

Modification of Strontium Oxide Concentration Stimulated Optical Properties of Er³⁺/Gd³⁺/Yb³⁺ Tri-doped Phosphate Glass

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ABSTRACT

A series of Er³⁺, Gd³⁺ and Yb³⁺ tri-doped phosphate glasses with compositions (48.5-x)P₂O₅ – 30Li₂O – 20ZnO – (x)SrO, where $0 \leq x \leq 5$ are prepared by melt quenching technique and their spectroscopic characterizations were made. The XRD patterns shows a broad peak which means the nature of the glass is amorphous. Glass samples are characterized via FTIR to examine the SrO concentration dependent structural properties. FTIR spectra revealed broad absorption bands (weak and strong) in wavenumber range of 1400 to 400 cm⁻¹. Thermal properties, including glass transition temperature (T_g), crystallization temperature (T_c), and crystal melting temperature (T_m) are obtained using DTA. The UV-Vis-NIR absorption spectra are recorded in the range of 200-800 nm. Using the UV absorption edge, the values of optical band gap energy (E_{opt}) and the Urbach energy (ΔE) are evaluated. It is demonstrated that SrO plays the role as an intermediate of glass formation and transforms the role to network-former or glass modifier depending on composition. The role of SrO in influencing the optical responses are analyzed and discussed. It is suggested that SrO contents assisted modification in the structure and absorption behaviour is attributed to the relaxing selection rules for forbidden transitions as well as reduction in the multi-phonon relaxation rate. Meanwhile, the observed optical improvements suggest that these glass compositions are potential for development of phosphate glass based efficient solid-state laser.

Keywords: Phosphate glass; strontium; erbium; gadolinium; ytterbium; tri-dopant

INTRODUCTION

Phosphate glasses have been widely studied in many fields such photonic applications, solid state laser, optical fiber, biomedical and many more due to their auspicious properties in several aspects [1]. Particularly, phosphate glasses properties such as low melting temperature, prominent transparency for visible light, low refractive index and dispersion, high luminous for ion doped concentration, and large emission and absorption cross sections are advantageous for white light emitting diodes (W-LEDs) [2]. However, typical pure phosphate glasses have relatively poor electric and thermal stability, which limits their applications. Glass composition can be optimized by adding other oxides such as Li₂O, ZnO and SrO to achieve more stable network glass structure.

Rare earth ions (REIs) materials such as Er^{3+} , Gd^{3+} and Yb^{3+} received great attention due to their wide range of applications in lasers, displays, solar cells, fibers, and amplifiers [3,4,5]. Lately, various type of oxides are being added to achieved desires luminescence and energy transfer properties. Emission signals are vigorously influenced by the concentration of REIs [6,7,8]. But first, a suitable concentration of SrO must be decided since adding other oxides such SrO are supposed to optimized for achieving stable glass network. The goal of the present study is to determine the effects of SrO addition while maintaining a constant tri-dopant concentration of phosphate glass network, on the structures and optical properties.

MATERIALS AND METHODS

Glass preparation

Phosphate glass $(49.7-x)\text{P}_2\text{O}_5-30\text{Li}_2\text{O}-20\text{ZnO}-x\text{SrO}-0.1\text{Er}_2\text{O}_3-0.1\text{Yb}_2\text{O}_3-0.1\text{Gd}_2\text{O}_3$, with ($x = 0, 1, 2, 3, 4$ and 5) are synthesized by using conventional melt-quenching technique. The nominal compositions and glass codes are summarized in Table 1. The batches are weighted and mixed thoroughly in an attrition mill. The batches are preheated and melted in alumina crucible at temperature $300\text{ }^\circ\text{C}$ for 1 h and $1050\text{ }^\circ\text{C}$ for 15 min. The homogenous melts are then quickly quenched on a stainless-steel plate and annealed at $300\text{ }^\circ\text{C}$ for 3 h to avoid thermal stress. Chemical powders of reagent grade purity were used to prepare this samples.

Table 1. Nominal compositions of $(49.7-x)\text{P}_2\text{O}_5-30\text{Li}_2\text{O}-20\text{ZnO}-x\text{SrO}-0.1\text{Er}_2\text{O}_3-0.1\text{Yb}_2\text{O}_3-0.1\text{Gd}_2\text{O}_3$

Sample code	P_2O_5 (mol%)	Li_2O (mol%)	ZnO (mol%)	SrO (mol%)	Er_2O_3 (mol%)	Yb_2O_3 (mol%)	Gd_2O_3 (mol%)
S1	49.7	30	20	0	0.1	0.1	0.1
S2	48.7	30	20	1	0.1	0.1	0.1
S3	47.7	30	20	2	0.1	0.1	0.1
S4	46.7	30	20	3	0.1	0.1	0.1
S5	45.7	30	20	4	0.1	0.1	0.1
S6	44.7	30	20	5	0.1	0.1	0.1

Glass characterization

The IR absorption and transmittance spectra are obtained using potassium bromide (KBr) pallet procedure. Highly purified KBr powder is mixed with ratio 1:100 of glass powder and desiccated. The samples are grounded in fine powder using a mortar and weighed. The mixture is then pressed with a pressure of 10 ton per square inch to yield a transparent pallet $\sim 0.3\text{ mm}$ thickness suitable for mounting. The room temperature IR spectra are recorded by a Perkin- Elmer Spectrum One FT-IR spectrometer in the range of $1400-400\text{ cm}^{-1}$ using 100 scans at a resolution of 4 cm^{-1} . DTA curves of the glass samples were obtained from differential thermal analyzer, where 25 mg glass powders heated in alumina crucible from room temperature to $800\text{ }^\circ\text{C}$ in static air, at heating rates of $10\text{ }^\circ\text{C}/\text{min}$.

Optical spectra measurement

Absorption spectra are recorded using UV3600Plus spectrometer in the wavelength range of 200-1600 nm. In many crystalline and non-crystalline semiconductors, the

absorption coefficient, $\alpha(\omega)$ depends exponentially on the $(\hbar\omega)$. This exponential dependence, known as the Urbach rule [9], can be written in the form:

$$\alpha(\omega) = B \exp(\hbar\omega/\Delta E),$$

where B is constant, and ΔE is the width of the band tails of the localized states.

For amorphous materials, $\alpha(\omega)$ at the fundamental edge is described by Mott and Davis [10]. The Mott and Davis equation was used to calculate direct and indirect optical band gaps using:

$$\alpha(\omega) = B[(\hbar\omega - E_{\text{opt}})^n / \hbar\omega],$$

where B is a constant, E_{opt} is the optical band gap energy for direct ($n = 1/2$) or indirect ($n = 2$) transitions.

RESULTS AND DISCUSSION

Glass forming ability

The XRD patterns of the glasses shows an amorphous state for all the studied compositions (Figure 1). The X-ray diffraction proved the amorphous nature of the specimens. A typical vitreous halo structure is reported between $2\theta = 20^\circ$ and 30° without any crystalline peaks for all glass samples concerned.

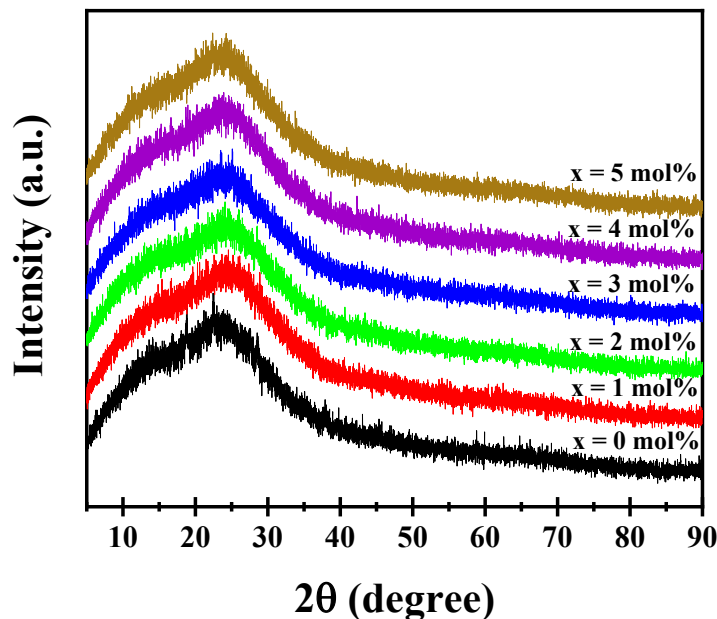


Figure 1. XRD patterns of $(49.7-x)\text{P}_2\text{O}_5-30\text{Li}_2\text{O}-20\text{ZnO}-x\text{SrO}-0.1\text{Er}_2\text{O}_3-0.1\text{Yb}_2\text{O}_3-0.1\text{Gd}_2\text{O}_3$ glasses

Infrared spectra

Figure 2 reveals the infrared spectra of the phosphate glass samples in a range of wavenumber from 400 to 1500 cm^{-1} . All the glasses had similar FT-IR spectra, the spectra of the mentioned glasses are characterized by the presence of five main absorption bands with the maxima located in the $1200-1300\text{ cm}^{-1}$, $1000-1200\text{ cm}^{-1}$, $900-950\text{ cm}^{-1}$, $700-800\text{ cm}^{-1}$ and $400-600\text{ cm}^{-1}$ wave number regions, and the detail data are listed in Table 2.

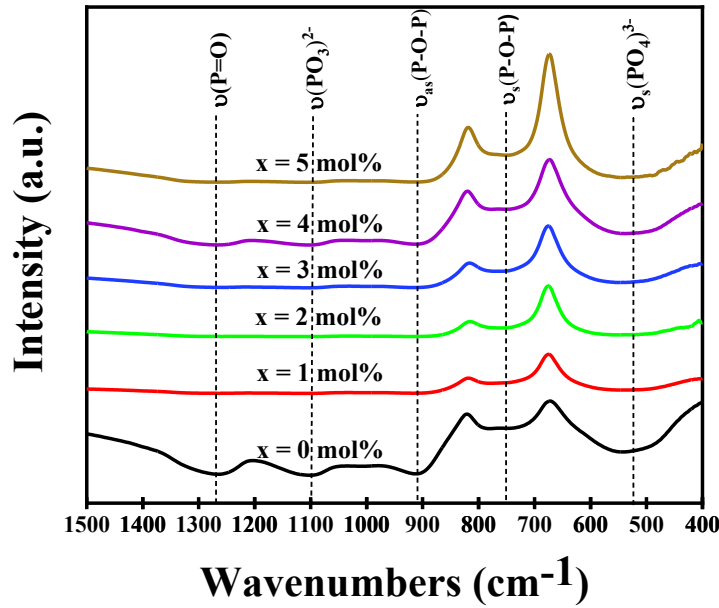


Figure 2. FT-IR spectra of
 $(49.7-x)\text{P}_2\text{O}_5-30\text{Li}_2\text{O}-20\text{ZnO}-x\text{SrO}-0.1\text{Er}_2\text{O}_3-0.1\text{Yb}_2\text{O}_3-0.1\text{Gd}_2\text{O}_3$ glasses

Table 2. Summary on positions (cm^{-1}) of various bands in the FT-IR spectra of the glass samples

Structural/sample code	S1 (± 2)	S2 (± 2)	S3 (± 2)	S4 (± 2)	S5 (± 2)	S6 (± 2)
$\nu(\text{P}=\text{O})$	1294	1292	1282	1275	1269	1258
$\nu(\text{PO}_3)^{2-}$	1106	1113	1115	1110	1099	1094
$\nu_{\text{as}}(\text{P}-\text{O}-\text{P})$	917	898	895	893	919	901
$\nu_{\text{s}}(\text{P}-\text{O}-\text{P})$	752	754	757	747	744	742
$\nu(\text{PO}_4)^{3-}$	536	554	526	530	525	522

The broad peak centered at $\sim 522 \text{ cm}^{-1}$ is allocated to fundamental frequencies of $\nu(\text{PO}_4)^{3-}$ or the harmonics of $\delta(\text{O}=\text{P}-\text{O})$, and a wide peak centered at $\sim 742 \text{ cm}^{-1}$ is attributed to the symmetric stretching vibration of P-O-P bonds occurring in ring type groups assigned with Q^2 metaphosphate units [11,12]. The band at $\sim 901 \text{ cm}^{-1}$ comes from asymmetric stretching vibration of P-O-P bonds in Q^2 units [13]. The peak at $\sim 1094 \text{ cm}^{-1}$ is associated to asymmetric stretching modes of $\nu(\text{PO}_3)^{2-}$ group associated with Q^1 phosphate units and that peak centered at $\sim 1258 \text{ cm}^{-1}$ is given by the asymmetric stretching vibration of doubly bonded oxygen $\nu_{\text{as}}(\text{P}=\text{O})$ and $(\text{PO}_2)^-$ modes from Q^2 units [14]. The peak intensity at $\nu_{\text{as}}(\text{P}-\text{O}-\text{P})$ shifts to the lower wavenumbers with an increase in SrO concentration. The shift indicates the increasing of phosphate chain length and angle which will lead to decreasing field strength of cation. The field strength of strontium ion is lower which causes the P-O-P bond angle to increase with the substitution of SrO, leading the peak to shift to lower wavenumber [15]. From these results, the broadening FT-IR spectra shows that the glass structures have the capability to tolerate with range of bonding states. The longer the phosphate chain, will lead to improvement of chemical durability as H_2O molecules are more difficult to hydrate the

phosphate molecule.

Thermal stability

Figure 3 presents the DTA curves of the glass samples $(49.7-x)\text{P}_2\text{O}_5-30\text{Li}_2\text{O}-20\text{ZnO}-x\text{SrO}-0.1\text{Er}_2\text{O}_3-0.1\text{Yb}_2\text{O}_3-0.1\text{Gd}_2\text{O}_3$ for heating rate of $10\text{ }^\circ\text{C}/\text{min}$, from which the glass transition temperature, T_g , peak crystallization temperature T_c and glass melting temperature T_m are obtained. As shown in Table 3, it is noticed that the concentration of SrO encourage the increase in T_g . This may be a consequence from an increase in the bond energy and strength of the glass network cause by the substitution of SrO with P_2O_5 . Meanwhile, T_c values shows decreases trend from $604\text{ }^\circ\text{C}$ to $555\text{ }^\circ\text{C}$ as the concentration of SrO increases. T_c values represent the crystallization peak which shows crystal growth of crystalline phases. Glass thermal stability depends on both T_g and T_c which important to acquire sufficient long-term stability. Higher T_g value is a reflection of the better composition and structure of glass. The temperature difference between T_c and T_g is a parameter that indicates the forming ability and thermal stability of glass network. Lower temperatures difference between T_c and T_g represents that the glass thermal stability is a good inhibition of nucleation and crystallization process. The DTA patterns is in agreement with previous report [16].

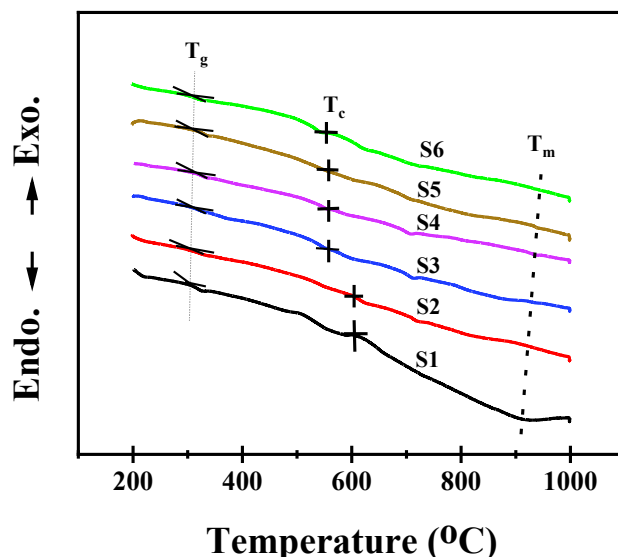


Figure 3. DTA curves of glass samples at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$

Table 3. Thermal stability parameters of $(49.7-x)\text{P}_2\text{O}_5-30\text{Li}_2\text{O}-20\text{ZnO}-x\text{SrO}-0.1\text{Er}_2\text{O}_3-0.1\text{Yb}_2\text{O}_3-0.1\text{Gd}_2\text{O}_3$ glasses

Sample code	T_g ($\pm 1\text{ }^\circ\text{C}$)	T_c ($\pm 1\text{ }^\circ\text{C}$)	T_m ($\pm 1\text{ }^\circ\text{C}$)
S1	301	604	911
S2	301	606	923
S3	307	559	929
S4	309	558	934
S5	311	558	940
S6	311	555	942

UV-Vis absorption spectra

The absorption spectra of glass samples are recorded at room temperature ranging from 400–900 nm of wavelength are shown in Figure 4. Absorption peaks are observed which are contributed by the excited state of $\text{Er}^{3+}/\text{Gd}^{3+}/\text{Yb}^{3+}$ tri-dopant. As expected, this transition presents the same absorption coefficient for all samples, since they all presents the same nominal composition of $\text{Er}^{3+}/\text{Gd}^{3+}/\text{Yb}^{3+}$ tri-dopant. The slight increase in some of the absorption peaks is believed to be due to the increasing SrO. The absorption bands attributed to each dopant were identified. The absorption peaks intensities around 1504 nm, 973 nm, 805 nm, 653 nm, 544 nm, 521 nm, 488 nm, 452 nm, 408 nm, 377 nm and 361 nm which correspond to the transitions from ground state of $^4\text{I}_{15/2}$ of Er^{3+} to the excited state of $^4\text{I}_{13/2}$, $^4\text{I}_{11/2}$, $^4\text{I}_{9/2}$, $^4\text{F}_{9/2}$, $^4\text{S}_{3/2}$, $^2\text{H}_{11/2}$, $^4\text{F}_{7/2}$, $^4\text{F}_{5/2}$, $^2\text{G}_{9/2}$, $^4\text{G}_{11/2}$ and $^4\text{G}_{9/2}$, respectively are in agreement with others [16,17]. The entire transitions are found to occur at the same place irrespective of the change in chemical composition. Comparing the absorption spectra with previous study [18] we acknowledge that, there are additional peak center at 927 nm attributed to an absorption broader band from ground state of $^2\text{F}_{7/2}$ of Yb^{3+} to excitation state $^2\text{F}_{5/2}$ of Yb^{3+} coinciding with the $^4\text{I}_{11/2}$ excitation state of Er^{3+} [19]. From the spectra, it is evidence that increasing SrO concentration increases absorbance peak at 521 nm.

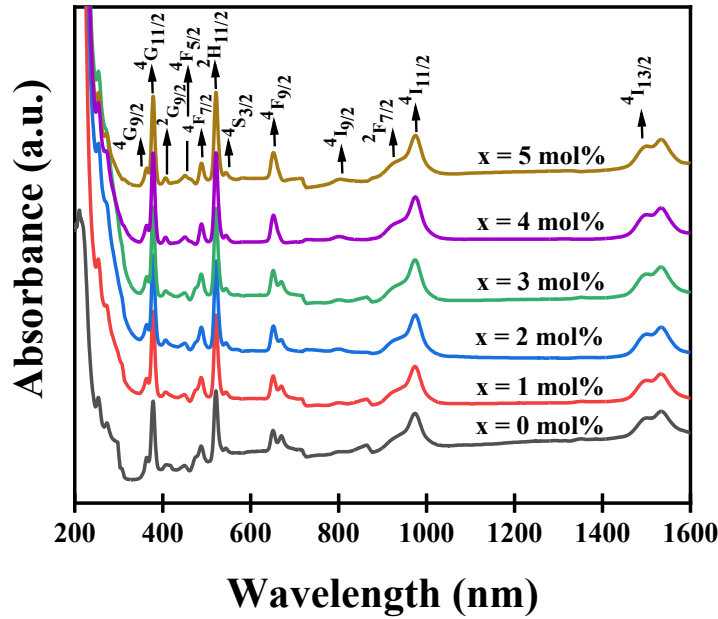


Figure 4. Absorption spectra of $(49.7-x)\text{P}_2\text{O}_5-30\text{Li}_2\text{O}-20\text{ZnO}-x\text{SrO}-0.1\text{Er}_2\text{O}_3-0.1\text{Yb}_2\text{O}_3-0.1\text{Gd}_2\text{O}_3$ glasses

Optical band gap energy (E_{opt}) and the Urbach energy (ΔE)

Tauc's plot representing $(\alpha\hbar\omega)^2$ versus $(\hbar\omega)$ is shown in Figure 5. The estimated E_{opt} and Urbach energy are listed in Table 4. The E_{opt} values are obtained in the linear region through extrapolation at $(\alpha\hbar\omega)^{1/2} = 0$. The values of E_{opt} decrease from 3.60 eV to 3.41 eV. This is owing to the fact that; the covalent nature of glass matrix decreases with increases of SrO concentration. But, with the increase of SrO concentrations up to 3 mol% and then increase to 3.59 eV with the increase of SrO concentration up to 5

mol%. This is due to the shortened of average chain length as the presence of the modifier change the network to more compact structure. Also, it opens up the chain by breaking those oxygen bonds, which form a bridge between the corners of PO_4 tetrahedra. Further addition of small amount of SrO altered the disorder and consequently increase the E_{opt} . The same trend is reported with Urbach energy when the SrO content is increase up to 3 mol%. The Urbach values decrease and then increase back to 0.28 eV when the concentration is increase up to 5 mol%. The Urbach energy decreases because the indirect nature of band gap become weaker. Meanwhile, when the Urbach energy increase, the effect gets weaker and makes the energy increased. The width of localized state in gap become smaller and the density of electrons with higher energy decreases thus reducing the electronic transition from valence band to conduction band. With an increase of SrO up until 5 mol%, the electronic transition is increased.

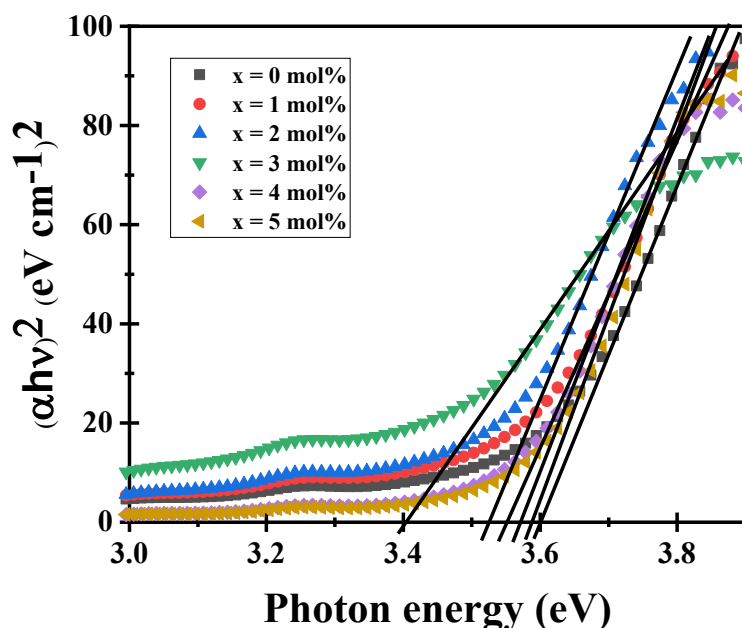


Figure 5. Tauc's plot to determine the direct band gap energy for different SrO concentration

Table 4. Optical band gap energy and Urbach energy value

Sample code	$E_{\text{opt}} (\pm 0.01 \text{ eV})$	$\Delta E (\pm 0.01 \text{ eV})$
S1	3.60	0.26
S2	3.54	0.25
S3	3.53	0.25
S4	3.41	0.24
S5	3.57	0.26
S6	3.59	0.28

CONCLUSIONS

The SrO dependent modification in local structures and enhancement in the absorbance of as tri-dopant phosphate glass are examined. The FTIR spectra reveals that the presence of SrO increased the depolymerization of the glass at Q1 and Q2 tetrahedral

site. The increase of T_g with the increase of SrO content is mainly attributed to the increase of bonding strength between phosphate chains. The structural and thermal properties show a strong correlation of rearrangement by SrO in phosphate glass network. All twelve UV-Vis absorption peaks intensities reveal slight enhancement. Optical band gap and Urbach energies calculated from absorption data shows considerably improvement in the optical response. The effects of SrO in altering the glass network and changing the absorption characteristics are interpreted and compared. The relationship between the optical properties and structural changes in the glass network due to the incorporating of SrO was established. The results improved structural and optical properties suggest that our method may constitute a basis for synthesizing phosphate glasses with controlled doping and addition of nanoparticles.

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REFERENCES

- [1] M. Itadani, A. Saitoh, Y. Masaoka, H. Takebe (2016). Low photoelastic and optical properties in RO–SnO–P₂O₅ (R = Zn, Ba, Sr) glasses, *Optics Letters* **41**, 45.
- [2] V. Kataria, S. Dixit, D. Singh Mehta (2019). Investigations on the up/downconversion of Gd₂O₂S: Er, Yb nanophosphor with both excitation wavelength and Yb³⁺–dependent emission color modulation, *J. Mater. Sci.* **54**, 13635.
- [3] E. Golis, E.I.S. Yousef, M. Reben, K. Kotynia, J. Filipecki (2015). Measurement of defect structures by positron annihilation lifetime spectroscopy of tellurite glass TeO₂–P₂O₅–ZnO–LiNbO₃ doped with ions of rare earth elements: Er³⁺, Nd³⁺ and Gd³⁺, *Solid State Science* **50**, 81.
- [4] K. Elena, N. Nikolay, B. Anastasiia (2020). Concentration dependence of upconversion luminescence of Er³⁺/Yb³⁺ in the fluorophosphate glasses with small phosphates content, *Optical Materials* **109**, 110279.
- [5] T. Jyothis, M. J.Q. Lauro, K. K. Venkata (2021). Optical properties of Ytterbium doped oxyfluoride glass-ceramic – Concentration and temperature dependence studies for optical refrigeration applications, *J. of Luminescence* **238**, 118278.
- [6] K. V. Ravi, G. Giridhar, V. Ravi Kumar (2017). The energy transfer efficiency from Yb³⁺ to Nd³⁺ in SrO–Pb₃O₄–ZnO–P₂O₅ glass system-Influence of lead ions, *J. of Luminescence* **187**, 281.
- [7] J. Dheraj, V. Sudarsan, R.K. Vatsa (2009). Luminescence studies on ZnO–P₂O₅ glasses doped with Gd₂O:Eu nanoparticles and Eu₂O₃, *J. of Luminescence* **129**, 439.
- [8] R.J. Amjad, M.R. Sahar, S.K. Ghoshal, S. Riaz (2012). Enhanced infrared to visible upconversion emission in Er³⁺ doped phosphate glass: Role of silver nanoparticles, *J. of Luminescence* **132**, 2714.
- [9] M. PrajnaShree, A. Wagh, Y. Raviprakash (2013). Characterization of pr6o11 doped zinc fluoroborate glass, *Eur. Sci. J.* **9**, 83-92.

- [10] S.K.J. Al-Ani, C.A. Hogarth, R.A. El-Malawany (1985). A study of optical absorption in tellurite and tellurite glasses. *J. Mater Sci* **20**(2), 661.
- [11] Y. Lai, X. Liang, S. Yang, P. Liu, Y. Zeng, C. Hu (2014). Raman and FTIR spectra of CeO₂ and Gd₂O₃ in iron phosphate glasses. *J. of Alloys and Compounds* **617**, 597-601.
- [12] X. Li, Z. Xiao, Y. He, Y. Wang, J. Luo, J. Shi, Q. Huang, L. Kong (2019). Crystalline behaviour, structure and properties of glasses in SrO–Fe₂O₃–P₂O₅ system, *J. of Non-Crystalline Solids* **523**, 119588.
- [13] Z. Ramzi, S. Touhtouh, W. Nachit, K. Benkhrouja, M. Taibi, A.Hajjaji (2016). Investigation of structural and physical properties of xSrO-(100-x)P₂O₅ glasses, *Mol. Cryst. Liq. Cryst.* **627**, 97.
- [14] P. Ramakrishna, R.K. Padhi, D.K. Mohapatra, H. Jena, B.S. Panigrahi (2022). Structural characterization, Gd³⁺ → Eu³⁺ energy transfer and radiative properties of Gd/Eu in codoped Li₂O–ZnO–SrO–B₂O₃–P₂O₅ glass, *Optical Materials* **125**, 112060.
- [15] A. Maity, S. Jana, S. Mitra (2022). Luminescence studies on varied concentration of Eu³⁺ doped SrO–ZnO–PbO–P₂O₅ glasses for photonic application, *Material Research Bulletin* **146**, 111595.
- [16] S.Y. Moustafa, M.R. Sahar, S.K. Goshal (2016). Erbium ions oscillator strength and emission enhancement in antimony phosphate amorphous matrix, *J. of Non-Crystalline Solids* **433**, 87.
- [17] A.A. Reddy, S.S. Babu, K. Pradesh, C.J. Otton, G.V. Prakash (2011). Optical properties of highly Er³⁺-doped sodium–aluminium–phosphate glasses for broadband 1.5μm emission, *J. of Alloys and Compounds* **509**, 4047.
- [18] F.G. Rego-Filho, N.O. Dantas, A.C.A. Silva, M.V.D. Vermelho, C. Jacinto (2017). IR-to-visible frequency upconversion in Yb³⁺/Tm³⁺ co-doped phosphate glass, *Optical Materials* **73**, 1.
- [19] R.F. Falci, T.C. Ranquine, N.O. Dantas, V. Anjos, M.J.V. Bell (2022). Upconversion and near infrared emission in Yb–Tm mediated by ZnTe crystals in oxide glasses, *Optical Materials* **124**, 111843.