Volume 65, Issue 8, 2021
Journal of Scientific Research
of
The Banaras Hindu University

# Effect Of Rare Earth Impurities on Physical, Structural and Optical Properties of Some Borate Based Glasses

Susheela K. Lenkennavar*[1]

*[1]Department of physics, Bangalore University, Bangalore -56, Karnataka, India
*E-mail: sushhh10@gmail.com

*Abstract:* **The present glass samples were prepared by using melt quenching technique. The prepared glasses were characterized optical properties by using absorption and photoluminescence (PL) spectral measurements and Structural properties by X-ray diffraction (XRD). The objective is to report detailed studies of glass matrix. The rare earth ions are used as optical activators, since they have excellent optical properties. Using proper optimization method we can make use of these lasers for photonic applications. From the luminescence spectrums it's clear that synthesized glass offers light yellow colour and can be an auspicious laser candidate. The physical parameters have been evaluated. The densities (ρ) of the glass samples were measured using Archimede's principle with toluene as an immersion liquid. Refractive indices (n) of samples were measured at 589.3 nm using an Abbe's refractometer and few physical parameters of the glasses like, molar volume ($V_m$), molar refractivity ($R_m$), polarizabilities ($\alpha_m$), concentration of rare earth ion ($N_i$) , polaron radius ($r_p$) , inter ionic distance ($r_i$), field strength(F), reflection loss ($R_L$%) and dielectric constant (ε). The detailed studies of them have been reported for the better understanding.**

***Index Terms:*** **X-Ray Diffraction, physical parameters, UV/Visible Spectroscopy, photoluminescence.**

## I. INTRODUCTION

Now a days the applications of lanthanides is extended to almost all important fields of technology. The lanthanides built-in glass host matrices due to its spectroscopic properties have been one of the most attractive areas for researchers. Photoluminescence of lanthanides ions were investigated for many application in some of the fields such as optical data storage, biomedical lasers, high-energy particle detector, laser printing, bar-code reading, environment friendly solid- state lighting, underwater and satellite communication, etc. [1-6]. The 4f electrons of lanthanides ions are shielded with 5s, 5p electrons and spin–orbit interactions exerts considerable influence on positions of their electronic energy levels. The characteristic of different emission properties of lanthanides ions basically take place which is caused by electronic transitions among these energy levels. The surrounding ligand-field or glass host matrices doped with lanthanides ions also shows a great influence on the lasing properties [7-14].

Up-conversion materials have drowned great attention from researchers. In the up-conversion process absorption of two or more photons will results in the emission of one photon and that too with a shorter wavelength than exciting light, in which emission energy of a photon is much higher than the excitation energy photon. The rare-earth ions act as the luminous centers hence RE are doped in the different hosts for the design of a number of luminescent materials [15-16]. Especially optical glasses doped with the holmium due to its abundant energy levels in the range of ultraviolet (UV) to infrared ray (IR), can be utilized in numerous applications such as data storage systems or data recording in HD quality, medical diagnostics, 3D displays, optical sensors [17-19]. The transition $^5I_7 \rightarrow {}^5I_8$ shows stimulation of $Ho^{3+}$ at about 2.0 μm which draw considerable attention in the past because of efficient optical pumping due to possible by co-doping with ions such as $Er^{3+}$, $Tm^{3+}$ and $Yb^{3+}$ [38].

In this work, we report the preparation of calcium sodium lead boro oxyfluoride glasses doped with holmium ions by melt quenching technique. The physical, structural and optical properties of holmium ions doped with calcium oxides, sodium oxides, lead fluoride and borate were investigated and for the better understanding the detailed studies of them have been reported.

## II. II. SYNTHESIS AND CHARACTERIZATION

### A. *Synthesis*

Oxide glasses with composition $10CaO\text{-}20Na_2O\text{-}10PbF_2\text{-}60B_2O_3\text{-}XHo_2O_3$ with X= 1 mol% were synthesized utilizing electric furnace by the conventional melt quenching technique and indicated as CNFB and CNFBH. The chemical composition of the 10g batch was weighted very precisely. In an agate mortar, the 10g batches chemical were grinded and mixed thoroughly, and taken in a porcelain crucible, chemical compositions were taken melted in the temperature range of 1030-1080 $^0$C in an electric furnace for 45 minutes and immediately poured on a brass mould which was preheated to get pellet form samples. Therefore by employing conventional melt-quench technique glasses were obtained. It includes or involves batch preparation, grinding or mixing, calcinations, melting, quenching and annealing.

### B. *Characterizations*

1) Few physical parameters were calculated. The density is measured using Archimedes principle. Refractive indices of samples were measured at 589.3 nm using an Abbe's refractometer. Using suitable expression few physical properties has been calculated as discussed in literature [19-32].

2) X-ray diffraction patterns of the present prepared glass samples calcium sodium lead boro oxyfluoride glasses doped with holmium ions were recorded to investigate the non-crystallinity utilizing advance XRD diffractometer RIGUKA ULTIMA IV.

3) The absorption spectra recorded at room temperature using Perkin Elmer Lambda-950 UV-Vis spectrometer.

4) The luminescence spectrum has been recorded by Spectroflourometer, Horiba Jobin Yvon Fluorolog-3.

## III. RESULTS AND DISCUSSION

### 1) *PHYSICAL PROPERTIES*

*Density (ρ) was estimated using ($W_a$) sample weight in air, ($W_b$) sample weight in liquid (toluene) ($\rho_x$=0.8669gcm$^{-3}$ , toluene of density) using*

$$\rho = \frac{W_a}{(W_a - W_b)\rho_x} \quad \text{.....(1).}$$

Molar volume ($V_m$) was calculated by using glass molecular weight (M.W),

$$V_m = \frac{M.W}{\rho} \quad \text{.....(2).}$$

Molar refractivity ($R_m$) is calculated using molar volume $V_m$ and refractive index,

$$R_m = \frac{n^2-1}{n^2+2}(V_m) \quad \text{....(3).}$$

The polarizabilities ($\alpha_m$) is calculated using Avogadro's number ($N_A$) and molar refractivity ($R_m$) by using relation,

$$\alpha_m = \frac{3}{4\pi N_A} R_m \quad \text{........(4).}$$

Rare earth(RE) ion concentration is calculated using relation,

$$N_i = \frac{x\,\rho NA}{y\,b} \quad \text{...... (5).}$$

Where, x is the weight of RE ion and y is molecular weight of rare earth ion.

The inter ionic distance ($r_i$) and polaron radius ($r_p$) is calculated using the concentration of RE ion ($N_i$),

$$r_i = \left[\left(\frac{1}{N_i}\right)^{1/3}\right] \quad \text{.....(6a)}$$

$$r_p = \left[\frac{1}{2}\left(\frac{\pi}{6N_i}\right)^{1/3}\right] \quad \text{.....(6b) respectively.}$$

Field strength (F) can be calculated by using charge of rare earth ion (Z) and polaron radius,

$$F = \left(\frac{Z}{r_p^2}\right) \quad \text{....(7)}$$

Dielectric constant (ε) is calculated form,

$$\epsilon = n^2 \quad \text{....(8).}$$

Reflection loss ($R_L$%) was calculated by using Refractive index,

$$R_L = \left(\frac{n-1}{n+1}\right)^2 \quad \text{....(9).}$$

For the better understanding purpose the preliminary physical properties of glass samples of calcium sodium lead boro oxyfluoride glasses and doped with holmium ions are estimated and reported as follows [19-32].

| Sl.No | Physical properties | CNFB | CNFBH |
|---|---|---|---|
| 1. | Refractive index (RI) | 1.612 | 1.692 |
| 2. | density (ρ) gm/cm$^3$ | 3.341 | 3.294 |
| 3. | Molar refractivity ($R_m$)cm$^{-3}$ | 10.59 | 11.02 |
| 4. | Molar volume ($V_m$)g/cm$^3$ | 26.87 | 27.92 |

| | | | |
|---|---|---|---|
| 5. | Molar polarizability ($\alpha_m$)×$10^{-24}$cm$^3$ | 4.19 | 4.26 |
| 6. | Reflection loss($R_L$)%, | 6.156 | 6.144 |
| 7. | Dielectric constant($\varepsilon$), | 2.815 | 2.828 |
| 8. | Concentration ($N_i$)×$10^{20}$ ions/cc. | - | 2.24 |
| 9. | Polaron radius ($r_p$)nm | - | 0.49 |
| 10. | Inter ionic distance ($r_i$) nm | - | 1.58 |
| 11. | Field strength(F) ×$10^{14}$cm$^2$ | - | 8.47 |

*2) X-RAY DIFFRACTION*

XRD pattern of prepared glass samples doped with holmium ions is displayed in Fig.1, which has no sharp peaks that is a clear indication of the absence of crystalline nature. The diffractograms exhibit just broad diffuse scattering at low angles which is characteristic of long-range structural disorder. That confirms the amorphous characteristics of the glass.

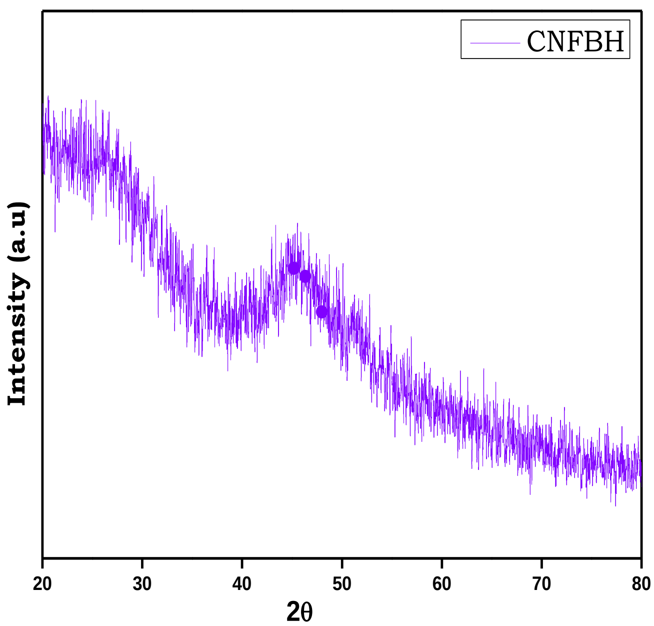


Fig 1. XRD pattern glass samples doped with holmium ions.

*3) OPTICAL ANALYSIS*

Using double beam spectrophotometer the spectral measurements were carried out. In the spectral range 300-900 nm absorption spectra were recorded using Pekin Elemer Lambda—35 UV-Vis spectrometer. In 1000-2200nm spectral range recorded using Perkin Elmer Lambda-950 UV-Vis spectrometer.

The UV-Vis-NIR spectra of Holmium incorporated calcium sodium lead boro oxyfluoride glass in 350-2000nm spectral range has been explicate in fig 2(a) and 2(b). Based on the energy separation of $Ho^{3+}$ free ions, observed intensity and absorption bands have been assigned in visible (300–700 nm) and as well as near-infrared (700–2000 nm) regions with all possible transitions from $^5I_8$ ground state to different energy levels. Form the $^5I_8$ ground state to excited states $^5G_5$, $^5G_6$, $^5F_2$, $^5F_3$, $^5F_4$, $^5F_5$, $^5I_5$, $^5I_6$, and $^5I_7$. The $Ho^{3+}$ ion has the electronic configuration of $4f^{10}$ with $^5I_8$ ground state. It gives a large number of well resolved absorption and emission transitions in the UV, Vis and NIR regions [33-37]. The two transitions of $Ho^{3+}$ in the absorption spectra, viz., $^5I_8 \rightarrow {}^5G_6$ and $^5I_8 \rightarrow {}^5H_6$ are hypersensitive [16-19]

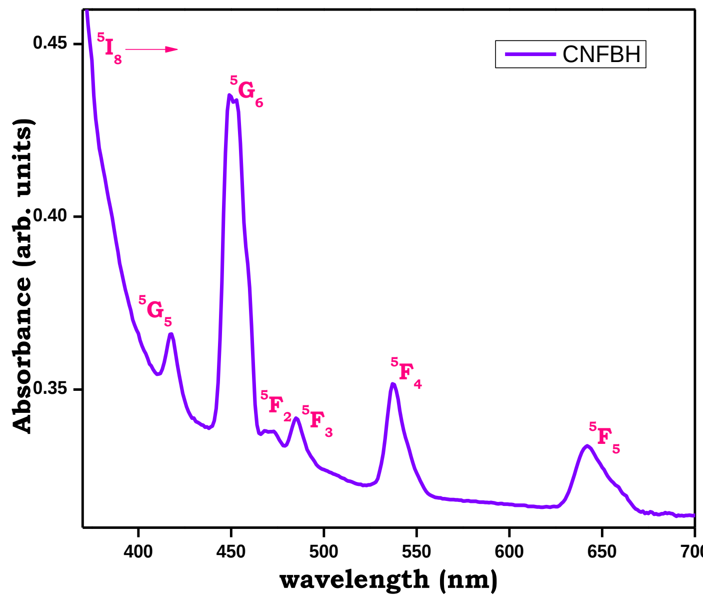


Fig 2(a). Absorption spectra of glass samples doped with holmium ions in the spectral range 300-900 nm

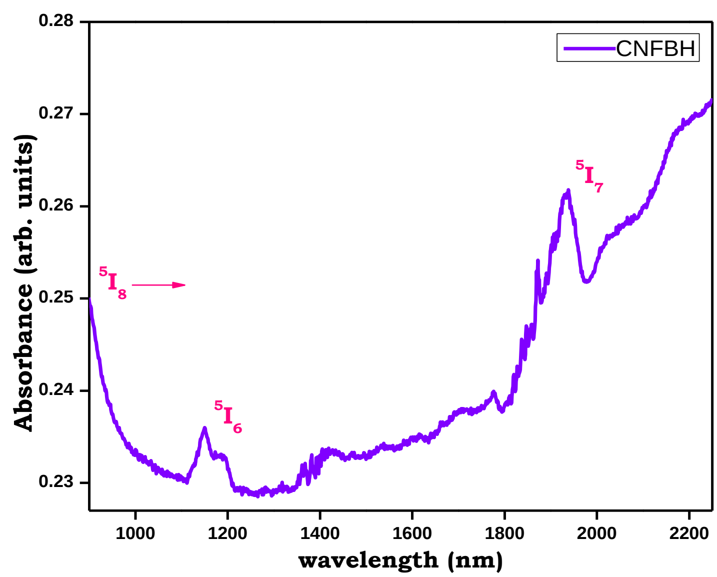

Fig 2(b). Absorption spectra of glass samples doped with holmium ions in the spectral range 900-2200 nm.

## IV. EMISSION PROPERTIES

The figure 3 shows photoluminescence spectra of $Ho^{3+}$ doped samples under 450 nm excitation and we observed that the sample revealed strong emission bands at 494 nm and 612 nm. The former is governed by the quadrupole selection rules ($\Delta S = 0$, $\Delta L$, $\Delta J < 2$). The transition from $^5F_3 \rightarrow {}^5I_8$ indicates green emission. The glass was exciting with 450 nm wavelength radiation, as a result two emission bands were obtained, the first emission bands is located at 494 nm, this corresponding to $^5F_3 \rightarrow {}^5I_8$ and, the second emission bands is located at 612 nm, this corresponding to $^5F_5 \rightarrow {}^5I_8$ 612 nm [38-42].

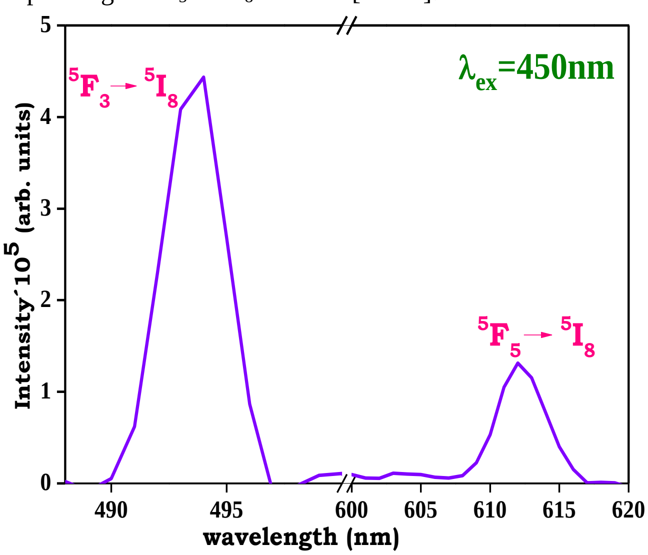


Fig 3. Emission spectra of glass samples doped with holmium ions.

## CONCLUSION

In this work the spectroscopic properties of holmium doped glass were investigated. The calcium sodium lead boro oxyfluoride glasses doped with holmium ions have been prepared by normal melt quench technique. The Powder X-Ray diffraction analysis of the prepared samples confirms the amorphous nature of the samples. To evaluate changes in the optical properties, the optical absorption and photoluminescence spectrum of polished samples have been recorded at room the temperature. The $Ho^{3+}$ ion has the electronic configuration of $4f^{10}$ with $^5I_8$ ground state. It gives a large number of well resolved absorption and emission transitions in the UV, Vis and NIR regions. All possible transitions from $^5I_8$ ground state to different excited states $^5G_5$, $^5G_6$, $^5F_2$, $^5F_3$, $^5F_4$, $^5F_5$, $^5I_5$, $^5I_6$, and $^5I_7$ were observed. The photoluminescence spectra of $Ho^{3+}$ doped samples under 450 nm excitation, the sample revealed strong emission bands at 494 nm and 612 nm.

## ACKNOWLEDGEMENTS

Author would like to thank (Late) Prof. R.V. Anvekar for his guidance and suggestions.

## REFERENCES

Reddy A A., Babu SS., Pradeesh K., Otton CJ., & Prakash GV. (2011). Optical properties of highly $Er^{3+}$-doped sodium–aluminium–phosphate glasses for broadband 1.5 µm emission. *Journal of Alloys and Compounds*. 509(9) 4047–4052.

Lenkennavar K S., Eraiah B., & Kokila MK. (2020). Rare earths doped oxy-fluoride glasses as candidates for generating tunable visible light. *Materials Today: Proceedings, Elsevier Publication.* 33(7), 2550-2554.

Dihingia P J., & Rai S. (2012). Synthesis of TiO2 nanoparticles and spectroscopic upconversion luminescence of Nd3+ -doped TiO2-SiO2 composite glass. *Journal of Luminescence.* 132, 1243-1251.

Lenkennavar S K., & Kokila M K (2019). Optical and Physical Properties of Sodium Calcium Lead fluoro Borate Glasses Incorporated with Praseodymium Ion.. *International Journal of ChemTech Research.* 12 (2), 90-94.

Dutta P., and Rai S. (2011). Optical transitions and frequency upconversions of $Ho^{3+}$ and $Ho^{3+}/Yb^{3+}$ ions in Al (NO3) 3–SiO2 sol–gel glasses. *Optik.* 122 (10), 858–863.

Lenkennavar S K., Eraiah B., & Kokila M K. (2020). Optical absorption spectra, energy band gap and tailing states determination in praseodymium doped PbO-Na2O-B2O3-MO (M= Ca, Ba, Sr) glasses, *AIP Conference Proceedings*, 2220, 080032-5.

Ofelt G. (1962). Intensities of Crystal Spectra of RareEarth Ions. *The Journal Of Chemical Physics*. 37, 511–520.

Lenkennavar S K., Madhu A., Eraiah B., & Kokila M K. (2017). Optical and Physical properties of Pr3+ doped sodium lead calcium borate glasses. *International Journal in Physical and Applied Sciences,* 4(7), 112-7

Abdel-Baki M., Abdel-Wahab F A., & El-Diasty F. (2012). One-photon band gap engineering of borate glass doped with ZnO for photonics applications. *Journal of Applied Physics* 111, 073506–073516

Lenkennavar S K., Madhu A., Eraiah B., & Kokila M K. (2018). The Luminescence and decay enhancement by variation in atomic size of alkaline earth metals in $Pr^{3+}$ incorporated sodium lead borate glass. *American Institute of Physics Conference Proceedings.* 1951, 090053-8

Yoon M J. (2009). Surface Modifications and Optoelectronic Characterization of TiO2-Nanoparticles: Design of New Photo-Electronic Materials. *Journal of the Chinese Chemical Society*. 56, 449–454.

Reisfeld R. (2001). Rare earths complexes in sol gel glasses. *Materials Science*. 20, 5–18.

Lenkennavar S K., Madhu A., Eraiah B., & Kokila M K. (2018). Luminescence study and CIE diagram of certain alkaline sodium lead borate glass for LED applications. *American Institute of Physics Conference Proceedings,* 1953, 030009-12.

Reben, M., & Sroda M. (2013) . Influence of fluorine on thermal properties of lead oxyfluoride glass . *Journal of Therm. Anal. Calorim.* 113(1) 77–81.

Xueying Wang., Hai Lina., & Dianlai Yang. (2007). Optical transitions and upconversion fluorescence in Ho3+/Yb3+ doped bismuth tellurite glasses. *Journal of Applied Physics* 101, 113535–113542.

Shi J W., Zheng J T., & Wu P. (2009). Preparation, characterization and ... holmium-doped titanium dioxide nanoparticles. *Journal Hazardous Materials* 161, 416–422.

Kamma I., & Rama Reddy B. (2010). Glass. *Journal of Applied Physics.* 107, 113102-11306,

Kim S J., Park S D., Jeong Y H., & Park S. (1999). Homogeneous Precipitation of TiO2 Ultrafine Powders from Aqueous TiOCl2 Solution. *Journal of American Ceramic Society*. 82(4), 927-932

FriebeleE J. (1991). Radiation effects in Optical Properties of Glass, D.R. Uhlmann, N.J. Kreidl, Eds. *American Ceramic Society*, Westerville 205–262.

Lenkennavar S K., Madhu A., Eraiah B., & Kokila M K. (2018). Effect of certain alkaline metals on Pr doped glasses to investigate spectroscopic Studies. *IOP Conf. Series: Materials Science and Engineering*. 310, 012052-59

Venkateswara Rao G., Veeraiah N., & Yadagiri Reddy P. (2003) Luminescence quenching by manganese ions in MO–CaF2–B2O3 glasses. *Optical Mater.* 22(2), 295-302.

Lenkennavar S K., Madhu A., Eraiah B., & Kokila M K. (2018). Influence of $Pr^{3+}$ ions on Physical, Optical and Structural Properties of Lead borate Glasses and Effect of γ Irradiation. *Journal Applicable Chem*. 7 (4), 933–948.

Lucacel RC., Marcus C., Timar V., & Ardelean I. (2005). FT-IR and Raman spectroscopic studies on B2O3–PbO–Ag2O glasses dopped with manganese ions. *Solid State Sciences.* 9 (9), 850-854.

Murali A., Sreekanth Chukrodhar R.P., & Lakashmana Rao J. (2005). EPR studies of Gd3+ ions in lithiumtetra borotellurite and lithiumlead tetra boro-tellurite glasses. *Physica B.* 364, 142-149.

Lenkennavar S K., Eraiah B., & Kokila M K. (2019). Luminescence behavior and decay lifetimes of different alkaline earth metals in sodium lead fluoroborate glass doped with $Pr^{3+}$. *American Institute of Physics AIP Conference Proceedings.* 2134, 050006-10

Sharma G., Singh., Radia K. (2006). Effects of Gamma Irradiation on Optical and Structural Properties of PbO–Bi2O3–B2O3 Glasses. *Radiation Physics and Chemistry*. 75(9), 959-966

El-Batal H A., Khalifa F A., & Azooz M A. (2001). Gamma ray interaction , crystallization and infrared absorption spectra of some glasses and glass-ceramics from the system Li2O , B2O3 , Al2O3. *Indian Journal of Pure and Applied Physics*. 39(9), 565-569.

Lenkennavar S K., Madhu A., Eraiah B., & Kokila M K. (2018). The Luminescence and decay enhancement by variation in atomic size of alkaline earth metals in Pr3+ incorporated sodium lead borate glass. *American Institute of Physics Conference Proceedings.*1953, 090025-29.

Kamitsos E. I. (2003). Infrared Studies of Borate Glasses. *Physics and Chemistry of Glasses*. 44(2), 79-84.

Kathleen MacDonald., Margaret A Hanson., & Daniel Boyd. (2016). Modulation of strontium release from a tertiary borate glass through substitution of alkali for alkali earth oxide. *Journal of Non-Crystalline Solids*, 443, 184-191.

Lenkennavar S K., Madhu A., & Kokila M K. (2019). Optical properties of $Dy^{3+}$ and $Nd^{3+}$ -ions doped oxyfluoride glasses. *International Archive of Applied Sciences and Technology*. 10(1), 106-110.

Myrtille O J.Y., Hunault, Laurence Galoisy., Gérald Lelong, Matt Newville., Georges Calas. (2016). Effect of cation field strength on $Co^{2+}$ speciation in alkali-borate glasses. *Journal of Non-Crystalline Solids.* 451, 101-115.

Arunkumar S., & Marimuthu K. (2013). Concentration effect of Sm3+ ions in B2O3–PbO–PbF2–Bi2O3–ZnO glasses – Structural and luminescence investigations. *Journal of alloys and compounds.* 565 (1) 104-114.

Sumiyoshi T., Sekita H., Arai T., Sato S., Ishihara M., & Kikuchi M (1999). Select. Top. Quantum Electron. *IEEE J.* 5, 936–943.

Lenkennavar S K., Eraiah B., & Kokila M K. (2020). Spectroscopic investigation of different nano metals doped to lead sodium calcium borate glasses. *Materials Today: Proceedings, Elsevier Publication,* 26(2), 1167–1174.

Boyer J., Vetrone F., Capobianco J., Speghini A., & Bettinelli M. (2003). Optical transitions and upconversion properties of doped glass. *J. Appl. Phys.* 93, 9460–9465.

Huang F., Liu X., Li W., Hu L., & Chen D. (2014). Energy transfer mechanism in $Er^{3+}$ doped fluoride glass sensitized by $Tm^{3+}$ or $Ho^{3+}$ for 2.7-\mu m emission. Chin. *Opt. Lett.* 12, 051601-14.

Ehrmann P.R., & Campbell J.H. (2002). Nonradiative energy losses and radiation trapping in neodymium-doped phosphate laser glasses. *Journal of the American Ceramic*. 85, 1061–1069.

Gao S., Fan X., Liu X., Liao M., & Hu L. (2015). Mechanical and∼ 2 μm emission properties of Tm3+-doped GeO2–TeO2 (or SiO2)–PbO–CaO glasses. *Opt. Mater*. 45,167–170.

Shin Y.B., & Cho W.Y, Heo. (1996). Multiphonon and cross relaxation phenomena in Ge As (or Ga) S glasses doped with $Tm^{3+}$. *J. Non-Cryst. Solids* 208, 29–35.

R. Reisfeld. (1982). Chalcogenide glasses doped by rare-earths-structure and optical properties, *Annales de chimie-science des materiaux,* 7, 147–160.

Luo Y., Zhang J., Sun J., Lu S., & Wang X. (2006). Spectroscopic properties of tungsten–tellurite glasses doped with Er3+ ions at different concentrations. *Opt. Mater.* 28, 255–258

***