

Er³⁺/Sm³⁺ Co-DOPED LUMINESCENT SODIUM LITHIUM PHOSPHATE GLASSES

S. Rashidah Misron, R. Arifin and S. K. Ghoshal

*Advanced Optical Material Research Group, Department of Physics,
Faculty of Science, Universiti Teknologi Malaysia,
81310 UTM Skudai, Johor, Malaysia.*

Corresponding author: ramliarifin@utm.my

ABSTRACT

Driven by the need of efficient luminescent glass materials we prepared a series of trivalent Erbium (Er³⁺)/ Samarium (Sm³⁺) co-doped sodium-lithium-phosphate (ErSmSLP) glasses via melt quenching method. Highly transparent glasses (both singly-doped and co-doped) of composition (49.5-x)P₂O₅-20Na₂O-30Li₂O-0.5Sm₂O₃-xEr₂O₃, where $x = 0.0$ to 1.0 mol% are acquired and their room temperature photoluminescence (PL) properties are determined as a function of co-dopants Er³⁺/Sm³⁺ concentration. The PL spectra of Er³⁺ doped phosphate glass (ErSLP) under 398 nm excitation exhibited six peaks at 500, 538, 560 595, 640, and 702 nm wavelength. The emission spectra of Sm³⁺ doped phosphate glass (SmSLP) under 403 nm excitations revealed a prominent orange emission at 598 nm originated from ⁴G_{5/2}→⁶H_{7/2} transition. Furthermore, the ErSmSLP glasses demonstrated PL intensity enhancement for Er³⁺ content of 1.0 mol%, which is attributed to the mechanism of energy transfer from Sm³⁺ to Er³⁺ ion. Our observation may be useful for the development of rare earth co-doped luminescent sodium-lithium-phosphate glass.

Keywords: Photoluminescence; Co-doped; Sodium Lithium Phosphate Glass; Rare Earth;

INTRODUCTION

Several unique properties of phosphate glasses make them attractive for varieties of technological applications. However, determination of glass optical, electrical, and physical properties together with composition optimization are prerequisite for selective applications [1]. Often, glass modifier, conditional former, and types of rare earth ions (REIs) are altered to upsurge the glass properties useful for enhanced performance. Phosphate glasses are thought to be the right competitor of traditional silicate glasses due to their easy fabrication, good chemical durability, excellent optical properties, ion exchange ability, very high solubility of REIs and non-clustering attributes. It is the high solubility of REIs in phosphate glasses that allows the introduction of a larger concentration of active ions into a small volume. Recently, REIs doped phosphate glasses are increasingly used in photonics, optical communications, micro surgery, high-power lasers, etc. [2-4]. Materials for laser operation must possess sharp

fluorescent lines, strong absorption bands, and reasonably high quantum efficiency for the fluorescent transition (stimulated emission).

The REIs are natural candidates to serve as active ions in solid-state laser materials because they exhibit a wealth of sharp fluorescent transitions (involving 4f-4f) presents several emissions representing almost every region of the visible and near-infrared portions of the electromagnetic spectrum [5, 6]. Luminescence emissions of RE doped glasses and crystals are suitable sources for laser development [6]. On the one hand, the $^4G_{5/2}$ level of Sm^{3+} ($4f^5$) ion display different emission channels with relatively high quantum efficiency. Samarium doped glass is well-known as a cladding for Nd-doped glass laser rods owing to its high absorption at 1064 nm but low absorption between 500 and 900 nm [7-8]. Conversely, Er^{3+} ion are well-known for excellent up-conversion emission and sensitization efficiency [9]. In addition to IR broad band line around 1.5 μm , Er^{3+} ions blue, green, and red emissions are prospective. Er^{3+} ions are exploited as an up-conversion luminescence center due to their more homogeneous energy level distribution, enabling longer lifetimes of metastable energy levels. In the short-wavelength region, Er^{3+} can emit blue ($^4F_{7/2} \rightarrow ^4I_{15/2}$, 488 nm), green ($^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$, 520/550 nm) and red ($^4F_{9/2} \rightarrow ^4I_{15/2}$, 660 nm), and the upconversion emissions of all these wavelengths have been observed when pumped with various wavelengths matching $^2H_{11/2}/^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ levels [10].

Combining these attractive features of REIs (Er^{3+} and Sm^{3+}) and SLP glass we inspect the feasibility of achieving enhanced luminescence under optimized co-dopants concentration, where energy transfer between these luminescence ions may be suitably exploited and tuned.

EXPERIMENTAL

Reagent grade chemicals of P_2O_5 , Na_2O , Li_2CO_3 , Er_2O_3 , and Sm_2O_3 in powdered form are used for the glass preparation. A 15 g batch of these glass constituents is weighed separately and thoroughly milled for 15 minutes to get homogeneous mixture. Then, the mixture is placed into alumina crucibles and sintered in a pre-heated electric furnace at 300°C for an hour. Next, the crucible containing the preheated mixture is transferred into another electric furnace at 950°C and melted for 15 minutes. Upon achieving the desired viscosity, the molten fluid is poured onto steel mold and annealed at 300 °C for 2 and half hours to relieve the internal stress. After that, the samples are cooled down slowly room temperature. Solid samples are cut and polished to desired dimension for further analyses. The room temperature luminescence spectra of as synthesized samples are recorded using Horiba FluoroMax4 Spectrofluorometer. Table 1 enlists the nominal compositions all the prepared ErSmSLP glasses together with their codes.

Table 1: Composition of ErSmSLP glass samples

Sample Codes	Composition (mol%)				
	P ₂ O ₅	Na ₂ O	Li ₂ O	Er ₂ O ₃	Sm ₂ O ₃
SmSLP	49.5	20	30	0	0.5
ErSLP	49.5	20	30	0.5	0
ErSmSLP1	49.3	20	30	0.2	0.5
ErSmSLP2	48.9	20	30	0.6	0.5
ErSmSLP3	48.5	20	30	1.0	0.5

RESULTS AND DISCUSSION

Figure 1 shows the PL spectra of ErSLP glass with 0.5 mol% of Er³⁺ (without Sm³⁺) under 398 nm excitations. It consists of six significant peaks centered at 500 nm, 538 nm, 560 nm, 595 nm, 640 nm, 702 nm which are assigned to the transitions from the excited states of ²H_{11/2}, ⁴S_{3/2}, and ⁴F_{9/2} to the ground states of Er³⁺ ion.

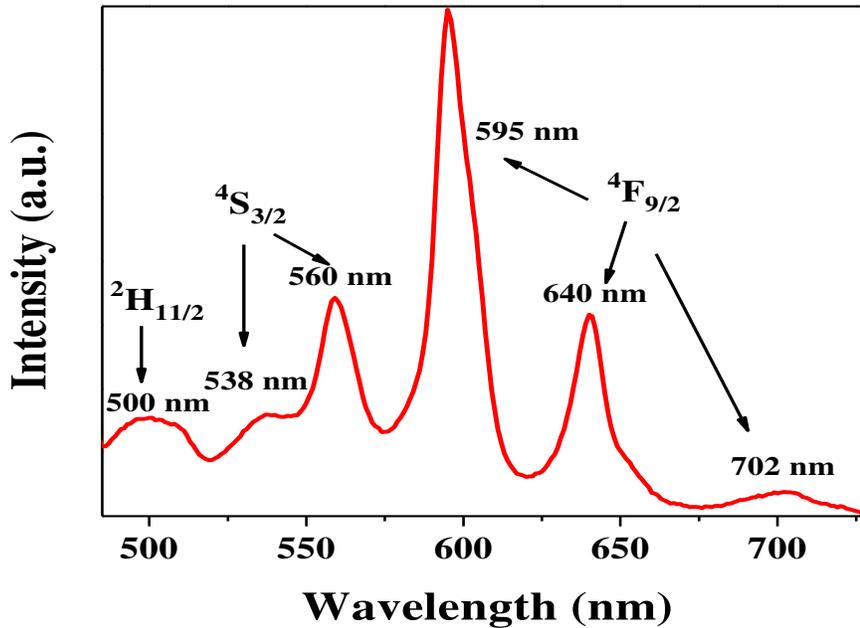


Figure 1: PL spectra of ErSLP glass (0.5 mol% Er³⁺)

Figure 2 displays the PL spectra of SmSLP glass with 0.5 mol% of Sm³⁺ (without Er³⁺) under 404 nm excitations. It consists of four significant peaks centered at 562 nm (yellow), 598 nm (orange), 644 nm (orange reddish) and 705 nm (red), which are allocated to the electronic transitions of ⁴G_{5/2}→⁶H_{(2j+1)/2}, where j = 2, 3, 4 and 5. The orange peak corresponding to the ⁴G_{5/2}→⁶H_{7/2} (598 nm) transition is found to possess

the highest intensity.

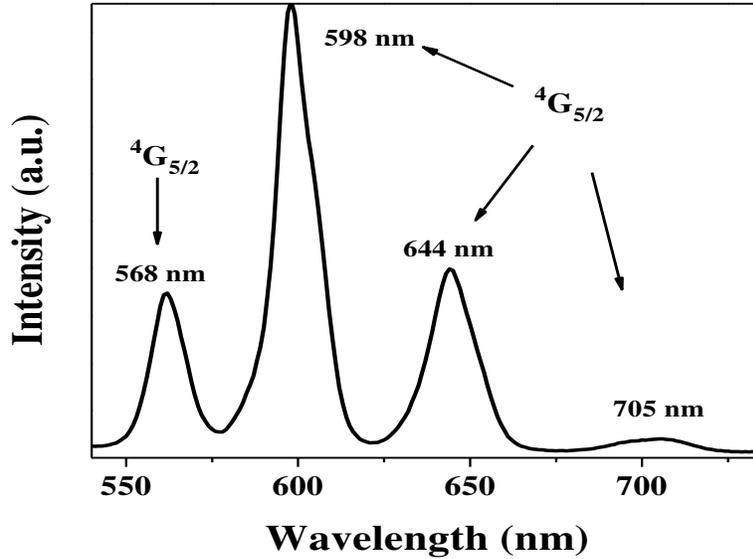


Figure 2: PL spectra of SmSLP glass (0.5 mol% Sm³⁺)

Figure 3 illustrates the PL spectra of all ErSmSLP glass under 488 nm excitations with varying Er³⁺ concentration. Four prominent peaks are evidenced, which are assigned to various transitions among Sm³⁺ excited states to the ground state such as ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ (560 nm), ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (596 nm), ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ (640 nm) and ${}^4G_{5/2} \rightarrow {}^6H_{11/2}$ (704 nm). Furthermore, the PL intensity of Sm³⁺ is found to greatly enhance with the increase of Er³⁺ ion concentration in the glass matrix. This enhancement is attributed to the energy transfer from Sm³⁺ to Er³⁺ ion due to the sensitization. [8] At lower Er₂O₃ concentrations, the average distance between the Er³⁺-Er³⁺ ions is high so the interactions between them is negligible this results high energy migration from Er³⁺ to Sm³⁺ ions. However, at higher Er₂O₃ concentration, the distance between Er³⁺ - Er³⁺ ions is low resulting in strong interactions between these ions. This leads to lower amount of energy transfer from Er³⁺ to Sm³⁺ ion.

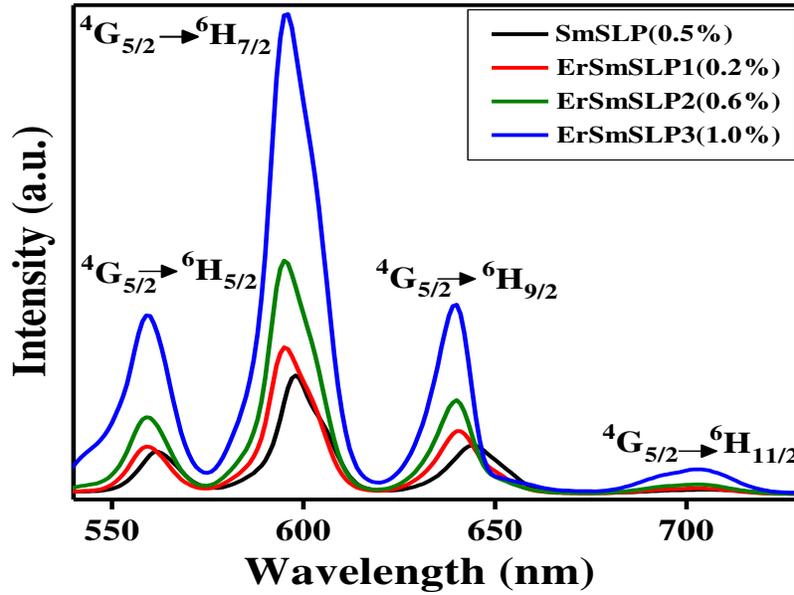


Figure 3: PL spectra of co-doped ErSmSLP glass samples (0.2-1.0 mol% Er³⁺)

Figure 4 depicts the partial energy levels diagram of Sm³⁺ and Er³⁺ ions showing the down conversion under excitation wavelength of 488 nm. The excited level gets populated through the ground state absorption (GSA). In this mechanism, a resonant photon pumped at 488 nm excitation promotes the populations of Er³⁺ from the ground state, ⁴I_{5/2} to the excited state ²H_{11/2}. The unstable ions in ²H_{11/2} relax radiatively (R) to ⁴S_{3/2} level. The relaxed Er³⁺ ions at ⁴S_{3/2} excited state transfer the energy (ET) to Sm³⁺ ions and populate ⁴F_{3/2} level of samarium. The unstable state ⁴F_{3/2} relaxes nonradiatively to ⁴G_{5/2} level. Some of the ions in ⁴G_{5/2} level relax radiatively to the ground state ⁶H_{5/2} level that results in yellow emission centered at 560 nm. There are other ions in ⁴G_{5/2} level relax radiatively to ⁶H_{7/2} level and produces orange emission centered at 596 nm. The Sm³⁺ ions are found relax radiatively to both states ⁶H_{9/2} and ⁶H_{11/2} to form peaks centered at 640 nm and 704 nm, respectively [8].

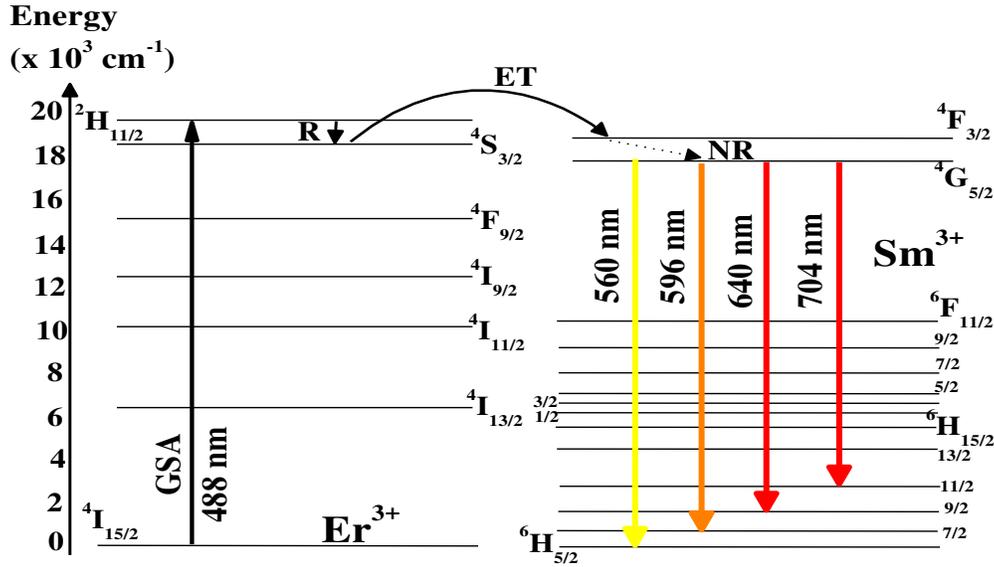


Figure 4: Energy level diagram for co-doped ErSmPSL glass samples

The network of phosphate glasses contains a polymeric structure that is controlled by the glass composition, which is in rough agreement with the predictions of Zachariassen et al [11]. Phosphate glass structure does not show any long range order or significant symmetry of atomic arrangement, but they do have short-range order. The glass-forming component in phosphate glasses is P_2O_5 , and the basic unit in the phosphate glass structure is the orthophosphate (PO_4^{3-}) tetrahedron, which is a phosphorus atom surrounded by four oxygen atoms connected to adjacent units by three of their four vertices. Usually, one place is occupied by a terminal with double-bonded oxygen atom (DBO) [11]. As one of the oxygen atoms is connected to the phosphorus atom by a double bond, only the three other oxygen atoms can act as bridges to other orthophosphate tetrahedra. By forming such bridges, individual orthophosphate tetrahedra can be linked to each other by covalent P–O–P bonds. The oxygens in these P–O–P linkages are commonly called bridging oxygens (BOs). The addition of glass modifier oxides and dopants which are Na_2O , Li_2O , Er_2O_3 and Sm_2O_3 to the glass, results in the cleavage of P–O–P linkages and the creation of non-bridging oxygens (NBOs) in the glass. The resulting glass structure is disrupted, containing not only covalent P–O–P bonds but also ionic cross-linkages between NBOs, and this process is called depolymerisation of the network [12].

CONCLUSION

Transparent and thermally stable SLP glasses co-doped with Er^{3+}/Sm^{3+} are prepared using melt quenching method. The influence of co-dopants on the fluorescence features is scrutinized. The inclusion of Er^{3+} as codopants in to the glass matrix has enhanced the PL peak intensity. The Er^{3+} ions mediated sensitization of the PL spectrum of co-doped

glasses is interpreted using partial energy level diagram. Generation of NBO and subsequent depolymerisation of the network together with energy transfer from Er^{3+} to Sm^{3+} is found to play a significant role towards PL intensity enhancement. These kinds of glasses are potential for fabricating orange light emitting devices in the fields of photonics and optoelectronics.

ACKNOWLEDGEMENTS

We acknowledge gratefully the financial support from Ministry of Higher Education through grant GUP/FRGS Vot. 07H99, 05H36, 4F650, and 4F424. The experimental assistance from Faculty of Science, Universiti Teknologi Malaysia is appreciated.

REFERENCES

- [1]. Altaf, M. and Ashraf, M. C. *Journal of Modern Physics*. **1** 201-205 (2010)
- [2]. Mura, E., Lousteau, J., Milanese, D., Abrate, S. and Vincenzo, M. S. *Journal of Non-Crystalline Solids*. **362**, 147–151 (2013)
- [3]. Amjad, R. J., Sahar, M. R., Ghoshal, S. K., Dousti, M. R., Samavati, A. R., Riaz, S. and Tahir, B. A. *Acta Physica Polonica A*. **123** (4) 746-749 (2013)
- [4]. Mura, E., Lousteau, J., Milanese, D., Abrate, S. and Vincenzo, M. S. *Journal of Non-Crystalline Solids*. **362** 147–151 (2013)
- [5]. Semwal, K., Bhatt, S.C. *International Journal of Physics*. **1** (1) 15-21 (2013)
- [6]. Dousti, M. R. *Measurement*. **56**, 117–120 (2014)
- [7]. Elisa, M., Sava, B. A., Vasiliu, I. C., Monteiro, R. C. C., Veiga, J. P., Ghervase, L., Feraru, I. and Iordanescu, R. *Journal of Non-Crystalline Solids*. **369**, 55–60 (2013)
- [8]. Reddy, C.P, Naresh, V., Babu, B.C., Buddhudu, S. *Advances in Materials Physics and Chemistry*. **4**, 165-171 (2014)
- [9]. Tripathi, G., Rai, V. K., Raia, A., Rai, S.B. *Spectrochimica Acta Part A*. **71**, 486–489 (2008)
- [10]. Fu, S. B., Chen, B. J., Zhang, J. S., Li, X. P., Zhong, H., Tian, B. N., Wang, Y. Z., Sun, M., Zhang, X. Q., Cheng, L. H., Zhong, H.Y. and Xia, H. P. *Applied Physics A*. **115**, 1329–1333 (2014)
- [11]. Moustafa, Y. M., El-Egili, K. *Journal of Non-Crystalline Solids*. **240**, 144-153 (1998)
- [12]. Brauer, D. S. (2012). *Phosphate Glasses, in Bio-Glasses: An Introduction*. Jones, J. R. and Clare, A. G. (Eds.). Chichester, UK: John Wiley & Sons, Ltd