

RADIO AND PHOTO LUMINESCENCE STUDIES OF MGO-BAO-P₂O₅ GLASSES DOPED WITH EU³⁺ ION FOR REDDISH ORANGE EMISSION MATERIAL APPLICATION

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Received: May 29, 2018; Revised: June 29, 2018; Accepted: July 02, 2018

Abstract

Trivalent europium doped magnesium barium phosphate (MgO-BaO-P₂O₅) glasses were prepared and investigated to evaluate their potential for photonic materials. The density, the molar volume and the refractive index were studied to assess the impact of Eu₂O₃ on studied glasses. Luminescence properties of glass samples have been recorded under photon, X-ray and laser excitations. It can be observed that, the emission centered at around 610 nm (⁵D₀→⁷F₂) is the most prominent. Also, the shapes of the emission peaks are similar in all the glasses excepting small variations in intensity of the transitions. From calculated chromaticity coordinates, it is suggested that the glass samples are most suitable for the development of photonic applications in reddish orange region.

Keywords: Europium oxide, Luminescence, Phosphate glass

Introduction

In recent years, there has been a renewed interest in the search for new materials to be used as hosts for rare earth (RE) ion for potential applications in the fields of lasers, optical amplifiers and display devices. Oxide glasses are one of the most interesting materials because of their cheap production cost, good thermal stability, simple manufacturing process and high doping

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capability (Ki-Soo Lim *et al.*, 2013; Deopa *et al.*, 2018). Among various glass materials such as phosphate, borate, vanadate, germanate and silicate, phosphate glasses are the best glass formers and attract many researchers due to their unique characteristics that include high transparency, low melting temperature, low viscosity, high ultraviolet (UV) transmission and high solubility of RE ion (Balakrishnaiah *et al.*, 2006; Langar *et al.*, 2017; Shajan *et al.*, 2017). It is a known fact that phosphate glasses are low chemical durability and high hygroscopic nature, which in literature reviews on the properties of glass in terms of its chemical and physical durability out that these can be improved by adding metal oxides like K₂O, MgO, BaO, Al₂O₃, (Balakrishnaiah *et al.*, 2006; Hraiech *et al.*, 2018) etc.

RE ion doped phosphate glasses are used in many optical devices due to their intense radiations in the visible (Vis), infrared (IR) and near infrared (NIR) regions under suitable excitation wavelengths. This is result of that high luminescence efficiencies which related with 4f–4f and 4f–5d electronic transitions (Ki-Soo Lim *et al.*, 2013; Nayab Rasool *et al.*, 2013). However, the luminescence efficiencies also depend on the concentration of RE ion and chemical composition structure of glass. Trivalent europium (Eu³⁺) ion shows great potential as orange/red light emission (around 610 nm) due to its ⁵D₀→⁷F₂ transition state. Therefore its compounds are promising for various optical applications such as high-density optical storage, color display devices and reddish orange emitting materials (Linganna and Jayasankar, 2012; Vijaya and Jayasankar, 2012). Many researchers have investigated the luminescence properties of Eu³⁺ doped in phosphate (Linganna and Jayasankar, 2012; Shajan *et al.*, 2017), borate (Rajagukguk *et al.*, 2016) and tellurite (Stambouli *et al.*, 2013) glasses for using as photonic applications.

In this study, magnesium barium phosphate glasses doped with various Eu³⁺ concentrations have been fabricated by melt-quenching technique. The physical, optical and luminescence properties of the glass samples were studied and reported to determine the

ability for using as display devices in reddish orange region.

Materials and Methods

Sample Preparation

Magnesium barium phosphate glasses doped with various concentrations of europium oxide were prepared by melt quenching technique in the compositions 30MgO:20BaO:(50-x)P₂O₅:xEu₂O₃ (where x = 0.00, 0.05, 0.10, 0.50, 1.00 and 2.00 mol%) which are labeled as MgBPEu000, MgBPEu005, MgBPEu010, MgBPEu050, MgBPEu100 and MgBPEu200, respectively. Raw chemicals of magnesium oxide (MgO), barium carbonate (BaCO₃), ammonium dihydrogen orthophosphate (NH₄H₂PO₄) and europium oxide (Eu₂O₃) were used for the preparation of the glasses. About 20 g of the batch composition was weighed and mixed thoroughly in porcelain crucible and melted at 1,200 °C for 3 h in an electric muffle furnace. Then the glass melt was poured in to a preheated graphite mold and annealed at 500°C for 3 h and then cooled down to room temperature to remove thermal stress and strain. Finally, these glass samples were cut and polished to flat surface as shown in Figure 1.

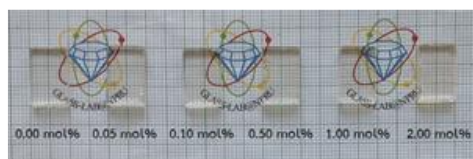


Figure 1. Photograph of magnesium barium phosphate glasses doped with Eu³⁺ ion

Measurements

The refractive index (*n*) of the glass samples was measured by sodium vapor lamp as a light source (589 nm) using Abbe refractometer (ATAGO) and mono-bromonaphthalene was used as the contact liquid. The density (*ρ*) of each glass samples was determined by the Archimedes method by using a 4-digit sensitive microbalance (AND, HR-200). The molar volume (*V_m*) was

calculated by dividing the total molecular weight (M_T) of each system by their density. The absorption spectra were recorded by UV-Vis-NIR spectrophotometer (Shimadzu, UV-3600) in the range of 350-2,400 nm. The excitation and emission spectra were measured by fluorescence spectrophotometer (Agilent Technologies Cary Eclipse) with xenon lamp as a light source. The radioluminescence (RL) of glass samples are record at room temperatuer under X-ray excitation. The RL spectra were measured using a Cu target x-ray generator (Inel, XRG3D-E), whose was operated at 50 kV and 30 mA, and the spectrometer (QE65 Pro, Ocean Optics) with an optical fiber to detect the emission spect. The laser induced emission spectrum was measured with a pulse width of 10 ns and repetition rate of 6.06 kHz (CNI, 266 nm UV solid state laser, MPL-F-266). The laser induced emission spectra were measured at low temperature in the range from 300 K to 10 K. CIE 1931 chromaticity diagram was used to determine color of the emission light obtained from the emission spectra.

Results and Discussion

Physical Properties

The physical properties of MgBPEu glasses are collected in Figure 2. The density is one of the essential physical properties that describes the structural modification in the network of the material. As seen from Figure 2(a), the density and the refractive index

increase with increasing Eu^{3+} concentration. Since, the molecular weight of Eu_2O_3 (351.93 g/mol) is higher than other oxides in glasses ($\text{MgO} = 40.30$ g/mol, $\text{BaO} = 153.33$ g/mol and $\text{P}_2\text{O}_5 = 141.94$ g/mol). Hence, addition of Eu_2O_3 at the cost of P_2O_5 increases the density of glasses. While, the refractive index of the glass increases when its density increases due to the replacement of P_2O_5 via Eu_2O_3 in glass composition, which Eu_2O_3 has higher density more than P_2O_5 . Theoretically, the refractive index, is a function of density and mean polarizability of the medium (Tan and Arndt, 1997). Therefore, the refractive index of a glass increases when its density increases (Chanthima *et al.*, 2017).

The molar volume is decreased as the Eu^{3+} concentration is in range of 0.00 to 0.50 mol%, which shows that the Eu_2O_3 acts as a partly former of the glass material making the structure is more packing and increase of connectivity in glass network. On the other hand, the molar volume of glass samples were increased as the Eu^{3+} concentration was beyond 0.50 mol% as shown in Figure 2(b). This result reflects that Eu_2O_3 entering into the glass network can act as a modifier and the creation of non-bridging oxygen (NBO) in glass network, indicating the reduction of glass connectivity and the increase of the molar volume of glass samples (Rajagukguk *et al.*, 2016). From the result of the molar volume, it indicates that the concentration of the Eu_2O_3 causing the Eu_2O_3 act as performed differently within the matrix.

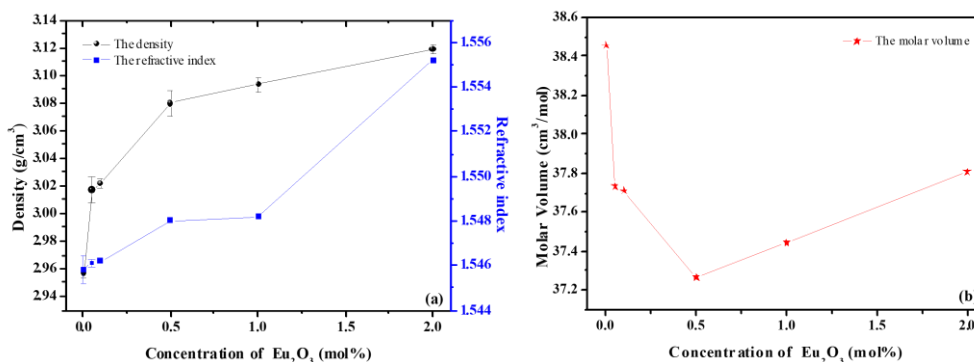


Figure 2. The density and the refractive index (a) and the molar volume (b) of glass samples

Optical Absorption

Figure 3 shows the absorption spectra of MgBPEu glasses recorded at room temperature in ultraviolet visible and near infrared (UV-Vis-NIR) regions. The absorption bands with different wavelengths are correlated to the electronic transition between the inner orbits of Eu³⁺ ion. These bands corresponding to the transitions ${}^7F_0 \rightarrow {}^5G_2$ (381 nm), ${}^7F_0 \rightarrow {}^5L_6$ (394 nm), ${}^7F_1 \rightarrow {}^5D_3$ (412 nm), ${}^7F_0 \rightarrow {}^5D_2$ (465 nm), ${}^7F_1 \rightarrow {}^5D_1$ (532

nm), ${}^7F_0 \rightarrow {}^7F_6$ (2091 nm) and ${}^7F_1 \rightarrow {}^7F_6$ (2209 nm) were observed. The absorption band positions in MgBPEu glasses are similar to those reported in other literatures (Linganna and Jayasankar, 2012; Vijaya and Jayasankar, 2012; Rajagukguk *et al.*, 2016). Among all absorption bands, the ${}^7F_0 \rightarrow {}^5L_6$ (394 nm) transition is found to be more intense than any other transitions, even this transition is forbidden by the ΔS and ΔL selection rules but allowed for the ΔJ selection rule (Linganna and Jayasankar, 2012; Rajagukguk *et al.*, 2016). Furthermore, the absorbance of MgBPEu glasses increases with increasing Eu³⁺ concentration.

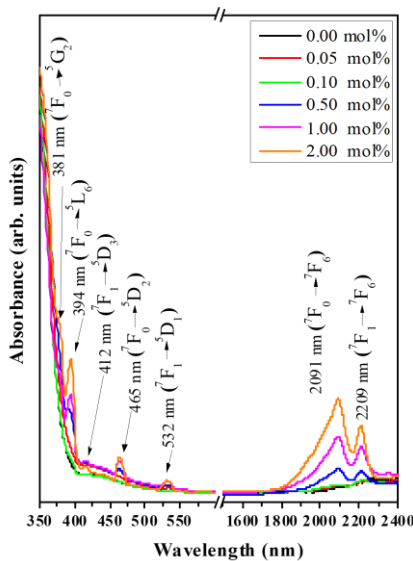


Figure 3. The absorption spectra of MgBPEu glasses in UV-Vis-NIR regions

Photoluminescence

Figure 4(a) shows the excitation spectra of Eu³⁺ doped magnesium barium phosphate glasses in the wavelength range of 350-550 nm, by monitoring the emission at 613 nm. From the excitation spectra, various bands are observed at 362, 382, 394, 414, 464, 525 and 533 nm corresponding to the transitions from the ground state to the excited states that are ${}^7F_0 \rightarrow {}^5D_4$, ${}^7F_1 \rightarrow {}^5G_2$, ${}^7F_0 \rightarrow {}^5L_6$, ${}^7F_1 \rightarrow {}^5D_3$, ${}^7F_0 \rightarrow {}^5D_2$, ${}^7F_0 \rightarrow {}^5D_1$ and ${}^7F_1 \rightarrow {}^5D_1$, respectively (Vijaya and Jayasankar, 2012). Among these excitation bands, the ${}^7F_0 \rightarrow {}^5L_6$ (394 nm) transition is found to be more prominent and it was used to record the emission spectra of MgBPEu glasses in the wavelength range of 550-750 nm.

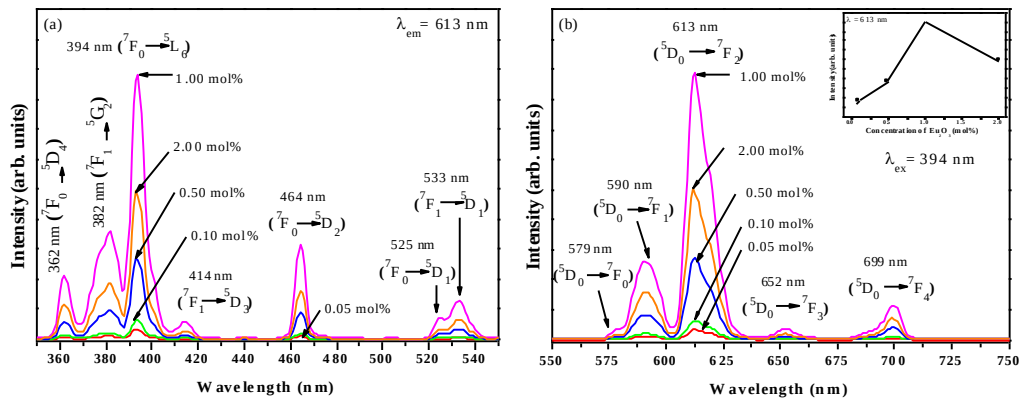


Figure 4. The density and the refractive index (a) and the molar volume (b) of glass samples

The emission spectra of MgBPEu glasses for different concentrations of Eu^{3+} ion under 394 nm excitation wavelength are shown in Figure 4(b). The emission spectra exhibited five emission bands centered at 579, 590, 613, 652 and 699 nm corresponds to $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively (Maheshvaran and Marimuthu, 2012). The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition ($\Delta J = 1$) is a magnetic dipole (MD) allowed transition and is not sensitive to the site symmetry around Eu^{3+} ion, whereas the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition ($\Delta J = 2$) is due to the electric dipole (ED) allowed transition and very sensitive to the coordination environment of Eu^{3+} ion, so $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition can indicate the symmetry around Eu^{3+} ion in glass matrix (Linganna and Jayasankar, 2012; Luciana *et al.*, 2010; Maheshvaran and Marimuthu, 2012; Stambouli *et al.*, 2013). The intensities of both excitation and emission peaks increase with increasing of Eu_2O_3 concentration upto 1.00 mol% and then decrease. Because of the rise in non-radiative decay channels, which are enhanced due to the concentration quenching effect (Linganna and Jayasankar, 2012). Therefore, the optimum concentration of Eu_2O_3 for MgBPEu glass is 1.00 mol% which makes the highest intensity of emission coming out from this glass.

The intensity ratio R (ratio between intensities of ED and MD transitions; ED/MD), known as the asymmetric ratio can be used to investigate the symmetry of the local environment the RE ion and relative strength of covalent/ionic bonding between Eu^{3+} ion. Higher ratio shows lower symmetry around the Eu^{3+} ion and higher Eu–O covalence (Maheshvaran and Marimuthu, 2012; Ramachari *et al.*, 2013). Also the R value provide valuable information in

developing laser sources. (Stambouli *et al.*, 2012). In this work, the intensity ratio of MgBPEu100 glass is found to be 3.44 and is smaller when compared to BBCE2 (Libin Xia *et al.*, 2017) and 2EB (Maheshvaran and Marimuthu, 2012) glasses and higher when compared to PbPEuP (Maheshvaran and Marimuthu, 2012) and BNaPbZnLiEu_2 (Rajagukguk *et al.*, 2016) glasses as presented in Table 1. Therefore, can be explained more laser potential of MgBPEu100 glass than PbPEuP and BNaPbZnLiEu_2 glasses.

CIE Chromaticity Diagram

The emitting color of MgBPEu glasses excited by 394 nm were investigated using the Commission International de l'Eclairage (CIE) 1931 chromaticity diagram to identify the dominant emission wavelength of glass samples for evaluating the material performance. The CIE color coordinates (x,y) of MgBPEu005, MgBPEu010, MgBPEu050, MgBPEu100 and MgBPEu200 glasses are found to be (0.647,0.352), (0.648,0.352), (0.648,0.352), (0.648,0.351) and (0.648,0.351), respectively. Figure. 5 presents the location of (x,y) color coordinate of the emission light of the MgBPEu glasses on CIE 1931 chromaticity diagram, which is fall in the reddish orange region, also confirms the suitability of MgBPEu glasses for using as reddish orange emitting applications under the excitation of 394 nm.

Radioluminescence

Figure 6(a) shows the radioluminescence (RL) spectra of MgBPEu glasses recorded under X-ray excitation at room temperature. Under the excitation of X-rays, the emission spectra of MgBPEu glasses in the region of 550-750 nm consist of five bands centered at 578 nm ($^5\text{D}_0$

Table 1. Comparison of intensity ratio of glass sample with other reported Eu^{3+} glasses

Glass system	Intensity ratio (R)	Reference
PbPEuP	2.08	(Maheshvaran and Marimuthu, 2012)
BNaPbZnLiEu_2	3.07	(Rajagukguk <i>et al.</i> , 2016)
MgBPEu100	3.44	Present work
BBCE2	4.01	(Libin Xia <i>et al.</i> , 2017)
2EB	4.24	(Maheshvaran and Marimuthu, 2012)

$\rightarrow^7F_0$), 590 nm ($^5D_0 \rightarrow ^7F_1$), 610 nm ($^5D_0 \rightarrow ^7F_2$), 651 nm ($^5D_0 \rightarrow ^7F_3$) and 700 nm ($^5D_0 \rightarrow ^7F_4$). It is observed that, the strongest emission band is centered at 610 nm and the emission intensity also increase with increasing of Eu₂O₃ concentration until 1.00 mol%, after that it decrease via concentration quenching effect. Although the excitation source was different, the spectral results were nearly identical to those from the photoluminescence. In addition, the light emission suggested that MgBPEu glasses have the potential to X-ray detections.

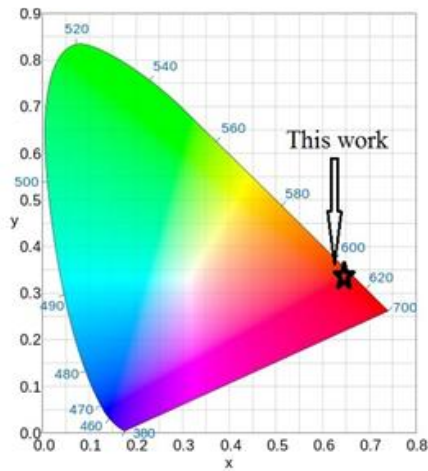


Figure 5. CIE chromaticity diagram of MgBPEu glasses

Temperature Dependence Luminescence

From the luminescence spectra, emission spectra of glass samples have been recorded under photon and X-ray excitations, it is observed that MgBPEu glass doped with Eu³⁺ concentration at 1.00 mol% is maximum intensity of emission, so they are selected for measurement the temperature dependence luminescence. Temperature dependence of emission spectra of MgBPEu100 glass is also investigated from 300 K to 10 K by exciting with 266 nm laser excitation as presented in Figure 6(b). The results indicate that the intensity of the emission peak is found to be increased with decreasing temperature. Even if the shape of the emission peaks are similar for all temperature, the emission intensity of the MgBPEu100 glass at 10 K was almost 2 times that at room temperature (300 K). This feature regards to the increase of non-radiative thermal quenching at high temperature causing a gradual decrease of the integrated emission efficiency (Park *et al.*, 2016; Luewarasirikul *et al.*, 2017).

Conclusions

Eu³⁺ doped magnesium barium phosphate glasses have been fabricated and their physical optical and luminescence properties were investigated. These glasses were prepared by the melt-quenching technique. The results

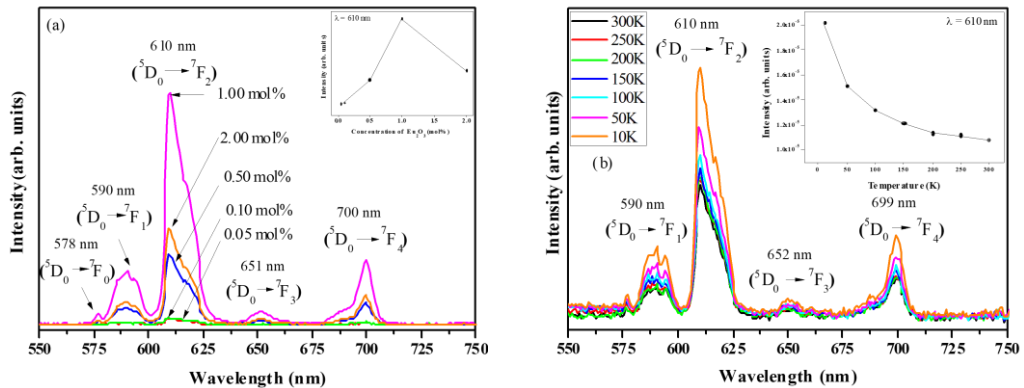


Figure 6. The RL spectra of MgBPEu glasses (a) and the temperature dependence luminescence of MgBPEu100 glass under laser induced emission spectra (b)

indicate that the density and the refractive index of glass samples increase when the concentration of Eu_2O_3 is increased. While, the molar volume of glass samples tends to decrease with increasing Eu_2O_3 content up to 0.50 mol% and then increases. From the result of molar volume, it indicates that the percentage of the Eu_2O_3 content also performs differently within the matrix. The absorption bands of glass samples were clearly observed in the UV–Vis–NIR regions. Emission spectra analysis of glass samples had been recorded under photon and X-ray excitations. Five emission bands of Eu^{3+} were observed and the strongest emission band centered at around 610 nm exhibits reddish-orange emission, which was confirmed by CIE chromaticity diagram. Although the excitation source was different, the spectral results were nearly identical to those from the photoluminescence. The optimum concentration of Eu_2O_3 for MgBPEu glass is 1.00 mol% which makes the highest intensity of emission coming out from this glass. Temperature dependence of luminescence was also studied under laser induced emission spectra. It is observed that the emission spectra of glass samples were increased with decreasing temperature from 300 K to 10 K. This result suggests that MgBPEu glasses can be good candidate as laser source and display devices in reddish orange region.

Acknowledgements

This work was supported by Thailand Research Fund (TRF) through the Research and Researchers for Industries (RRI) Ph.D. Program (Grant No. PHD61I0006).

References

- Balakrishnaiah, R., Babu, P., Jayasankar, C.K., Joshi, A.S., Speghini, A., and Bettinelli, M. (2006). K–Ba–Al-phosphate and fluorophosphate glasses. *J. Phys.: Condens. Matter*, 18:165-179.
- Chanthima, N., Kaewkhao, J., Tariwonga, Y., Sangwanate, N., and Sangwanate, N.W. (2017). Luminescence study and Judd-Ofelt analysis of $\text{CaO-BaO-P}_2\text{O}_5$ glasses doped with Nd^{3+} ions. *Mater. Today*, 4:6091-6098.
- Deopa, N., Rao, A.S., Choudhary, A., Saini, S., Navhal, A., Jayasimhadri, M., Haranath, D., and Vijaya Prakash, G. (2018). Photoluminescence investigations on Sm^{3+} ions doped borate glasses for tricolor W-LEDs and lasers. *Mater. Res. Bull.*, 100:206-212.
- Hraiech, S., Sdiri, N., Horchani-Naifer, K., and M. Ferid. (2018). Thermal and optical properties of Er^{3+} doped phosphate glasses. *J. Non-Cryst. Solids*, 482:73-77.
- Ki-Soo Lim, Vijaya, N., Kesavulu, C.R., and Jayasankar, C.K. (2013). Structural and luminescence properties of Sm^{3+} ions in zinc fluorophosphate glasses. *Opt. Mater.*, 35:1557-1563.
- Langar, A., Bouzidi, C., Elhouichet, H., Gelloz, B., and Ferid, M. (2017). Investigation of spectroscopic properties of Sm-Eu codoped phosphate glasses. *Displays*, 48:61-67.
- Libin Xia, Linsheng Wang, Qinghui Xiao, Zicheng Li, Weixiong You and Qian Zhang. (2017). Preparation and luminescence properties of Eu^{3+} -doped calcium bismuth borate red-light-emitting glasses for WLEDs. *J. Non-Cryst. Solids*, 476:151-157.
- Linganna, K., and Jayasankar, C.K. (2012). Optical properties of Eu^{3+} ions in phosphate glasses. *Spectrochim. Acta, Part A*, 97:788-797.
- Luciana, R.P., Kassab, P., Diego, S., da Silva and Cid B. de Arajo. (2010). Influence of metallic nanoparticles on electric-dipole and magneticdipole transitions of Eu^{3+} doped germanate glasses. *J. Appl. Phys.*, 107:113506 1-5.
- Luewarasirikul, N., Kim, H.J., Meejitpaisan, P., Kaewkhao, J. (2017). White light emission of dysprosium doped lanthanum calcium phosphate oxide and oxyfluoride glasses. *Opt. Mater.*, 66:559-566.
- Maheshvaran, K., Marimuthu, K. (2012). Concentration dependent Eu^{3+} doped boro-tellurite glasses-Structural and optical investigations. *J. Lumin.*, 132:2259-2267.
- Nayab Rasool, Sk., Rama Moorthy, L., and Jayasankar, C.K. (2013). Optical and luminescence properties of Dy^{3+} ions in phosphate based glasses. *Solid State Sci.*, 22:82-90.
- Park, J.M., Ha, D.H., Kaewjeang, S., Maghanemi, U., Kothan, S., Kaewkhao, J., and Kim, H.J. (2016). Luminescence properties of Ce^{3+} doped gadolinium-calcium-silicaborate glass scintillator. *Radiat. Meas.*, 90:166-169.
- Rajagukguk, J., Kaewkhao, J., Djamal, M., Hidayat, R., Suprijadi, Ruangtawee, Y. (2016). Structural and optical characteristics of Eu^{3+} ions in sodium-leadzinc-lithium-borate glass system. *J. Mol. Struct.*, 1121:180-187.
- Ramachari, D., Rama Moorthy, L., and Jayasankar, C.K. (2013). Phonon sideband spectrum and vibrational analysis of Eu^{3+} -doped niobium oxyfluorosilicate glass. *J. Lumin.*, 143:674-679.
- Shajan, D., Murugasen, P., and Sagadevan, S. (2017). Studies on structural, optical and spectral properties of europium oxide doped phosphate glasses. *Optik*, 136:165-171.

- Stambouli, W., Elhouichet, H., Gelloz, B., and Ferid, M. (2013). Optical and spectroscopic properties of Eu³⁺-doped tellurite glasses and glass ceramics. *J. Lumin.*, 138:201-208.
- Tan, C.Z., and Arndt, J. (1997). The mean polarizability and density of glasses. *Physica B*, 229: 217-224.
- Vijaya, N., and Jayasankar, C.K. (2012). Structural and spectroscopic properties of Eu³⁺-doped zinc fluorophosphate glasses. *J. Mol. Struct.*, 1036:42-50.