

Spectral analysis of Nd³⁺ & Er³⁺: B₂O₃-(TeO₂/CdO/ZnO)-Li₂O-AlF₃ glasses

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We report here on the development and optical spectral analysis of Nd³⁺ & Er³⁺ (0.5 mol %) ions doped three new glasses in the following composition: 10TeO₂-69.5 B₂O₃-10 Li₂O- 10 AlF₃, 10CdO- 69.5 B₂O₃-10 Li₂O- 10 AlF₃, 10ZnO- 69.5 B₂O₃-10 Li₂O- 10 AlF₃. From the measured Vis-NIR absorption spectra of Nd³⁺: glasses have revealed ten absorption bands at 430, 459, 511, 526, 583, 626, 686, 746, 803 and 874 nm corresponding to the transitions of ⁴I_{9/2} → (²P_{1/2}, ²D_{5/2}), ²G_{9/2}, ⁴G_{9/2}, (⁴G_{7/2}, ⁴K_{13/2}), (⁴G_{5/2}, ²G_{7/2}), ²H_{11/2}, ⁴F_{9/2}, (⁴F_{7/2}, ⁴S_{3/2}), (⁴F_{5/2}, ⁴H_{9/2}), and ⁴D_{3/2} respectively. NIR emission spectra of (0.5 mol %) Nd³⁺: B₂O₃-(TeO₂/CdO/ZnO)-Li₂O-AlF₃ glasses have revealed three emission transitions (⁴F_{3/2} → ⁴I_{J=9/2, 11/2 & 13/2}) at 906, 1079 and 1349nm measured under excitation wavelength 514.5nm with an Ar⁺ laser (514.5nm). Similarly from the measured Vis-NIR absorption spectra of Er³⁺: glasses have revealed nine absorption bands at 377, 405, 450, 486, 519, 543, 649, 973 and 1529 nm which correspond to the transitions of ⁴I_{15/2} → ⁴G_{11/2}, (²G_{9/2}, ⁴F_{9/2}), ⁴F_{5/2}, ⁴F_{7/2}, (²H_{11/2}, ⁴G_{11/2}), ⁴S_{3/2}, ⁴F_{9/2}, ⁴I_{11/2} and ⁴I_{13/2} respectively. With an excitation at λ_{exci} =375nm, a bright green emission (⁴S_{3/2} → ⁴I_{15/2}) at 547 nm has been observed from these erbium glasses. NIR emission spectra of (0.5 mol %) Er³⁺: B₂O₃-(TeO₂/CdO/ZnO)-Li₂O-AlF₃ glasses have revealed one NIR emission transition (⁴I_{13/2} → ⁴I_{15/2}) at 1547 nm under excitation wavelength 514.5nm with an Ar⁺ laser (514.5 nm).

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1. Introduction

Over the past several years a great deal of work has been carried out on different rare earth (4fⁿ) ions and also transition metal (3dⁿ) ions in crystals and glassy matrices for various device and optical component development applications [1-10]. In order to improve the glass quality and its optical performance from B₂O₃ glasses, suitable quantity (10mol %) of TeO₂, CdO and ZnO have been added separately as the network modifiers [NWF] alongside two other property improving network modifiers namely Li₂O and AlF₃. More interestingly, we have succeeded in developing these newly proposed glasses with an excellent transparency & UV and IR transmission ability. Both Cd and Zn belong to the group IIB transition elements and whereas Te belongs to the chalcogens group. Those two elements (Cd,Zn) of IIB transition elements and one chalcogen (Te) element have significantly improved the transmission ability and moisture resistance and transparency in the UV and IR wavelength regions for their utilization as optical materials of potential importance with the suitable dopant ions in those matrices for their applications.

Oxide glasses are more appropriate for practical applications, due to their high chemical durability and good thermal stability compared to fluoride, chalcogenide and chloride glasses. But oxide glasses have high

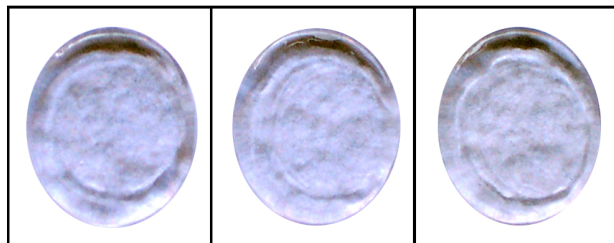
multiphonon relaxation rates (1400 cm⁻¹) which causes high non-radiative energy losses causing a low decrement of emission efficiency in glasses. Fluoride glasses have low multiphonon rates (700cm⁻¹) compared to oxide, tellurite or chalcogenide glasses though they possess low thermal stability. Mixing of oxide and fluoride ions in the preparation of glasses will combine the properties of both these ions i.e., oxyfluoride glasses will exhibit good thermal stability, moisture resistance and low multiphonon rates which have the value in between oxide and fluoride based glasses for a better emission efficiency [11-13]. B₂O₃ is a glass forming oxide, AlF₃,Li₂O is a conditional glass formers and with these two chemicals in the glass matrix a low rate of crystallization, moisture resistance, stable and transparent glasses could be achieved. Addition of CdO/ZnO/TeO₂ to such glass matrices, different properties could significantly be modified, as network modifiers. Such glasses with rare earth ions have several potential applications. Rare earth ions are incorporated into these glasses in order to characterize their optical properties. From the literature, it has been noticed that Nd³⁺, Er³⁺ doped glassy materials have attracted a great deal of attention due to their applications in lasers and fiber optic amplifiers[14-19]. Glasses based on B₂O₃ and TeO₂ with metal oxides have been studied in [20]. We have recently analyzed the spectral properties of Cu²⁺ ions

doped in B_2O_3 -(TeO_2 /CdO/ZnO)- Li_2O - AlF_3 glasses [21]. Since there are no reports so far made on the optical analysis of Nd^{3+} and Er^{3+} : B_2O_3 -CdO/ZnO/ TeO_2 - Li_2O - AlF_3 glasses, we have undertaken the present work.

2. Experimental procedure

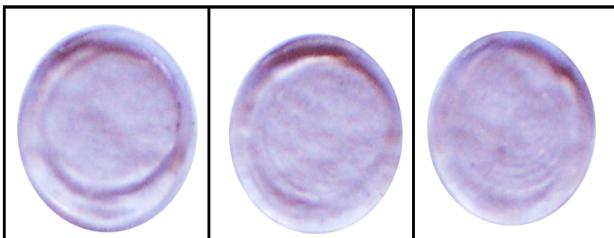
2.1 Glasses Preparation

The glass samples without Nd^{3+} , Er^{3+} ions were prepared by the conventional melt quenching method in the chemical composition of $[10(TeO_2/CdO/ZnO)-70B_2O_3-10Li_2O-10AlF_3]$. We then prepared Nd^{3+} , Er^{3+} glasses in the composition of $10(TeO_2/CdO/ZnO)-69.5B_2O_3-10Li_2O-10AlF_3-0.5(Nd_2O_3/Er_2O_3)$. The starting materials used in the present work were reagent grade of H_3BO_3 , ZnO, CdO, TeO_2 , AlF_3 , Li_2CO_3 , Nd_2O_3 and Er_2O_3 . All chemicals were weighed appropriately, powdered finely and mixed thoroughly. Each batch weighing about 10g was melt in ceramic crucibles by placing them in an electrical furnace for an hour, at $950^\circ C$. These melts were quenched in between two brass plates to produce 2-3 cm diameter optical glass discs of 0.3cm thickness each. The glasses thus obtained were all annealed at $200^\circ C$ for an hr to remove thermal strains. Figs. 1&2 present the photographs of the glasses studied in the present work.



Nd^{3+} : TeO_2 Nd^{3+} : CdO Nd^{3+} : ZnO

Fig.1: Photograph of 0.5 mol% Nd^{3+} : $10(TeO_2/ZnO/CdO)-69.5B_2O_3-10Li_2O-10AlF_3$ glasses.



Er^{3+} : TeO_2 Er^{3+} : CdO Er^{3+} : ZnO

Fig. 2: Photograph of 0.5 mol% Nd^{3+} : $10(TeO_2/ZnO/CdO)-69.5B_2O_3-10Li_2O-10AlF_3$ glasses.

2.2 Measurements

Powder X-ray diffraction (XRD) spectra was obtained on a Shimadzu XD3A diffractometer with a Ni-filter and $Cu K_{\alpha}$ ($=1.542\text{\AA}$) radiation with an applied voltage of 30KV and 20 mA anode current, calibrated with Si at the rate of $2^\circ/\text{min}$. The Vis-NIR absorption spectra for the Nd^{3+} , Er^{3+} doped glasses were measured on a Varian-Cary Win Spectrometer (JASCO V-570). Both the excitation and visible emission spectra of Er^{3+} glasses were measured on a SPEX Fluorolog -2 Fluorimeter (Model II) with datamax software to acquire the data with a Xe-arc lamp (150W) as the excitation source. NIR photoluminescence spectra of the Nd^{3+} & Er^{3+} glasses were also measured on a Horiba Triax-550 grating monochromator (JOBIN YVONHORIZA) equipped with a liquid nitrogen cooled InGaAs photo detector (Electro-Optical System -Inc) in the wavelength range of 800-2400 nm and a lock-in-amplifier (SR 830 DSP, Standard Research Systems) with an Ar^+ laser (514.5nm) (LEXEL MODEL 85 ION LASER, 5Mw-200mW) as the excitation source.

3. Results and discussion

3.1. Nd^{3+} : Glasses

The X-ray diffraction patterns of 0.5mol% of Nd^{3+} : $10(TeO_2/CdO/ZnO)-70B_2O_3-10Li_2O-10AlF_3$ glasses are given in Fig.3, which confirm the amorphous nature of the glasses.

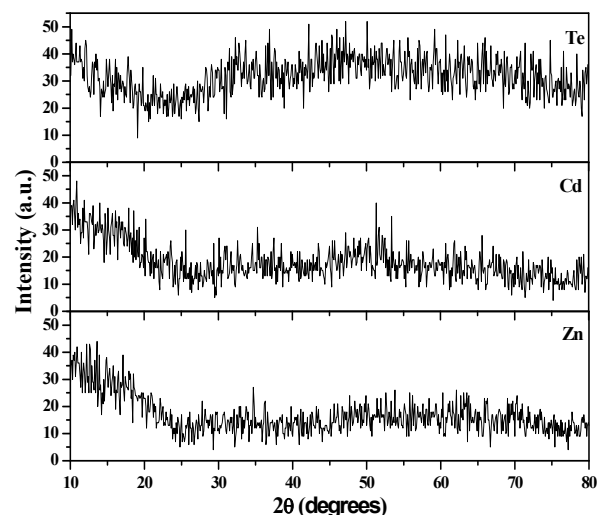


Fig.3. XRD profile of Nd^{3+} : $10(TeO_2/ZnO/CdO)-69.5B_2O_3-10Li_2O-10AlF_3$ glasses

Vis-NIR absorption spectra of Nd^{3+} glasses are shown in Fig. 4 for a comparison.

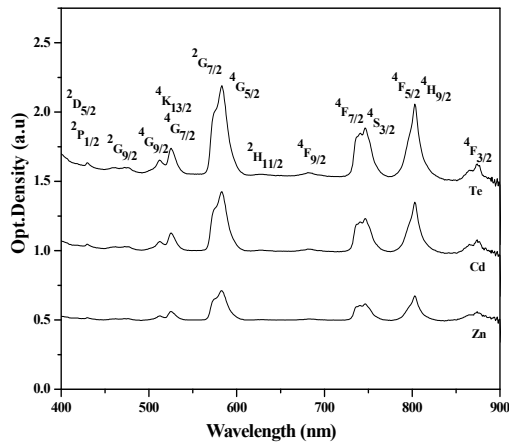


Fig. 4. Vis-NIR absorption spectrum of Nd³⁺:10(TeO₂/CdO/ZnO)-69.5 B₂O₃-10Li₂O-10AlF₃ glasses.

All samples have revealed ten absorption bands such as $^4I_{9/2} \rightarrow ^4F_{3/2}$, ($^4F_{5/2}$, $^4H_{9/2}$), ($^4F_{7/2}$, $^4S_{3/2}$), $^4F_{9/2}$, $^2H_{11/2}$, ($^4G_{5/2}$, $^2G_{7/2}$), ($^4G_{7/2}$, $^4K_{13/2}$), $^4G_{9/2}$, $^2G_{9/2}$, ($^2P_{1/2}$, $^2D_{5/2}$) and were all considered. It is clear from the figure that, the overall appearance of the spectra of Nd³⁺ ion in all three glass hosts are similar but band relative intensities are changing. The luminescence spectra of Nd³⁺: glasses in the region 800-1500 nm under excitation wavelength 514.5nm with an Ar⁺ laser (514.5 nm) are shown in Fig.5.

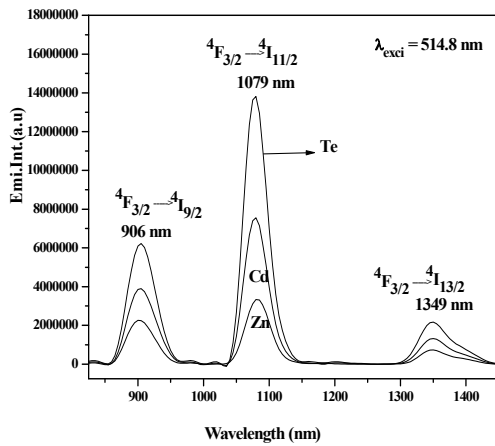


Fig. 5. NIR emission spectra of Nd³⁺:10(TeO₂/CdO/ZnO)-69.5 B₂O₃-10Li₂O-10AlF₃ glasses.

From the measured photoluminescence spectra of Nd³⁺: glasses, three bands are identified at 906 nm, a strong band at 1079 nm and another band at 1349 nm and are assigned 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 respectively. Among them, $^4F_{3/2} \rightarrow ^4I_{11/2}$ is a lasing transition having a prominent intensity. It is observed that as the ZnO/CdO/TeO₂ with AlF₃/LiF change the spectral intensities significantly. From NIR emission spectra it is obvious that the intensity of TeO₂ is stronger than that of CdO and ZnO glasses.

3.2. Er³⁺: Glasses

The X-ray diffraction patterns of 0.5mol% of Er³⁺: 10(TeO₂/CdO/ZnO)-69.5B₂O₃-10 Li₂O-10 AlF₃ glasses are given in Fig.6, which confirm the amorphous nature of the glasses.

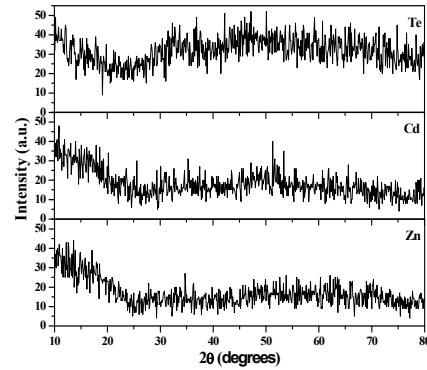


Fig. 6. XRD profile of Er³⁺: 10(TeO₂/ZnO/CdO)-69.5B₂O₃-10Li₂O-10AlF₃ glasses.

Vis-NIR absorption spectra of Er³⁺: glasses are shown in Figs. 7a&b, with nine distinctive & sharp absorption bands at 377, 405, 450, 486, 519, 543, 649, 973 and 1529nm, and those are assigned to the electronic transitions appropriately. From these absorption spectra, well defined absorption bands such as $^4I_{15/2} \rightarrow ^4I_{13/2}$, $^4I_{11/2}$, $^4F_{9/2}$, $^4S_{3/2}$, ($^4G_{11/2}$, $^2H_{11/2}$), $^4F_{7/2}$, $^4F_{5/2}$, ($^4F_{9/2}$, $^2G_{9/2}$) and $^4G_{11/2}$ have been considered. It is clear from the figure that, the overall appearance of the spectra of Er³⁺ ion in all three glass hosts are similar but band relative intensities are changing.

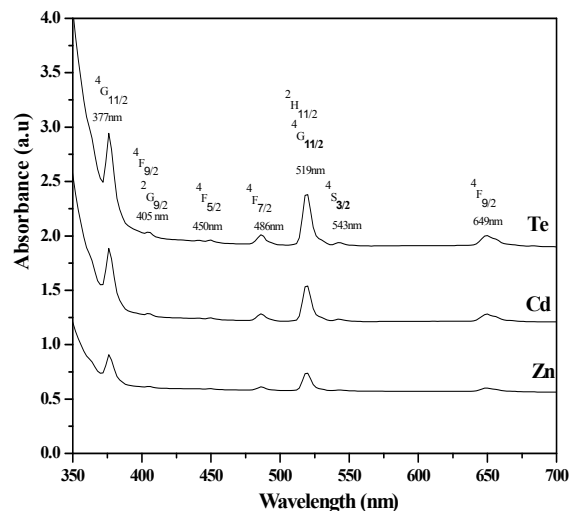


Fig. 7a. Visible absorption spectrum of Er³⁺:10(TeO₂/CdO/ZnO)-69.5 B₂O₃-10Li₂O-10AlF₃ glasses.

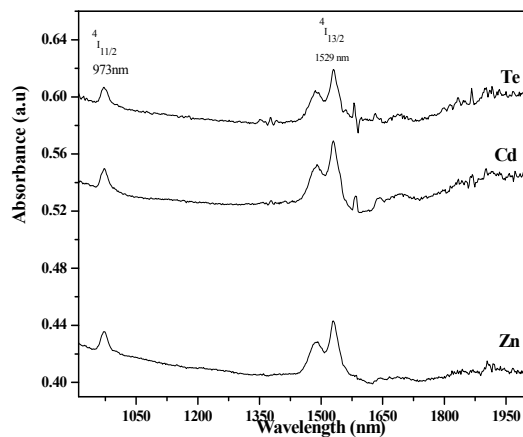


Fig. 7b. NIR absorption spectrum of Er^{3+} :10($\text{TeO}_2/\text{CdO}/\text{ZnO}$) - 69.5 B_2O_3 -10 Li_2O -10 AlF_3 glasses.

The visible luminescence spectra of Er^{3+} : glasses in the region 500-700 nm with an excitation at 375 nm ($^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}$) is shown in Fig.9. Since the excitation energy in this case falls in the absorption edge of the host glass itself, the excitation of erbium ion can take place partially via its ($^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}$) absorption and also energy transfer from the excited state of the host. The measured visible photoluminescence spectra of Er^{3+} : glasses show strong green emission at 547 nm ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$). The excitation spectrum (Fig.8) exhibits a strong excitation at 375 nm which indicates that a significant fraction of the Er^{3+} ions of the glasses are excited to the $^4\text{S}_{3/2}$ state when the glasses are excited with 375 nm.

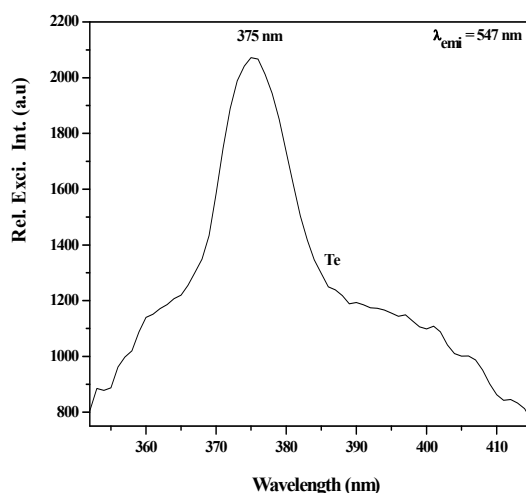


Fig. 8. Excitation spectrum of Er^{3+} :10($\text{TeO}_2/\text{CdO}/\text{ZnO}$) - 69.5 B_2O_3 -10 Li_2O -10 AlF_3 glasses.

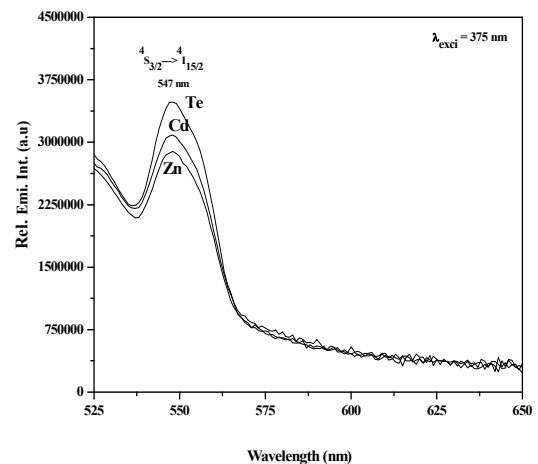


Fig. 9. Visible emission spectra of Er^{3+} :10($\text{TeO}_2/\text{CdO}/\text{ZnO}$) - 69.5 B_2O_3 -10 Li_2O -10 AlF_3 glasses.

Fig.10 shows an NIR emission ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$) at 1547nm with an Ar^+ laser (514.5 nm) excitation. The transition $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ is a lasing transition with a prominent intensity with little changes on adding the $\text{ZnO}/\text{CdO}/\text{TeO}_2$.

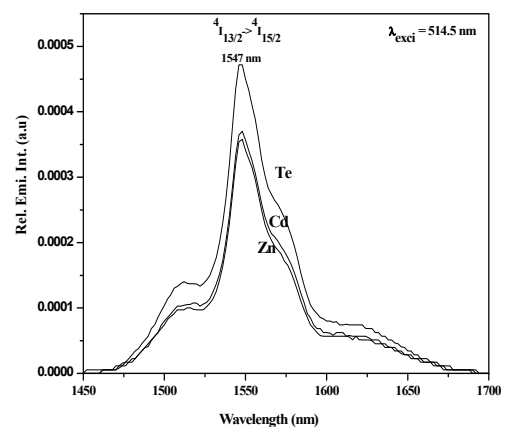


Fig. 10. NIR emission spectra of Er^{3+} :10($\text{TeO}_2/\text{CdO}/\text{ZnO}$) - 69.5 B_2O_3 -10 Li_2O -10 AlF_3 glasses.

For (0.5mol %) of Er^{3+} : glasses, the excitation-dependent photoluminescence spectra are shown in Fig.11, and it indicates that these emission peaks do not show any apparent shift with the change in excitation power. In addition, NIR emission intensity depends on excitation source power as shown in Fig.11. The integrated PL intensity has a linear dependence on the excitation power (Fig.12). The luminescence parameterization of the Er^{3+} glasses has successfully been carried out by the absorption and emission spectral results.

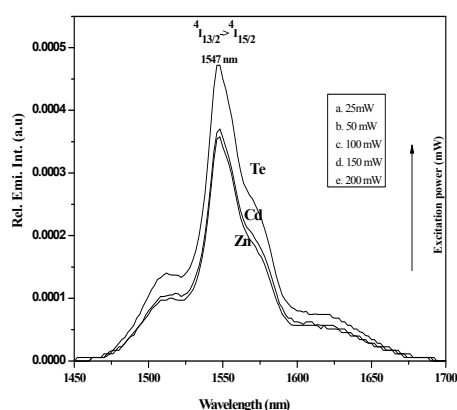


Fig.11. Excitation-dependent photoluminescence spectra of Er³⁺:10(TeO₂/CdO/ ZnO) - 69.5 B₂O₃-10Li₂O-10AlF₃ glasses. The arrow indicates the excitation source power.

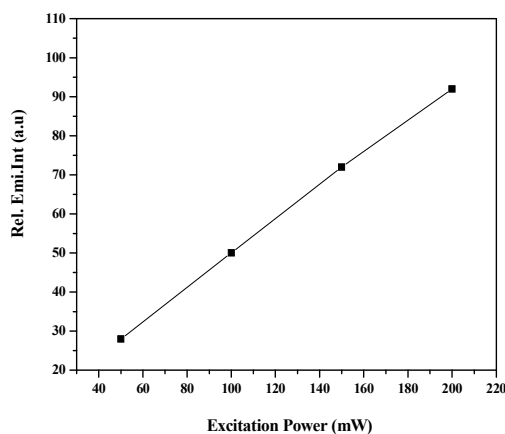


Fig.12. Emission (at 1547nm) intensity dependence on source power change for Er³⁺:10(TeO₂/CdO/ ZnO) - 69.5 B₂O₃-10Li₂O-10AlF₃ glasses.

4. Conclusions

In summary, it could be concluded that we have successfully developed highly transparent, moisture resistant and more stable (0.5 mol %) Nd³⁺, Er³⁺ ions doped 10(CdO/ZnO/TeO₂) - 69.5B₂O₃ - 10 Li₂O -10AlF₃ glasses. Keeping in view these encouraging properties, glasses have been considered to examine their amorphous nature from their XRD spectra. Optical analyses of these glasses have been carried out based on the measurement of their absorption, excitation and emission spectra in the visible and NIR region. Apart from analyzing their optical properties, we could also notice a bright green emission (Er³⁺ glasses) under an UV source. From the measured NIR emission spectra of Nd³⁺ and Er³⁺ doped 10(CdO/ZnO/TeO₂) - 69.5B₂O₃ - 10 Li₂O -10AlF₃ glasses, the NIR emission at 1079 nm of Nd³⁺ glasses and NIR emission at 1547 nm of Er³⁺ glasses have been observed. From these glasses, the glasses with TeO₂ have demonstrated encouraging emission and absorption

spectral results. Among three glasses, the glasses that contain TeO₂ have demonstrated encouraging emission and absorption results. Thus, we could suggest that 10TeO₂ - 69.5B₂O₃ - 10 Li₂O -10AlF₃ with as the luminescent ions Nd³⁺ and Er³⁺ based on NIR emission performance at 1079 nm (Nd³⁺) and 1547nm (Er³⁺) and also based on their visible emission performance for their use in development of solid state lasers and fiber optical amplifiers.

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