UDC 666.29

B.J.R.S.N. Swamy [a], N. Narasimha Rao [a], P. Naresh [b], P. Raghava Rao [a], A. Chitti Babu [c], N.Ch. Ramesh Babu [d]

IMPACT OF Eu^{3+}/Tb^{3+} IONS ON $PbO-NaF-B_2O_3$ GLASSES OPTICAL ABSORPTION SPECTRA

[a] Department of Physics, Krishna University Dr.MRAR College of PG Studies, Nuzvid, AP, India
[b] Department of Physics, Velagapudi Ramakrishna Siddhartha Engineering College, Vijayawada, AP, India
[c] Department of Physics, Sir. C.R. Reddy College of Engineering, Eluru, Andhra Pradesh, India
[d] Department of Physics, Rajiv Gandhi University of Knowledge & Technologies (AP-IIIT), Nuzvid, A.P, India

The optical characteristics of glasses have become an increasingly established and developing aspect. This article presents the optical characteristics of the Ln^{3+} ion in lead sodium fluoroborate glass, which has the composition 10 PbO−19 NaF−70 B_2O_3−1.0 Ln_2O_3 (where Ln=Eu and Tb, all in mol.%). Glass samples were processed using the conventional melt-quenched approach, and the glassy nature was confirmed by the X-ray diffraction patterns. The optical absorption spectra of $PbO-NaF-B_2O_3$ glasses with Eu^{3+} ions exhibit distinct absorption bands that were assigned to the transitions $^7F_0 \rightarrow {}^5L_6$, $^5D_3$, $^5D_2$, and $^7F_1 \rightarrow {}^5D_1$. Judd-Ofelt (JO) factors (Ω_2, Ω_4, Ω_6) were determined from the absorption spectra. By using least square fit analysis, oscillator strength (f) was evaluated and presented. Regarding the three J-O parameters (Ω_2, Ω_4 and Ω_6), Ω_2, that is related to structural adjustments in the area of the Ln^{3+} ion, indicates slow adjustments of the covalent surroundings.

Keywords: B_2O_3 glass, optical absorption spectra, Eu_2O_3, Tb_2O_3, Ln^{3+} ions, J-O parameter.

DOI: 10.32434/0321-4095-2024-153-2-99-103

Introduction

Due to their amorphous nature, glasses show signs of optical isotropy. In the realms of science and technology, these translucent materials have attracted a lot of attention [1].

B_2O_3 is one of the most powerful and fundamental glass formers among several types of glass formers. It has received top-notch attention due to its interesting technology-related properties. Borate atoms form structural units of [BO_4] or [BO_3] through coordination with tetra- and tri-oxygen atoms. These units form B−O−B linkages that enhance the optical properties of glasses through metal-oxygen bonds and non-bridging oxygen atoms [2,3].

The optical and structural properties of oxide glasses are significantly enhanced by adding Pb^{2+} divalent ions [4,5]. Due to their optical transparency across a wide wavelength range, alkali fluoroborate glasses, in particular, make excellent laser hosts. Phenomenological parameters associated with the radiative properties of a glass composition can be chosen according to the Judd-Ofelt concept, which was developed to compute the intensities of electric dipole transitions between 4f states [6,7].

Glasses with europium doping are commonly used as effective red phosphors because of their narrow emission band and long radiative lifetime [8]. Tb_2O_3 glasses should find extensive use in the disciplines of optics, electricity, magnetism, information, communications, systems, and in other related fields due to their exceptional magneto-optical properties [9].

Considering the inherent drawbacks of the up conversion phenomenon, a significant amount of

energy is expended during the non-radiative processes, requiring high pump power to produce laser output. According to ref. [10], the energy level system of Tb^{3+} ions makes it feasible to produce the green pulsed laser.

Experemental

The melting and quenching processes were employed to prepare the glasses for the current study [11]. Within the glass-forming region of the system, the composition chosen for the present study is 10PbO−19 NaF − 70 B_2O_3 − 1.0 Ln_2O_3 (with Ln = Eu and Tb), all in mol.%. The detailed chemical compositions and their codes are displayed in Table 1. Schematic representation of the preparation of glass samples is shown in Fig. 1.

Table 1

Composition of glass samples (mol.%)

Sample code	Content, mol.%			
	PbO	NaF	B_2O_3	Ln_2O_3
Eu_2O_3 glass	10	19	70	1.0 Eu_2O_3
Tb_2O_3 glass	10	19	70	1.0 Tb_2O_3

The Philips PW 1830 X-ray diffraction spectrometer was used to record the XRD patterns. The optical absorption spectra of the samples were recorded at ambient temperature in the spectral wavelength range of 300−2200 nm, with a spectral resolution of 0.1 nm using a JASCO Model V-670 UV−vis−NIR spectrophotometer.

Results

The pattern of X-ray diffraction for PbO−NaF−B_2O_3:Ln_2O_3 (Ln=Eu, Tb) glasses was recorded in the vicinity of $15^0 \leq 2\theta \leq 75^0$ for the glass series as depicted in Figure 2. The lack of clear peaks in the pattern reveals that the samples are amorphous.

The spectral absorption of PbO−NaF−B_2O_3 glasses with Eu^{3+} ions reveals the following pronounced absorption bands (Fig. 3):

$^7F_0 \rightarrow {}^5L_6$, $^5D_3$, $^5D_2$, and $^7F_1 \rightarrow {}^5D_1$.

Through the use of least square fit analysis, oscillator strength (f) was evaluated. Table 2 displays these variables.

Table 2

The absorption energies as well as oscillator strength (f) for PbO−NaF−B_2O_3:Eu_2O_3 glasses

Transition	Energy, cm^{-1}	$f_{exp} \cdot 10^{-6}$	$f_{theor} \cdot 10^{-6}$
$^7F_0 \rightarrow {}^5L_6$	25369	61.4	61.4
$^7F_0 \rightarrow {}^5D_3$	24038	32.45	32.43
$^7F_0 \rightarrow {}^5D_2$	21490	8.4	6.90
$^7F_1 \rightarrow {}^5D_1$	18668	19.24	18.57

The following absorption bands were visible in the absorption spectrum of PbO−NaF−B_2O_3:Tb_2O_3 glasses (Fig. 4): $^7F_6 \rightarrow {}^5D_4$, $^5G_6$, $^5L_{10}$, $^5G_5$, and $^5L_9$. Absorption energies as well as oscillator strength (f) of the studied glasses are shown in Table 3.

The bonding parameter (δ) [12] has also been calculated for each pair of glasses and is depicted in Table 4. A higher value of δ indicates a more covalent environment for the Ln^{3+} ions. The highest values of

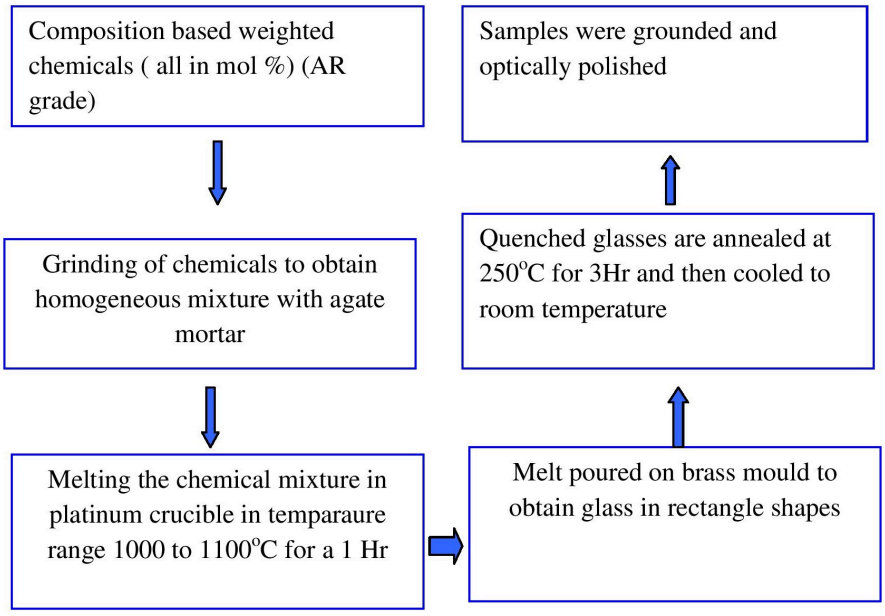

Fig. 1. Schematic representation of preparation of glasses

δ obtained for the Eu_2O_3 glass among the two alkaline earth oxide modifier glasses denote the most covalent environment of Eu^{3+} in this glass. The sequence of J-O parameters observed for all the glasses is: $\Omega_2>\Omega_4>\Omega_6$. Table 4 displays the data on the Ln^{3+} ion Ω_λ parameters in the glass matrices.

Discussion

B_2O_3 is a prominent glass-forming component that participates in glass networks with tetrahedral structures. Typically, modifiers like PbO disrupt the B−O−B linkage to form B−O terminations, thereby depolymerizing or modifying the structure. Upon comparing the theoretically calculated oscillator strengths with the experimental values, it was found that the calculated and experimental oscillator strengths generally agree well, except for the Ln^{3+} ions.

Positive transition energies and spectral patterns of Ln^{3+} ions shed some light on their coordination [13]. The environment of Ln^{3+} ions in glasses systems is described by the value of Ω_λ for Ln^{3+} ions. In glass systems, rare earth ions are randomly dispersed over non-equivalent sites, as demonstrated by simulation and optical studies [14]. The presence of large modifier ions in glasses leads to an increased average distance between the B−O−B chains, resulting in a weaker surrounding field for Tb^{3+} ions and consequently a lower value of Ω_2. Conversely, the ability of Eu^{3+} ions to occupy distinct coordination states leads to higher values of Ω_2 in the current glass systems.

The value of the bonding parameter (δ) provides additional evidence to support this claim; the bonding parameter (δ) follows the order of Eu_2O_3 glass>Tb_2O_3 glass, indicating a highly covalent environment for Ln^{3+} ions in Eu_2O_3 glasses and highly ionic conditions in Tb_2O_3 glasses. [15]. The optical absorption spectrum profiles of Ln^{3+} ion-doped PbO−NaF−B_2O_3 glasses were measured, revealing the following transitions:

Table 3

The absorption energies and oscillator strength (f) for PbO−NaF−B_2O_3:Tb_2O_3 glasses

Transition	Energy, cm^{-1}	$f_{exp}\cdot10^{-6}$	$f_{theor}\cdot10^{-6}$
$^7F_6\rightarrow{}^5D$	20530	3.10	2.86
$^7F_6\rightarrow{}^5G_6$	26035	21.2	18.42
$^7F_6\rightarrow{}^5L_{10}$	27202	22.91	20.08
$^7F_6\rightarrow{}^5G_5$	27194	23.45	24.10
$^7F_6\rightarrow{}^5L_9$	28256	25.92	23.61

$^7F_0\rightarrow{}^5L_6$, $^5D_3$, $^5D_2$, $^7F_1\rightarrow{}^5D_1$ for Eu_2O_3-doped glass,

and

$^7F_6\rightarrow{}^5D_4$, $^5G_6$, $^5L_{10}$, $^5G_5$, $^5L_9$ for Tb_2O_3-doped glass.

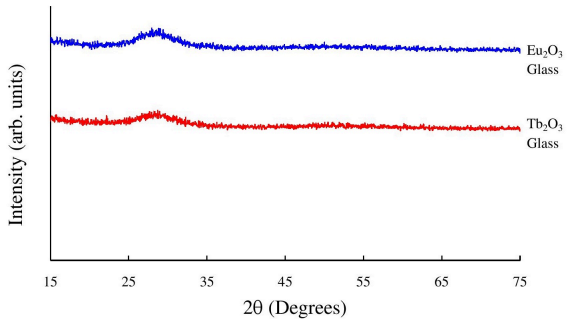

Fig. 2. X-ray diffraction pattern of PbO−NaF−B_2O_3:Ln_2O_3 (Ln=Eu, Tb) glasses

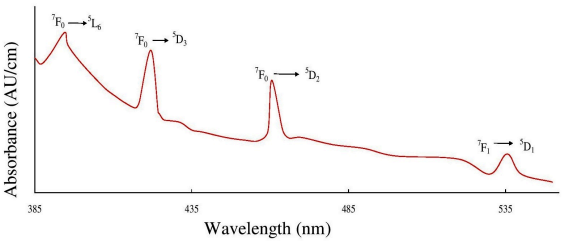

Fig. 3. Optical absorption spectrum of PbO−NaF−B_2O_3 glasses doped with Eu^{3+} ions

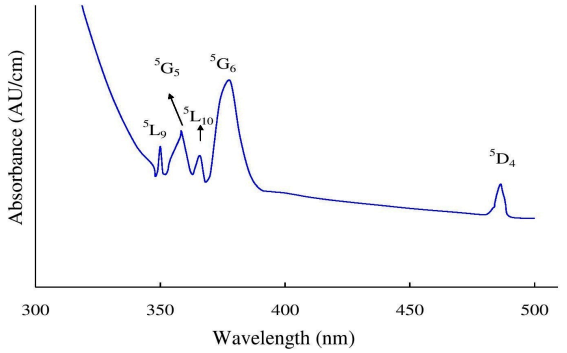

Fig. 4. Optical absorption spectrum of PbO−NaF−B_2O_3 glasses doped with Tb^{3+} ions

Table 4

J-O parameters of PbO−NaF−B_2O_3 glasses with Ln_2O_3

Glass	$\Omega_2\cdot10^{20}$, cm^2	$\Omega_4\cdot10^{20}$, cm^2	$\Omega_6\cdot10^{20}$, cm^2	Ω_4/Ω_6	Bonding parameter δ
Eu_2O_3 glasses	260	183	102.1	1.79	0.16
Tb_2O_3 glasses	88.40	83	14.24	5.82	0.11

The bonding parameter provides information regarding the covalent surroundings of Ln^{3+} ions within the glass matrix. The highest values of the bonding parameter δ found for the glasses indicate the highest covalent environment of Eu^{3+} ions among the glasses doped with Ln^{3+} ions.

Conclusions

The optical absorption of the $PbO-NaF-B_2O_3$ glass system was studied with varying concentrations of Ln_2O_3 (Ln=Eu, Tb). The optical absorption spectra of these ions in both glass systems were adequately described using the Judd-Ofelt hypothesis. The values of the Judd-Ofelt parameters Ω_λ, particularly Ω_2, which is related to the structural changes around the Ln^{3+} ions, indicated a gradual shift in the covalent environment with varying Ln_2O_3 concentrations. The highest bonding parameter values were observed in the glasses doped with Ln^{3+} ions, and the Eu_2O_3 doped glasses showed the highest covalent environment.

REFERENCES

1. *Optical* basicity and electronic polarizability of zinc borotellurite glass doped La^{3+} ions / Halimah M.K., Faznny M.F., Azlan M.N., Sidek H.A.A. // Results Phys. – 2017. – Vol.7. – P.581-589.

2. *Effect* of variable oxidation states of vanadium on the structural, optical, and dielectric properties of $B_2O_3-Li_2O-ZnO-V_2O_5$ glasses / Arya S.K., Danewalia S.S., Arora M., Singh K. // J. Phys. Chem. B. – 2016. – Vol.120. – P.12168-12176.

3. *Shaaban K.S., Abo-Naf S.M., Hassouna M.E.M.* Physical and structural properties of lithium borate glasses containing MoO_3 // Silicon. – 2019. – Vol.11. – P.2421-2428.

4. *XRD and FTIR structural* investigations of erbium-doped bismuth–lead–silver glasses and glass ceramics / Bosca M., Pop L., Borodi G., Pascuta P., Culea E. // J. Alloys Compd. – 2009. – Vol.479. – P.579-582.

5. *Murugan G.S., Varma K.B.R.* Characterization of lithium borate–bismuth tungstate glasses and glass-ceramics by impedance spectroscopy // Solid State Ionics. – 2001. – Vol.139. – P.105-112.

6. *Digonnet M.J.F.* Optical and electronic properties of rare earth ions in glasses // Rare-earth-doped fiber lasers and amplifiers, revised and expanded edition, 2nd edition. – CRC Press, 2001.

7. *Ofelt G.S.* Intensities of crystal spectra of rare-earth ions // J. Chem. Phys. – 1962. – Vol.37. – P.511-520.

8. *Luminescence* of europium-doped $BaO-Bi_2O_3-B_2O_3$ glasses / Egorysheva A.V., Volodin V.D., Chistyakov A.A., Kuzishchin Yu.A., Skorikov V.M., Dudkina T.D. // Inorg. Mater. – 2010. – Vol.46. – P.1384-1390.

9. *Zhou L., Zhu Z.* Study of magneto-optical properties of $GeO_2-B_2O_3-P_2O_5-ZnO-Tb_2O_3$ glass doped with different rare-earth ions // J. Non-Cryst. Solids. – 2022. – Vol.576. – Art. No. 121241.

10. *Performance* and wavelength tuning of green emitting terbium lasers / Metz P.W., Marzahl D.T., Huber G., Krankel C. // Opt. Express. – 2017. – Vol.25. – P.5716-5724.

11. *Paul A.* Chemistry of glasses. – Dordrecht: Springer, 1982.

12. *Spectroscopy* and energy transfer in Tb^{3+}/Sm^{3+} co-doped lead borate glasses / Pisarska J., Kos A., Soltys M., Gorny A., Pietrasik E., Pisarski W.A. // J. Lumin. – 2018. – Vol.195. – P.87-95.

13. *Yonezawa S., Kim J.H., Takashima M.* Preparation and properties of rare-earth-containing oxide fluoride glasses // Functionalized inorganic fluorides. – Wiley, 2010.

14. *Impact* of Eu^{3+} ions on physical and optical properties of $Li_2O-Na_2O-B_2O_3$ glass / Razak N.A., Hashim S., Mhareb M.H.A., Alajerami Y.S.M., Azizan S.A., Tamchek N. // Chin. J. Chem. Phys. – 2016. – Vol.29. – P.395-400.

15. *Spectroscopic* and physical properties of erbium doped $Li_2O-BaO-P_2O_5$ glasses / Ramesh Babu N.Ch., Raghava Rao P., Narasimha Rao N., Swami B.J.R.S.N., Vasu Babu M., Naga Raju G., et al. // Mater. Today Proc. – 2018. – Vol.5. – P.26314-26321.

Received 03.01.2023

ВПЛИВ ІОНІВ Eu^{3+}/Tb^{3+} НА ОПТИЧНІ СПЕКТРИ ПОГЛИНАННЯ СКЛА $PbO-NaF-B_2O_3$

Б.Дж.Р.С.Н. Свамі, Н. Нарасімха Рао, П. Нареш, П. Рагхава Рао, А. Чітті Бабу, Н.Ч. Рамеш Бабу

У статті наведені оптичні характеристики іонів Ln^{3+} у склі зі свинцево-натрієвим фторборатом складу 10 PbO–19 NaF–70 B_2O_3–1.0 Ln_2O_3 (де Ln=Eu та Tb, все в мол.%). Зразки скла були оброблені за допомогою звичайного методу розплавлення і швидкого охолодження, а скляна природа була підтверджена за допомогою рентгенівської дифракції. Оптичні спектри поглинання скла $PbO-NaF-B_2O_3$ з іонами Eu^{3+} виявляють виражені смуги поглинання, які були віднесені до переходів $^7F_0 \rightarrow {}^5L_6$, $^5D_3$, $^5D_2$ та $^7F_1 \rightarrow {}^5D_1$. Фактори Джадда-Офельта (Ω_2, Ω_4, Ω_6) були визначені з оптичних спектрів поглинання. За допомогою аналізу методом найменших квадратів, були оцінені та наведені сили осциляторів (f). Стосовно трьох параметрів Джадда-Офельта (Ω_2, Ω_4 та Ω_6), Ω_2, який пов'язаний з структурними коригуваннями на ділянці іонів Ln^{3+}, вказує на повільні коригування ковалентних оточень.

Ключові слова: B_2O_3 скло; оптичні спектри поглинання; Eu_2O_3; Tb_2O_3; іони Ln^{3+}; параметр Джадда-Офельта.

IMPACT OF Eu^{3+}/Tb^{3+} IONS ON $PbO-NaF-B_2O_3$ GLASSES OPTICAL ABSORPTION SPECTRA

B.J.R.S.N. Swamy [a], N. Narasimha Rao [a, *], P. Naresh [b], P. Raghava Rao [a], A. Chitti Babu [c], N.Ch. Ramesh Babu [d]

[a] Department of Physics, Krishna University Dr.MRAR College of PG Studies, Nuzvid, AP, India

[b] Department of Physics, Velagapudi Ramakrishna Siddhartha Engineering College, Vijayawada, AP, India

[c] Department of Physics, Sir. C.R. Reddy College of Engineering, Eluru, Andhra Pradesh, India

[d] Department of Physics, Rajiv Gandhi University of Knowledge & Technologies (AP-IIIT), Nuzvid, AP, India

[*] e-mail: nnrphy@gmail.com

The optical characteristics of glasses have become an increasingly established and developing aspect. This article presents the optical characteristics of the Ln^{3+} ion in lead sodium fluoroborate glass, which has the composition 10 PbO–19 NaF–70 B_2O_3–1.0 Ln_2O_3 (where Ln=Eu and Tb, all in mol.%). Glass samples were processed using the conventional melt-quenched approach, and the glassy nature was confirmed by the X-ray diffraction patterns. The optical absorption spectra of $PbO-NaF-B_2O_3$ glasses with Eu^{3+} ions exhibit distinct absorption bands that were assigned to the transitions $^7F_0 \rightarrow {}^5L_6$, $^5D_3$, $^5D_2$, and $^7F_1 \rightarrow {}^5D_1$. Judd-Ofelt (JO) factors (Ω_2, Ω_4, Ω_6) were determined from the absorption spectra. By using least square fit analysis, oscillator strength (f) was evaluated and presented. Regarding the three J-O parameters (Ω_2, Ω_4 and Ω_6), Ω_2, that is related to structural adjustments in the area of the Ln^{3+} ion, indicates slow adjustments of the covalent surroundings.

Keywords: B_2O_3 glass; optical absorption spectra; Eu_2O_3; Tb_2O_3; Ln^{3+} ions; J-O parameter.

REFERENCES

1. Halimah MK, Faznny MF, Azlan MN, Sidek HAA. Optical basicity and electronic polarizability of zinc borotellurite glass doped La^{3+} ions. *Results Phys*. 2017; 7: 581-589. doi: 10.1016/j.rinp.2017.01.014.

2. Arya SK, Danewalia SS, Arora M, Singh K. Effect of variable oxidation states of vanadium on the structural, optical, and dielectric properties of $B_2O_3-Li_2O-ZnO-V_2O_5$ glasses. *J Phys Chem B*. 2016; 120: 12168-12176. doi: 10.1021/acs.jpcb.6b08285.

3. Shaaban KS, Abo-Naf SM, Hassouna MEM. Physical and structural properties of lithium borate glasses containing MoO_3. *Silicon*. 2019: 11: 2421-2428. doi: 10.1007/s12633-016-9519-4.

4. Bosca M, Pop L, Borodi G, Pascuta P, Culea E. XRD and FTIR structural investigations of erbium-doped bismuth–lead–silver glasses and glass ceramics. *J Alloys Compd*. 2009; 479: 579-582. doi: 10.1016/j.jallcom.2009.01.001.

5. Murugan GS, Varma KBR. Characterization of lithium borate–bismuth tungstate glasses and glass-ceramics by impedance spectroscopy. *Solid State Ionics*. 2001; 139: 105-112. doi: 10.1016/S0167-2738(00)00825-0.

6. Digonnet MJF. Optical and electronic properties of rare earth ions in glasses. In: *Rare-Earth-Doped Fiber Lasers and Amplifiers, Revised and Expanded Edition*, 2nd Edition. CRC Press; 2001. doi: 10.1201/9780203904657.

7. Ofelt GS. Intensities of crystal spectra of rare-earth ions. *J Chem Phys*. 1962; 37: 511-520. doi: 10.1063/1.1701366.

8. Egorysheva AV, Volodin VD, Chistyakov AA, Kuzishchin YuA, Skorikov VM, Dudkina TD. Luminescence of europium-doped $BaO-Bi_2O_3-B_2O_3$ glasses. *Inorg Mater*. 2010; 46: 1384-1390. doi: 10.1134/S0020168510120204.

9. Zhou L, Zhu Z. Study of magneto-optical properties of $GeO_2-B_2O_3-P_2O_5-ZnO-Tb_2O_3$ glass doped with different rare-earth ions. *J Non-Cryst Solids*. 2022; 576: 121241. doi: 10.1016/j.jnoncrysol.2021.121241.

10. Metz PW, Marzahl DT, Huber G, Krankel C. Performance and wavelength tuning of green emitting terbium lasers. *Opt Express*. 2017; 25: 5716-5724. doi: 10.1364/OE.25.005716.

11. Paul A. *Chemistry of glasses*. Dordrecht: Springer; 1982. doi: 10.1007/978-94-009-5918-7.

12. Pisarska J, Kos A, Soltys M, Gorny A, Pietrasik E, Pisarski WA. Spectroscopy and energy transfer in Tb^{3+}/Sm^{3+} co-doped lead borate glasses. *J Lumin*. 2018; 195: 87-95. doi: 10.1016/j.jlumin.2017.11.020.

13. Yonezawa S, Kim JH, Takashima M. Preparation and properties of rare-earth-containing oxide fluoride glasses. In: Tressaud A. editor. *Functionalized inorganic fluorides*. Wiley; 2010. doi: 10.1002/9780470660768.ch18.

14. Razak NA, Hashim S, Mhareb MHA, Alajerami YSM, Azizan SA, Tamchek N. Impact of Eu^{3+} ions on physical and optical properties of $Li_2O-Na_2O-B_2O_3$ glass. *Chin J Chem Phys*. 2016; 29: 395-400. doi: 10.1063/1674-0068/29/cjcp1511226.

15. Ramesh Babu NCh, Raghava Rao P, Narasimha Rao N, Swami BJRSN, Vasu Babu M, Naga Raju G, et al. Spectroscopic and physical properties of erbium doped $Li_2O-BaO-P_2O_5$ glasses. *Mater Today Proc*. 2018; 5: 26314-26321. doi: 10.1016/j.matpr.2018.08.082.