation using Scherrer equation. Meanwhile, the crystallization temperature, T_c determined using Differential thermal analysis (DTA). The fluorescence spectra of Nd³⁺ ions exhibit emission transition of ²P_{3/2}→⁴I_{9/2}, ⁴G_{7/2}→⁴I_{9/2}, ²H_{11/2}→⁴I_{9/2}, and ⁴F_{9/2}→⁴I_{9/2} under 765 nm excitation wavelengths.

Introduction

Tellurite glass is of technical and scientific interests on the account of their easy fabrication at low temperature, high refractive index, and extended infrared transmission. It has been considered as a promising material for its widespread use in optical fiber technology [1]. Since the strong rare-earth ions-host interaction results in efficient upconversion emissions, tellurium has been recognized to be suitable glass host for the laser application [2]. Additionally, most tellurite glasses have a great rare-

earth ion solubility and low phonon energy which enables to design efficient laser and amplifier devices [3]. Therefore, the combination of rare earth with tellurite glasses has been a key to the development of many areas like optical sensing, biochemical studies and biomedical [4,5].

Previously, there are many studies succeeded in spectroscopic characterization of tellurite glass doped with neodymium. Neodymium doped all-solid-state laser sources have been identified as the most efficient laser sources for numerous applications in the fields of high-resolution spectroscopy. The development of low threshold high gain host media for Nd^{3+} ion doping was encouraged by the applications in these areas. It is obvious that the enlargement of host material for Nd^{3+} ions requires optimum material properties. They are characterized by a low content of OH^- groups and a low frequency phonon spectrum. These properties make it possible to reduce excitation losses due to multiphonon relaxation and in addition, the OH^- free tellurite glasses which is used as host material for Nd^{3+} -doped laser glasses have been a subject of increasing interest for optoelectronic applications. This glasses has high refractive index and low phonon energies [6].

In this work, we prepared neodymium doped tellurite glass via melt quenching technique and the x-ray diffraction pattern confirmed the nature of nanoglass using Scherrer equation. The effect of dopant concentration on the thermal and photoluminescence properties of this nanoglass were also investigated.

Experimental

Nd^{3+} doped magnesium-tellurite glasses of compositions $(75-x)\text{TeO}_2-15\text{MgO}-10\text{Na}_2\text{O}-x\text{Nd}_2\text{O}_3$, where $x=0, 1.0, 2.0$, and 3.0 . The system was prepared by melt quenching technique. They were heated in furnace and melted in the range $850\text{ }^\circ\text{C}$ - $900\text{ }^\circ\text{C}$ depending on the glass composition. The glass samples were annealed for about 2 hours at $300\text{ }^\circ\text{C}$ to remove thermal stress before being

cooled down to room temperature. Thermal properties of the glass were analysed using DTA, Perkin Elmer DTA-7 Series System. The glass was then heat treated near T_c for 3 hours. The existence of nanoglass was calculated using the Scherrer equation [1] given by:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of X-ray radiation ($\text{CuK}\alpha$ 1.5406×10^{-10}) and β is the FWHM of the peak at 2θ . The luminescence spectra is obtained by using Nanosecond Luminescence Spectroscopy System, Ekspla Model NT340/1 excited at 765nm using tunable Nd: YAG laser system. Each sample was scanned for radiation spectral wavenumber in the range of $200 - 900 \text{ cm}^{-1}$ at room temperature.

Result and discussion

Table 1 shows the compositional ratios of the series of TeO_2 - Na_2O – MgO glass system doped with Nd^{3+} that have been prepared by melt-quenching technique. The glasses were visually transparent, but color was different due to different % of Nd^{3+} doping as shown in Fig.1.

Table-1. Series of $(75-x)\text{TeO}_2$ -15 MgO -10 Na_2O - $x\text{Nd}_2\text{O}_3$ ($x=0,1.0,2.0$,and 3.0) glass system.

No. of Sample	TeO_2 (mol %)	MgO (mol%)	Na_2O (mol%)	Nd_2O_3 (mol%)
S1	75	15	10	0
S2	74	15	10	1
S3	73	15	10	2
S4	72	15	10	3

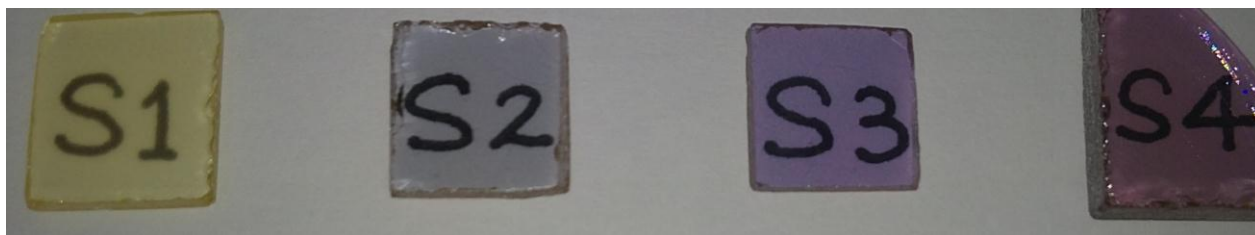


Fig. 1. Digital photograph of the Nd^{3+} doped Tellurite Glass.

Differential Thermal Analysis. The glass transition temperature T_g , crystallisation temperature T_c , and melting temperature T_m from a single DTA scan were calculated and compared in tables 2. The result is shown in Fig. 2. The T_g , T_c , and T_m temperatures all have increased with increasing Nd_2O_3 concentration in the glass system. The increasing of T_g is because of the changes in structural network. The natures of our result are in conformity with the work of Nazabal et. al [7].

Table-2. DTA results of $(75-x)\text{TeO}_2-15\text{MgO}-10\text{Na}_2\text{O}-x\text{Nd}_2\text{O}_3$ ($x=0, 1.0, 2.0$, and 3.0) tellurite glasses.

No.	of T_g	T_c	T_m	Stability	Tendency
Sample				$S=T_c-T_g$	$k_g = \frac{T_c-T_g}{T_m-T_c}$
S1	300.43	368.42	516.00	67.99	0.46
S2	303.41	373.27	891.94	69.86	0.13
S3	307.87	378.92	892.97	71.05	0.14
S4	323.32	391.49	568.98	68.17	0.38

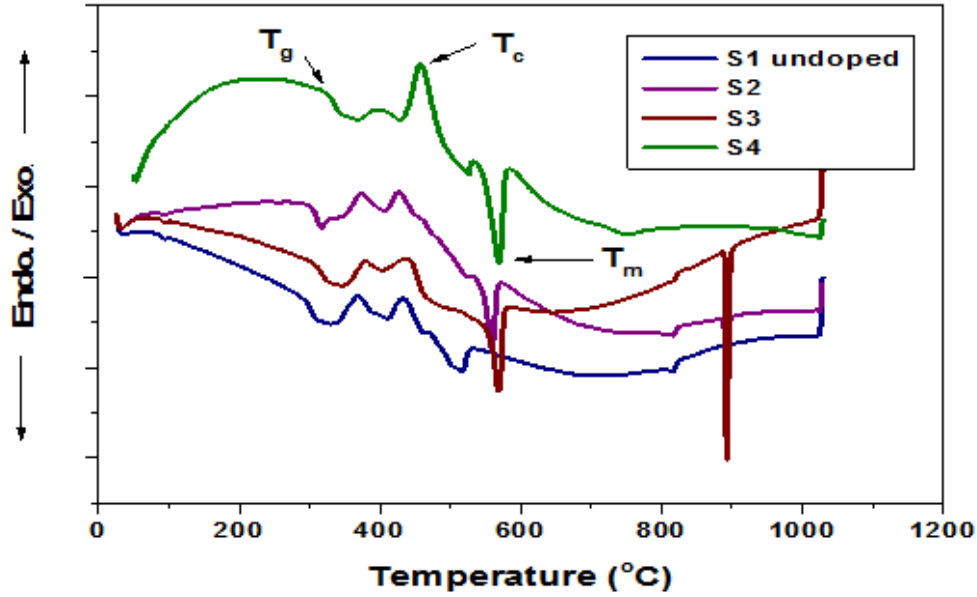


Fig. 2. Shows the thermal characteristic of the glass as measured by differential thermal analysis (DTA).

Thermal stability of glasses is one of the most important properties for glasses perform fabrication and is a measure of degree of disorder of glassy state. There are two widely used parameters for evaluating thermal stability of glasses from characteristic temperatures. These equations are defined as follows [8]:

$$S = T_c - T_g \quad (2)$$

$$k_g = \frac{T_c - T_g}{T_m - T_c} \quad (3)$$

The glass thermal stability is assessed by employing S and k_g parameters. The S value is an implication of the devitrification tendency of glass when heated above T_g . It defines the temperature range for glass drawing. The larger S and the smaller difference between crystallization temperature, T_c and melting temperature T_m slow down crystallization process and facilitate glass formation. The increasing stability with dopant concentration as observed by us is in consistent with the study of Nazabal et. al [7].

X-Ray Diffraction. Fig. 3 shows the x-ray diffraction spectra of sample 1 after heat treatment which without Nd_2O_3 . It can clearly be seen that the glass is still dominated by the amorphous structure and the peaks are related to nanocrystalline structures having varying sizes as shown in Fig. 2. The main peak is used to calculate the crystalline size using Scherrer equation and found to be in the range of 2-14 nm. The XRD pattern of this sample is identical to the previous sample, showing peak at 26.5° is superimposed; these peak can be attributed to TeO_2 crystalline phases [9]. From the FWHM of the intense diffraction peak of transparent tellurite nanoglass, the average crystallite size as obtained in range 2 – 14 nm. This result is in agreement with the observation of Kaur et. al [9].

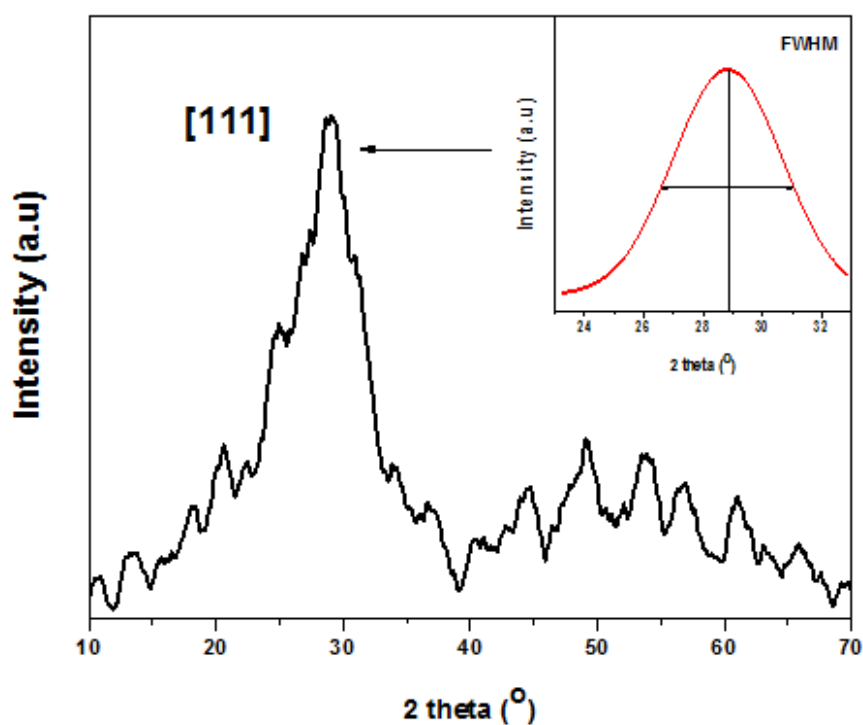


Fig. 3. XRD pattern of the glass system after heat treated.

Photoluminescence Spectra. Fig. 4 shows visible up-conversion emission characteristic spectrum of radiation emanating from a neodymium-doped tellurite nanoglass with excitation at the wavelength of 765 nm. It can be seen from Fig. 3 that apart from a green emission transition at 547 nm corresponding to the $^4\text{G}_{7/2} \rightarrow ^4\text{I}_{9/2}$ transition of the neodymium ions, a relatively weak ultraviolet emission transition at 373 nm ($^2\text{P}_{3/2} \rightarrow ^4\text{I}_{9/2}$) and red emission transition at 656 nm and 713 nm ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{9/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{9/2}$) respectively are also observed. The up-conversion luminescence

transition spectrum of ${}^4D_{3/2} \rightarrow {}^4I_{J+1}$ or ${}^2P_{3/2} \rightarrow {}^4I_J$ ($J=13/2, 11/2, 9/2$) was found to be essentially similar as those reported in Refs.10 and 11 and energy transfer ${}^4G_{7/2}$ has been previously reported [12]. An additional, the ultraviolet emission at about 345 nm is observed by Que et. al [13].

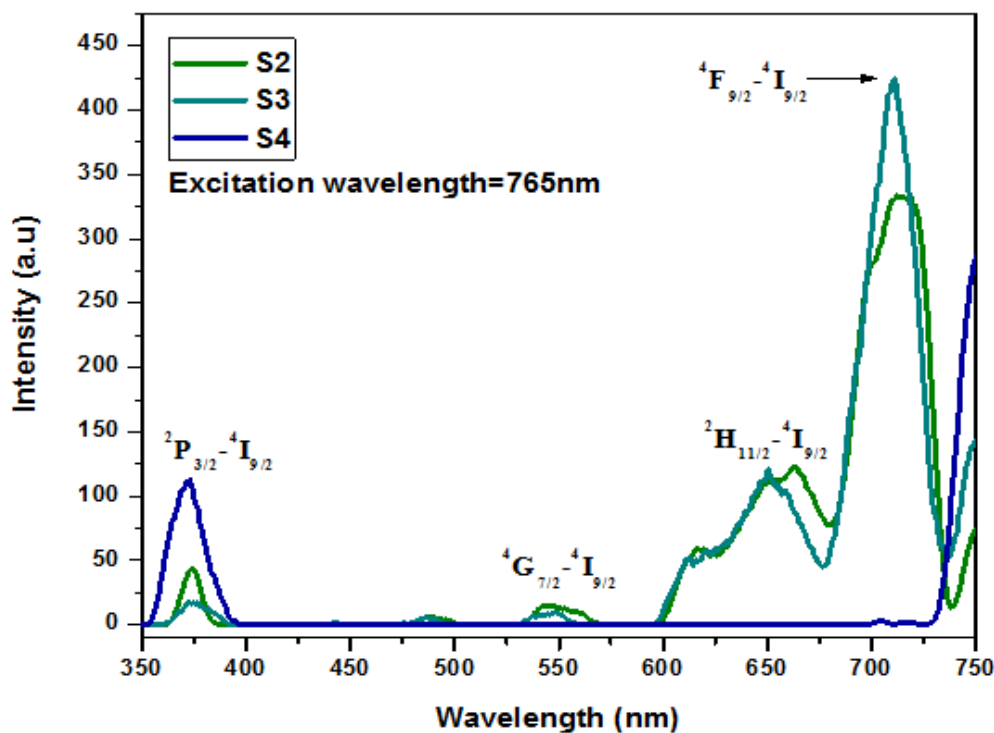


Fig. 4. Emission spectrum from the heat treated neodymium-doped $\text{Na}_2\text{O-MgO-TeO}_2$ nanoglass with different concentration of neodymium.

Based on Fig. 4, it can also be seen that the red emission intensity increases with Nd concentration. The intensity not make any different at green band and ${}^2H_{11/2} \rightarrow {}^4I_{9/2}$ transition of emission band but there is slightly shift of the peaks position which indicates the interaction of ions between Nd^{3+} sites. It can be observed that the intensity of ${}^2P_{3/2} \rightarrow {}^4I_{9/2}$ transition increases due to the increasing concentration of Nd but peaks of S4 can be seen disappeared at transition in range 450 nm-725 nm. It is because at the high Nd concentration, the luminescence will be quenched by energy transfer processes due to interactions between Nd ions and OH^- groups.

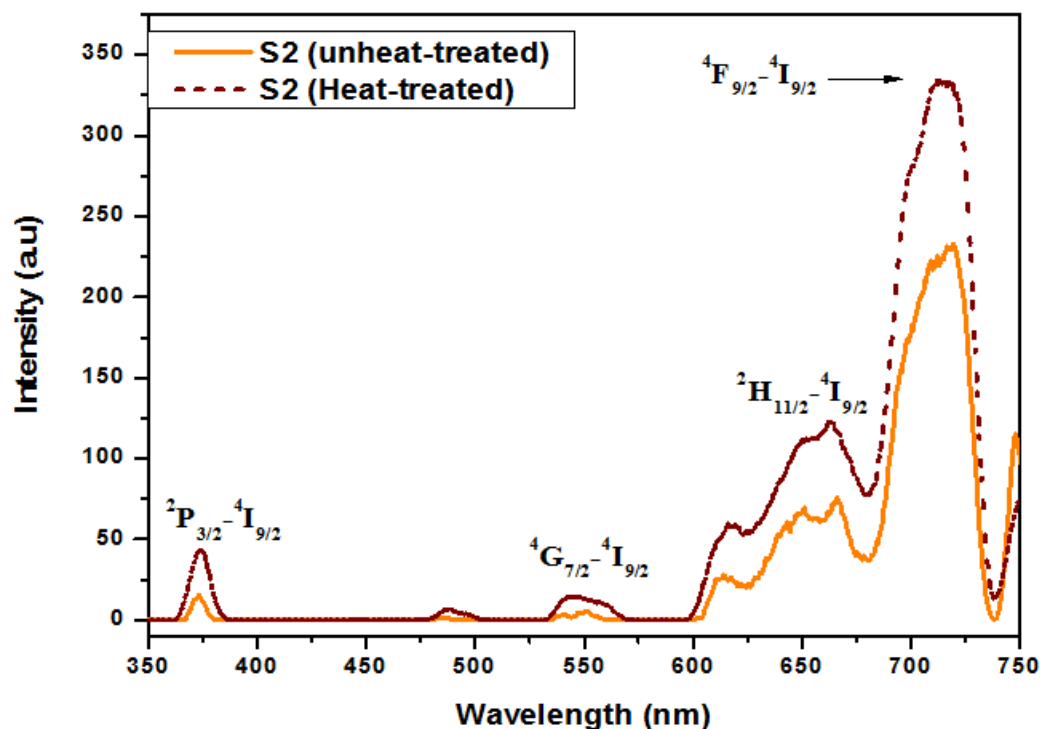


Fig.5. Comparison of the emission spectra from Na₂O-MgO-TeO₂ glass containing 1 mol% Nd₂O₃ with heat-treated and unheat-treated glass under an excitation of 765 nm.

Emission spectra of 1 mol% Nd in heat-treated and unheat-treated glass system is shown in Fig. 5 using 765 nm excitation wavelength. The emission peaks are appeared at 373 nm, 547 nm, 656 nm, and 713 nm (same as Fig.4). The 765 nm excitation is dominated by the emission near 713 nm which is the transition from the thermally populated $^4F_{7/2}$ state to $^4I_{9/2}$ [14]. The intensity of heat-treated sample shows enhancement compared to un-treated one.

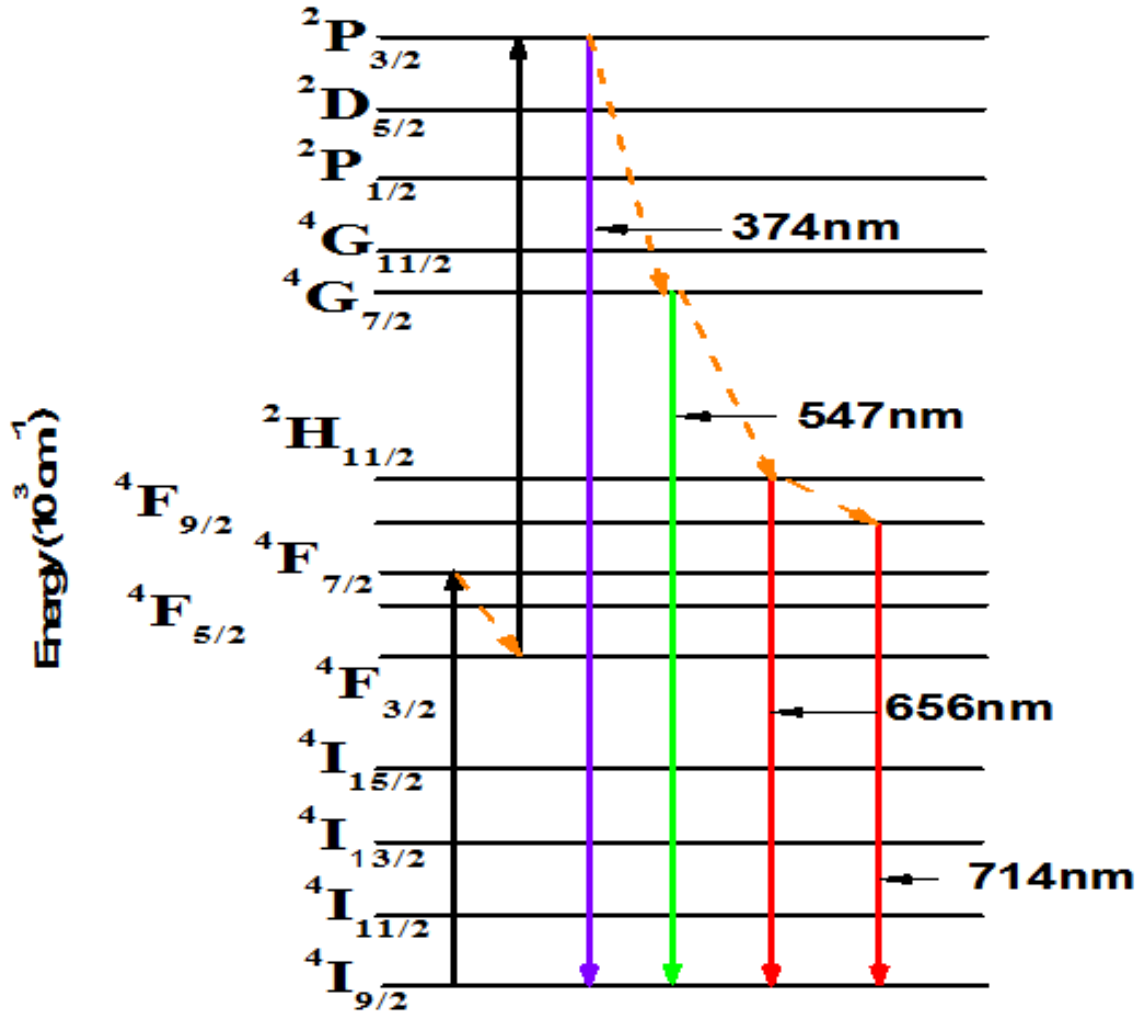


Fig. 6. Energy-level scheme describing the up-conversion emission from the neodymium-doped $\text{Na}_2\text{O-MgO-TeO}_2$ nanoglass upon an excitation at 765 nm.

Fig. 6 is a schematic diagram describing the mechanism of the up-conversion emission from a neodymium ion via a two-photon absorption process. In this process, Nd^{3+} ions are pumped with 765 nm excitation wavelength through the ground state absorption (GSA) they excite to the $^4\text{F}_{7/2}$ level. Using excited state absorption (ESA) mechanism [14], the electron rapidly decays nonradiatively to the metastable $^4\text{F}_{3/2}$ state. Ref. 15 reported that this metastable state has a quite long lifetime and thus the electron has a high chance to absorb a second 765 nm photon before the electron further decays downwards. Finally, it gets excited to the $^2\text{P}_{3/2}$ state. Afterwards, some electrons will decay radiatively to the $^4\text{I}_{9/2}$ state as shown in the energy diagram of Fig. 6. As they populated the $^2\text{P}_{3/2}$

level, some of the Nd^{3+} ions relaxed radiatively to $^4\text{I}_{9/2}$ level thus emitting the emission spectra centered at 374 nm. Some of the Nd^{3+} ions are found relax non-radiatively to lower level $^4\text{G}_{7/2}$, $^2\text{H}_{11/2}$, and $^4\text{F}_{9/2}$. The Nd^{3+} ions at $^4\text{G}_{7/2}$ are then decay to $^4\text{I}_{9/2}$ by emitting the emission spectra centered at 547 nm in green region. Whereby, the Nd^{3+} ions that emitting the red emission spectra are centered at 656 and 714 nm as the decay to $^2\text{H}_{11/2}$ and $^4\text{F}_{9/2}$ level respectively [16]. Our observation is tallies with the report of Wright [15].

Conclusion

Some conclusions can be made and summarize as follows: the system of neodymium-doped Na_2O - MgO - TeO_2 nanoglass with different Nd_2O_3 concentration has successfully been made by melt-quenching technique. Differential thermal analysis (DTA) has been employed to verify the glass transition (T_g), crystallization (T_x) and melting temperatures (T_m). The nanostructured of the glass was determined by calculating the crystalline size using the Scherrer method and it was in the range of 2-11 nm. The analysis detail on the visible emission process from the glass system to verify its luminescence performance was carried out successfully. The results showed that the emission of four visible luminescence bands centered on 374, 547, 656, and 714 nm as to correspond to the $^2\text{P}_{3/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{G}_{7/2} \rightarrow ^4\text{I}_{9/2}$, $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{9/2}$, and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{9/2}$ transitions of the Nd^{3+} ions respectively.

Acknowledgments

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