การเตรียมแก้วเพื่อศึกษาและวิจัยโดยใช้ขี้เถ้าแกลบในจังหวัดสุพรรณบุรีแทนการใช้ซิลิกอนไดออกไซด์ที่เจือด้วยเพรซีโอดิเมียม

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บทคัดย่อ

ในงานวิจัยนี้ ตัวอย่างของขี้เถ้าแกลบถูกเก็บมาจากจังหวัดสุพรรณบุรี และถูกนำมาใช้เพื่อศึกษาการนำขี้เถ้าแกลบมาใช้แทนซิลิกอนไดออกไซด์ในการเตรียมตัวอย่างแก้วที่เจือด้วยเพรซีโอดีเมียม ขี้เถ้าแกลบถูกเผาแคลไซน์ที่อุณหภูมิต่างๆ และศึกษาองค์ประกอบทางเคมี ตัวอย่างแก้วที่มีสูตรทางเคมี SiO_2(RHA)-B_2O_3-Na_2O-CaO-Pr_2O_3 ถูกเตรียมด้วยเทคนิคการหลอมเหลวแล้วทำให้เย็นลงอย่างรวดเร็ว และศึกษาสมบัติต่างๆ ด้วยเครื่องมือทางวิทยาศาสตร์ ผลการศึกษาพบว่า เมื่อเพิ่มปริมาณความเข้มข้นของ Pr_2O_3 จะส่งผลให้ความหนาแน่นและปริมาตรเชิงโมลของตัวอย่างแก้วเพิ่มขึ้น และยังพบว่าความเข้มของแถบการดูดกลืนในช่วงความยาวคลื่น 200 - 2,500 นาโนเมตร มีค่าเพิ่มขึ้นตามความเข้มข้นของ Pr_2O_3 นอกจากนี้เมื่อใช้แสงที่มีความยาวคลื่น 444 นาโนเมตร เพื่อกระตุ้นให้เกิดการเปล่งแสงของแก้ว จะพบลักษณะการเปล่งแสงของ Pr^{3+} ในช่วงความยาวคลื่น 605 นาโน-เมตร

คำสำคัญ: ขี้เถ้าแกลบ แก้ว ขยะทางการเกษตร เพรซีโอดีเมียม

Glass preparation for investigation and study with Suphan Buri province rice husk ash instead of silicon dioxide doped with praseodymium

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Abstract

In this work, the local rice husk ash collected from rice paddy in Suphan Buri province was used to study the utilization as a SiO_2 chemical substitute to fabricate the glass samples doped with praseodymium. The ash was calcined at various calcination temperatures and studied its chemical components. The glasses with formular SiO_2(RHA)-B_2O_3-Na_2O-CaO-Pr_2O_3 were prepared by melt - quenching technique and were studied through various scientific instruments to obtain their properties. The measurements revealed that as the Pr_2O_3 concentration increased, the density along with the molar volume increased. The intensity of all absorption bands increases with Pr_2O_3 concentration when measuring the absorption spectra of glasses in the 200 - 2,500 nm range. Additionally, using a 444 nm excitation wavelength, the photoluminescence characteristics of Pr^{3+} doped-SiO_2(RHA)-B_2O_3-Na_2O-CaO-Pr_2O_3 glasses were seen and found the emitted light around the 605 nm band.

Keywords: rice husk ash, glasses, agricultural waste, praseodymium

1. Introduction

Rice husk is a significant by-product after the milling process is produced over million tonnes annually in Thailand [1]. The rice husk ash (RHA) was residue during the combustion process of to generate heat and electricity, which was considered as an agricultural waste that usually create the disposal problems and environmental pollution. Many researches reported on the use of the RHA but it still small amount. Therefore, it is critical to find a long-term application for the ashes [2]. Many studies focus on the use of RHA in the production of concrete, glass, and ceramics have recently been conducted. Because of it has high silica content (more than 50% by weight), biomass ash is useful in these industries. The ash, on the other hand, is determined by the source for optical purposes, low cost, manufacturing process, high transparency at room temperature, constant hardness and composition are all characteristics of glasses made from source material [3-4].

The major glass-forming ingredients of borosilicate glass are silica and boron oxide [5]. Silicate glasses outperform oxide glasses in terms of glass formation [6]. The thermal expansion coefficient of borosilicate glass is low. It has a low melting point and can be used at quite high temperatures [7]. The researchers employed a host comprising silicon dioxide and borate for a range of purposes. Pr^{3+} has been proposed as a phosphor activator [8-9]. There has been a lot of interest in Pr^{3+}-doped glass, because of its extensive luminescent uses and coverage in the visible and near-infrared wavelength ranges. Solid-state lasers have been used in a variety of applications. There is a fiber laser and a fiber amplifier. Additionally, among the RE ions, Pr^{3+} has promised near-infrared luminescence, particularly in the wavelength band within the enlarged low-loss [9].

In this work, the researchers have been investigated the use of the RHA in glass manufacture instead of SiO_2 chemicals and investigated the physical and optical features of Pr^{3+} doped RHA glasses to reduce the cost of chemicals.

2. Materials and Methods

2.1 The RHA samples

The RHA samples from Suphan Buri province were collected, then removed unwanted substances and dust attached the samples by using sieve. The RHA were calcined in an electrical furnace at temperatures of 200, 400, 600, 800, and 1000 °C. The EDXRF, X-ray fluorescence spectrometer (PANalytical MiniPal 4) was carried out to study their chemical compounds and SiO_2 content (Table 1).

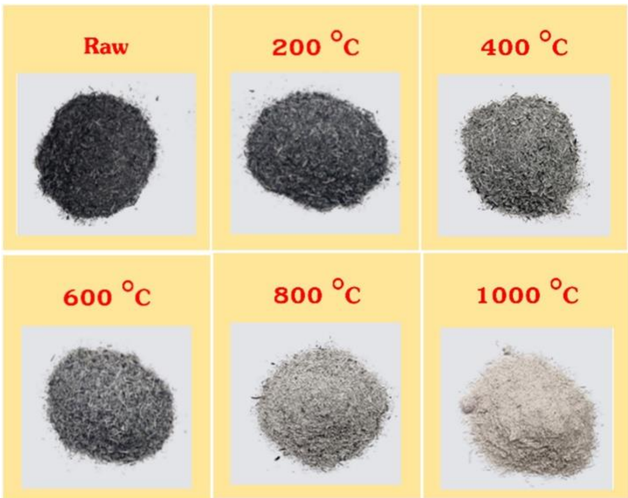

Figure 1 The raw RHA and calcined RHA samples at different temperatures.

Table 1 The chemical analysis of the RHA samples.

Calcination temperature ($^{\circ}C$)	Chemical composition (% wt)			
	SiO_2	K_2O	CaO	Fe_2O_3
Raw	95.724	2.911	0.774	0.107
200 $^{\circ}C$	95.361	2.856	0.756	0.049
400 $^{\circ}C$	96.115	2.840	0.775	0.145
600 $^{\circ}C$	95.436	3.087	0.765	0.106
800 $^{\circ}C$	96.897	2.324	0.664	0.080
1,000 $^{\circ}C$	97.585	1.638	0.622	0.066

As seen in Figure 1, the difference in color of RHA samples were obtained due to the amount of carbon contains in the samples. The XRF analysis data in Table 1 showed that calcined RHA at any temperature compose of SiO_2 more than 95%. Moreover, heating up the RHA with higher temperate, the SiO_2 content increased while the impurities content such as K_2O, CaO, and Fe_2O_3 decreased. At 1,000 $^{\circ}C$, it yielded SiO_2 with the highest amount so, this RHA sample was selected for SiO_2 source in glass preparation process.

2.2 Glass preparation

The glass samples with chemical formular of (55-x)SiO_2-25B_2O_3-10Na_2O-10CaO-xPr_2O_3 were prepared using the calcined RHA at temperature of 1,000 $^{\circ}C$ as SiO_2 source and x is the concentration of Pr_2O_3 ranging from 0.0 to 1.50 mol%.

First step, the constituent chemical powders for each concentration were weighed about 30 grams in alumina crucible. Then the mixed powder was heated from room temperature to 1,200 $^{\circ}C$ in an electric furnace and kept for 3 hours. After the mixture was completely dissolved, it was then poured on a pair of stainless-steel sheets at room temperature. To prevent the thermal stress occurs in glass sample, the glass was annealed at 500 $^{\circ}C$ for 3 hours. Following that, all glass samples were appropriately cut and polished into appropriate shape for further investigation.

Table 2 Chemical formular for the RHA glasses doped with Pr_2O_3

Concentration of Pr_2O_3 (mol%)	Sample code	Glass formula
0.0	Pr1	55.0SiO_2-25B_2O_3-10Na_2O-10CaO-0.0Pr_2O_3
0.1	Pr2	54.9SiO_2-25B_2O_3-10Na_2O-10CaO-0.1Pr_2O_3
0.3	Pr3	54.7SiO_2-25B_2O_3-10Na_2O-10CaO-0.3Pr_2O_3
0.5	Pr4	54.5SiO_2-25B_2O_3-10Na_2O-10CaO-0.5Pr_2O_3
1.0	Pr5	54.0SiO_2-25B_2O_3-10Na_2O-10CaO-1.0Pr_2O_3
1.5	Pr6	54.5SiO_2-25B_2O_3-10Na_2O-10CaO-1.5Pr_2O_3

2.3 Characterization

To examine some properties of glass samples, various techniques/instruments were conducted. The Archimedes' principle was employed to find out the density of glass samples following the equation (1) and purified water was used as the immersion fluid [8].

$$\rho = \frac{W_{air}}{W_{air} - W_{water}} \times \rho_{water} \quad (1)$$

Where the density of purified water (ρ_{water}) is about 0.9982 g/cm^3. The W_{air} and W_{water} are the weights of glasses in both air and water, respectively. Three measurements for each glass sample were conducted to ensure the errorless.

The molar volume can be directly calculate using the following equation [8] and use the density value from the measurement as mentioned in previously part.

$$V_m = \frac{M_T}{\rho} \quad (2)$$

The abbe refractometer (ATAGO) was a useful instrument to carried out the measurement of refractive index and using 1-bromonaphthalene as an adhesive solvent. The optical absorption spectra of glass samples were measured using a UV - Visible - NIR spectrophotometer (Shimadzu, UV-3600) in range of 200 - 2,500 nm and compared with other studies to find out the characteristic absorption bands of glasses doped with Pr_2O_3. Moreover, a fluorescence spectrophotometer (Agilent, Cary Eclipse) was carried out to study the luminescence spectra. All studies were performed at room temperature.

3. Results and Discussion

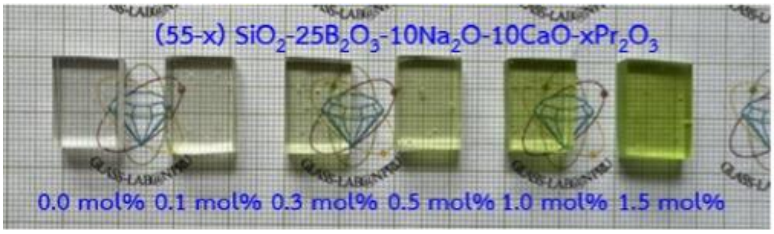

Figure 2 The photograph of the RHA glass samples doped with different Pr_2O_3 concentration.

The photograph of RHA glass samples made doped with Pr_2O_3 were shown in Figure 2. All glasses were transparent and homogeneous. Due to the color of glass varies with the concentration of dopants, it found that more concentration of Pr_2O_3, more intense green color has been observed.

The result in Figure 3(a) shows that density of glass samples observed to be increase with increasing of Pr_2O_3 concentration due to the molecular weight of Pr_2O_3 is heavier than that of SiO_2. Hence replaces SiO_2 (or RHA) with Pr_2O_3, the density of samples increased.

Along with the density result, the molar volume of glasses doped with Pr_2O_3 showed the similar trend. As seen in Figure 3(b) it was found that when more Pr_2O_3 was added, Pr^{3+} would break the bridgingoxygen bond which acts as a modifier. Thus, increasing the space in the glass, increasing the molar volume of glasses.

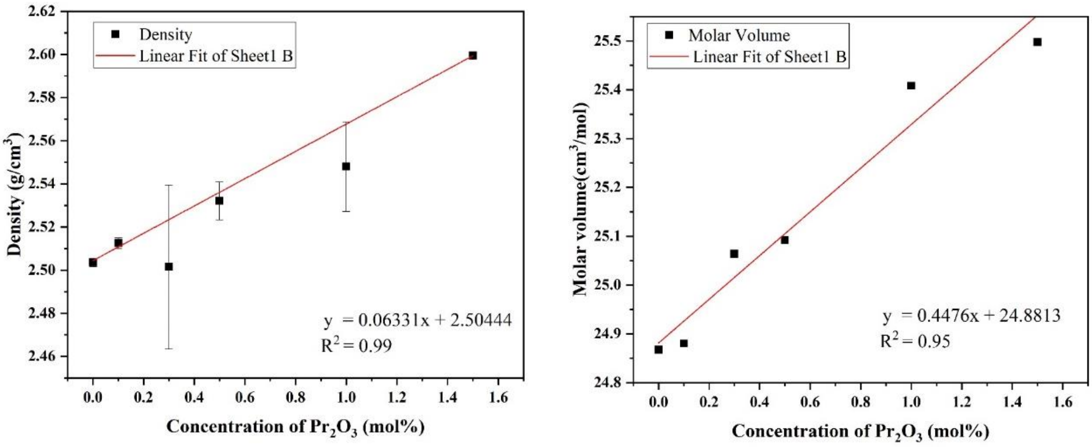

Figure 3 The variation of (a) density and (b) molar volume of the RHA glasses doped with different concentration of Pr_2O_3.

From Figure 4, the refractive index of RHA glass doped with Pr_2O_3 increased. From the equation n = c/v, as the density increases, the light passing through the glass slows down, and the refractive index increases with the density of the glasses.

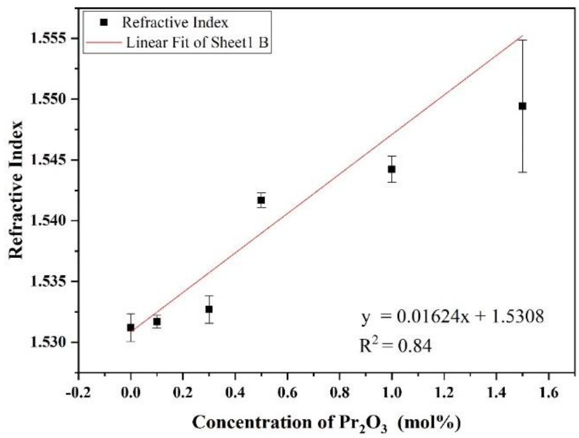

Figure 4 The refractive index of the RHA glasses doped with Pr_2O_3.

The optical absorption measurements on the RHA glasses were illustrated in Figure 5. It found that all samples doped with Pr_2O_3 the same pattern in characteristic absorption bands. The absorption bands of Pr^{3+} represent the transitions from the ground state $^3H_4$ to various excited states such as $^3P_2$ (444 nm), $^3P_1$(471 nm),$^1D_2$ (589 nm),$^1G_4$ (1,007 nm),$^3F_4$ (1,417 nm),$^3F_3$ (1,513 nm) and $^3F_2$ (1,917 nm), respectively. When increasing in concentration of Pr_2O_3, it could be also observed that the absorption bands were increased.

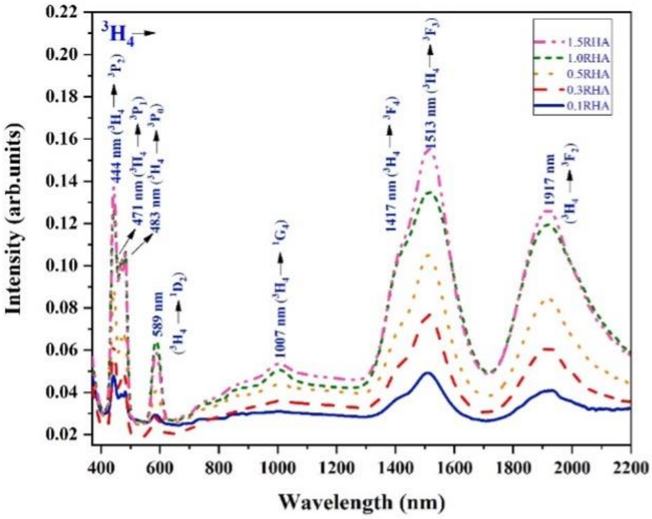

Figure 5 The absorption spectra of the RHA glasses from doped with Pr_2O_3.

For the photoluminescence study, all doped glasses were monitored the emitted light by excited them at 444 nm excitation wavelength. It found in Figure 6(b) that the intensity of emitted light increased with increased of Pr_2O_3 content and it reached the maximum intensity with Pr_2O_3 concentration at 0.3 mol%. After that the intensity of emitted light decreased at 0.5, 1.0, 1.5 mol% of Pr_2O_3 concentration caused by an increase in non-radiative decay channels, which has been updated due to the concentration quenching effect [11]. In addition, the partial energy level diagram of involved in the Pr^{3+} ion emission mechanism in the RHA glasses is shown in Figure 7.

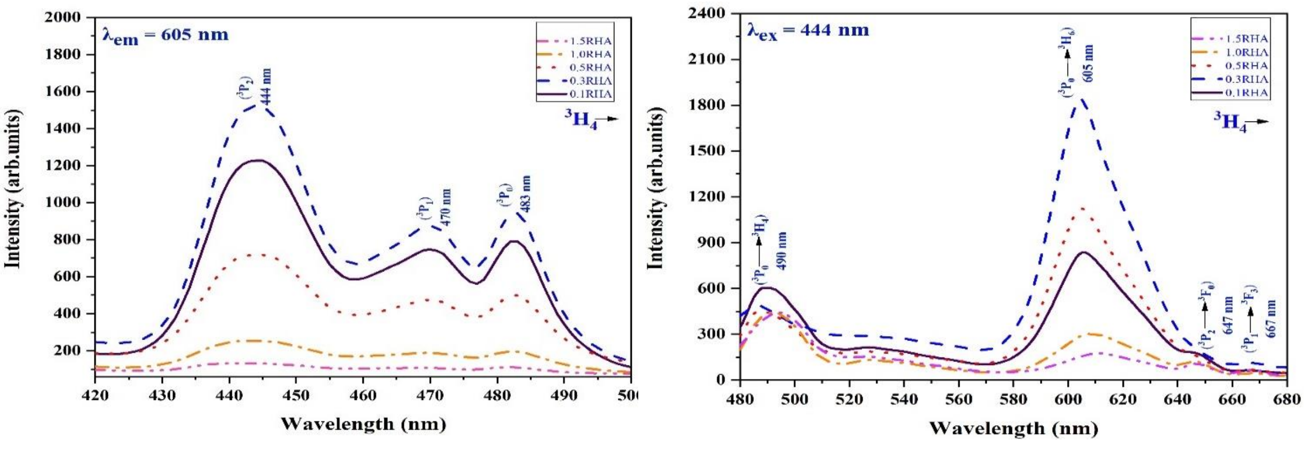

Figure 6 The (a) excitation and (b) emission spectra of the RHA glasses doped with Pr_2O_3.

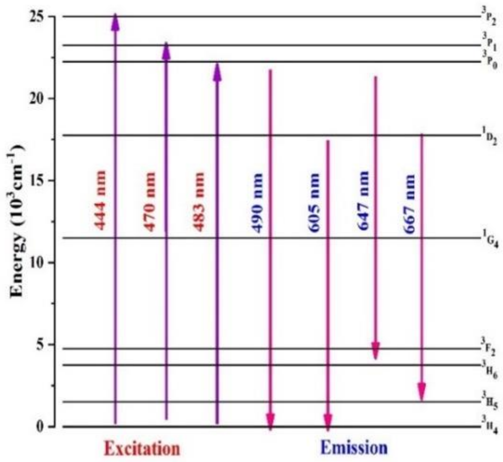

Figure 7 The partial energy level diagram of the RHA glasses doped with Pr_2O_3.

The CIE-1931 chromaticity was employed to investigate color coordinated of emitted light of the RHA glasses doped with Pr_2O_3. Due to the Pr3 sample (or glass doped with 0.3 mol% of Pr_2O_3) released the strongest intensity, its coordinates (x = 0.48, y = 0.41) were plotted in the chromaticity diagram. From Figure 8, the color coordinates located in the yellow-green region.

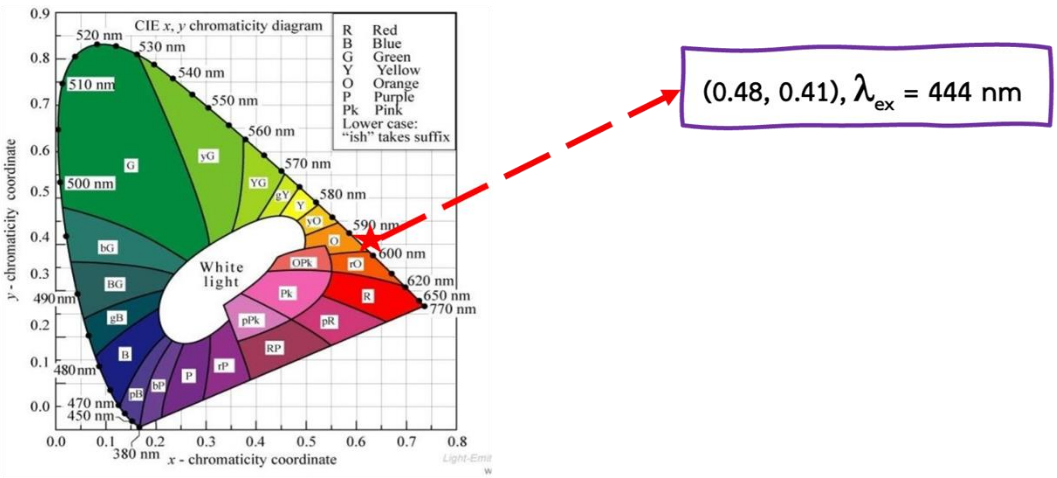

Figure 8 The CIE-1931 chromaticity diagram presents color coordinates of emitted light with excitation at 444 nm for the Pr3 glass sample.

4. Conclusion

The glasses samples doped with Pr_2O_3 using the calcined RHA at 1,000 $^\circ$C as SiO_2 source have been prepared. The properties such as density, molar volume, refractive index, optical absorption spectra and photoluminescence spectra were studied. The density, molar volume, and refractive index increased with increasing Pr_2O_3 concentration. The glasses doped with Pr_2O_3 exhibited characteristic absorption bands in visible and near-infrared regions located around 444, 471, 589, 1007, 1417, 1513 and 1917 nm. With the excitation at 444 nm, the glasses emitted light at 490, 605, 647 and 667 nm, respectively. The highest emission intensity was occurred with Pr_2O_3 concentration at 0.3 mol%. After that the intensity of emitted light decreased with increasing of Pr_2O_3 concentration due to the concentration quenching effect. The CIE-1931 showed that in emitted light of glass sample with 444 excitation wavelength fallen in to the yellow-green region. Hence, these RHA glass samples could be applied as the green laser medium. Moreover, the results from this study can be implied that the utilization of RHA as SiO_2 source in glass manufacturing can reduce production cost, as well as decreased the quantity of agricultural waste that can cause in health and environmental problems.

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References

[1] Tuscharoen, S., Kaewkhao, J., Limsuwana, P., Chewpraditkul, W. (2012) Structural, Optical and Radiation Shielding Properties of BaO-B_2O_3-Rice Husk Ash Glasses. Procedia Engineering, 32(734-739). https://doi.org/10.1016/j.proeng.2012.02.005

[2] Rueangtaweep, Y., Srisittipokakun, N., Boonin, K., Yasaka, P., Kaewkhao, J. (2013) Characterization of Rice Straw and Utilization inGlass Production, Adv Mat Res. 748(304-308). https://doi.org/10.4028/www.scientific.net/AMR.748.304

[3] Srisittipokakun, N., Ruangtaweep, Y., Rachniyom, W., Boonin, K., Kaewkhao, J. (2017) CuO, MnO_2 and Fe_2O_3 doped biomassash as silica source for glass production in Thailand. Results in Physics. 7(3449-3454). https://doi.org/10.1016/j.rinp.2017.09.010

[4] Wantana, N., Kaewnuam, E., Ruangtaweep, Y., Valiev, D., Stepanov, S., Yamanoi, K., Kim, H.J., Kothan, S., Kaewkhao, J. (2021) Tunable orange, yellow and white emission of Pr^{3+}-doped tungsten gadolinium borate glasses. Journal of Non-Crystalline Solids. 554(120603). https://doi.org/10.1016/j.jnoncrysol.2020.120603

[5] Zhang, L., Dong, G., Peng, M., Qiu, J. (2012) Comparative investigation on the spectroscopic properties of Pr^{3+}-doped boro-phosphate, boro-germo-silicate and tellurite glasses. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 93(223-227). https://doi.org/10.1016/j.saa.2012.02.076

[6] Zaman, F., Kaewkhao, J., Rooh, G., Srisittipokakun, N., H.J. (2016) Optical and luminescence properties of Li_2O-Gd_2O3-MO-B_2O_3-Sm_2O_3 (MO=Bi_2O_3, BaO) glasse. Journal of Alloys and Compounds. 676(275-285). https://doi.org/10.1016/j.jallcom.2016.03.176

[7] Yonphan, S., Srisittipokakun, N., Kaewkhao, J. (2021) Physical and Optical Properties of CuO doped in Glasses Prepared from Rice Husk Ash in Suphan Buri Province, Thailand. Journal of Physics. 2013(012002). https://doi.org/10.1088/1742-6596/2013/1/012002

[8] Damdeea, B., Kirdsiri, K., Kaewkhao, J. (2018) Studies of Luminescence Properties of Praseodymium Ions in Gadolinium Barium Borate Based Glasses for Reddish-Orange Lighting Applications. Materials Today: Proceedings. 43(2516-2524). https://doi.org/10.1016/j.matpr.2020.04.611

[9] Masaia, H., Okad, G., Kawaguchi, N., Yanagida, T. (2019) Optical and luminescent properties of Pr-doped Li_2O-MgO-Al_2O_3-SiO_2 glasses. Optical Materials. 88(1-6). https://doi.org/10.1016/j.optmat.2018.11.011

[10] Steven V., M. Mikko, D. Olli (2018) A review of biomass ash properties towards treatment and recycling. Renewable and Sustainable Energy Reviews. 96 (479-486) https://doi.org/10.1016/j.rser.2018.07.025

[11] Shunichi, K., Hirokazu, M., Go, O., Noriaki, K., Takayuki, Y. (2017) Photoluminescence and radioluminescence in Pr-doped lanthanum aluminoborate glasses. Journal of Asian Ceramic Societies. 5 (385-390). https://doi.org/10.1016/j.jascer.2017.08.003

[12] L. Zhang, G. Dong, M. Peng, J. Qiu (2012) Comparative investigation on the spectroscopic properties of Pr^{3+}-doped boro-phosphate, boro-germo-silicate and tellurite glasses.

[13] Sun, Y., Yu, F., Liao, M., Wang, X., Li, Y., Hu, L., Knight, J. (2020) Emission properties of Pr^{3+}-doped aluminosilicate glasses at visible wavelengths. Journal of Luminescence. 220(117013). https://doi.org/10.1016/j.jlumin.2019.117013