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Development of Sm^{3+} doped $ZnO\text{-}Al_2O_3\text{-}BaO\text{-}B_2O_3$ glasses for optical gain medium

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ABSTRACT

Sm^{3+} doped $ZnO\text{-}Al_2O_3\text{-}BaO\text{-}B_2O_3$ glasses have been prepared and characterized. These glasses have been developed by melt and quenching technique. The characterization includes the physical, optical, luminescence, and radiative properties. The lasing potential of glass samples such as oscillator strengths, JO parameter, stimulated emission cross-sections, radiative transition probability, and branching ratios have been calculated by using Judd-Ofelt theory. The results show that the maximum intensity of emission spectra of the prepared glass sample is at the wavelength of 598 nm due to the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition, excited by λ_{ex} = 403 nm. From CIE 1931 chromaticity, the title glasses were found to be a potential material for laser application in the orange region.

1. Introduction

Optoelectronics has become an important role in our daily life. Many devices use the principle of optoelectronics such as laser, optical data communication, lighting and display, manufacturing, health care, security, and safety. It is well known that the conventional technology has the limitation of their ability like low speed, capacity, and accuracy. Meanwhile, optoelectronic devices provide faster detection, sensitive and simple fabrication. For instance, the optoelectronics in safety and security field is more sensitive and accuracy to detect hazards materials. Moreover, nowadays the conventional fluorescent light bulb has been replaced by LED or OLED due to the higher quality and the ability to save energy. The most notable of these devices is the intensity of the light emission that depends on the gain medium. The luminescence of gain medium can be applied in the light industry [1], organic light emitting diodes and an optical fiber for telecommunications [2]. The glass as host matrix can be doped with rare earth ions with high concentration, possesses a unique structure which influences the environment around rare earth ion and effects the strong emission in the visible to near infrared region [1–9]. Among the rare earth elements, samarium becomes more interesting to be observed due to the emission in the yellow and orange region [5,6].

The components of the present glass medium are glass formers, modifiers, and intermediates. The addition of glass formers is to improve the rigidity and the viscosity of glass medium while the intermediate needs to make the glass more stable. Borate glass was used as a glass former due to the stability of thermal, chemical, and mechanical properties [10,11]. Previous researches have been reported about Sm^{3+} doped in various host glasses. The glass properties such as optical, luminescence, and radiative have been measured. For laser medium applications, long luminescence lifetime of Sm^{3+} is required. The lifetime of Sm^{3+} doped in niobium phosphate [12], lead fluorophosphates [13], lead germanate tellurite [14], zirconium tungsten tellurite [15], and fluorosilicate [16] glass are found to be lower than lithium lead alumino borate [17] and zinc mixed alkali borate glass [18]. However, the phonon energy of borate glass (1400 cm^{-1}) is higher than phosphate (1200 cm^{-1}), silicate (1100 cm^{-1}), and tellurite (700 cm^{-1}) [19]. The high phonon energy influences the increase of non-radiative decays and decreases the luminescence efficiency. The addition of metal alkali in glass system can reduce phonon energy [20]. In all these studies, Sm^{3+} ions were excited by ultraviolet region and observed several transitions from $^4G_{5/2}$ to $^6H_{7/2}$ and $^6H_{5/2}$ [1–9,13,21,22]. The CIE 1931 chromaticity diagram of Sm^{3+} ion doped glasses was fell down in the orange to reddish orange region [6,7,23]. Therefore, Sm^{3+}-doped glasses can be used as a gain medium, emitting orange devices and scintillator [6].

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Multi-metal component borate glass doped with lanthanide ion (Ln^{3+}) has been popular for study and development in the spectroscopic properties. For example, lead alumino borate [24], zinc lead borate [25], zinc bismuth borate [26] zinc lithium sodium borate [27] and zinc alumino bismuth borate glasses all were used as host for Ln^{3+}. Especially in case of zinc alumino bismuth borate glass, it was widely researched for photonic applications by doping with variety of Ln^{3+} such as Tb^{3+} [28], Nd^{3+} [29], Pr^{3+} [30], Dy^{3+} [31], Eu^{3+} [32], Er^{3+} [33], Ho^{3+} and even Sm^{3+} [18]. However, high amount of bismuth in glass causes a glass specimen to be yellow which degrade the absorption and luminescence properties. Replacing bismuth with barium in this glass composition can open a new way of challenge. The metal oxide such as ZnO, Al_2O_3, and BaO was added in glass system to reduce the thermal expansion, increase chemical, mechanical, and thermal stability. Furthermore, ZnO possesses wide band gap, large exciton binding energy, and intrinsic emitting property, while the addition of Al_2O_3 and BaO can increase the rare earth ion solubility [18,27,34].

In this research, Sm^{3+} was doped in borate glass combined with zinc, alumina, and barium oxide. This Sm-doped borate glasses were developed and characterized through physical, optical, photoluminescence, radiative and lasing properties. The optical properties such as oscillator strength (f), branching ratios (β_R), radiative transition probability (A_R), and stimulated emission cross-section (σ_λ) were calculated using Judd-Ofelt theory [35,36].

2. Experimental

The composition of glass samples are $10ZnO{:}10Al_2O_3{:}20BaO{:}(60-x)B_2O_3{:}xSm_2O_3$ with x = 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, and 2.5 mol % and were prepared by the melt-quenching method as reported by [37–39]. Glass specimens label consist of ZABBSm0.1, ZABBSm0.3, ZABBSm0.5, ZABBSm1.0, ZABBSm1.5, ZABBSm2.0 and ZABBSm2.5, respectively. All the raw material is procured from Sigma-Aldrich with a purity of 99.99%. The materials were mixed and melted at 1100 °C for 3 h and then annealed at 500 °C for 3 h. Finally, the glass medium was cut to required size of 1.5 × 1.0 × 0.35 cm^3 and polished as shown in Fig. 1. Physical, optical and photoluminescence properties were characterized and compared with other reported data. The physical properties such as density, molar volume, and refractive index have been determined. The density of the glass sample, satisfying Archimedes law, has been determined using the following equation,

$$\rho_{sample} = \left(\frac{w_{air}}{w_{air} - w_{liquid}}\right) \times \rho_{liquid} \quad (1)$$

Where ρ_{liquid} is the density of water (1 g/cm^3), w_{air} and w_{liquid} are sample weight in the air and water, respectively. The weight in the air (w_{air}) and water (w_{liquid}) was measured with an accuracy of milligrams by using AND HR-200 type system. The refractive index was measured by using an Abbe refractometer (ATAGO) of NAR-2T Liquid type. The absorption spectrum was measured by using Shimadzu 3600 UV-VIS-NIR spectrophotometer with halogen and deuterium lamp as a light source. Excitation and emission spectra were measured by Cary Eclipse fluorescence spectrophotometer (Agilenttechnology Inc.). The light source of the instrument is a xenon flash lamp. All of the measurements were executed at room temperature. Radiative properties were analyzed by using Judd-Ofelt theory and determined the lasing potential of the glass sample. Judd-Ofelt theory also used to determine several characteristic properties such as Judd-Ofelt parameters $\Omega_{\lambda = 2,4,6}$, oscillator strengths (f_{cal} and f_{exp}), branching ratios (β_R), radiative transition probabilities (A_R), and cross-sections (σ).

3. Results and discussion

3.1. Density and molar volume

The density of glass samples are presented in Fig. 2(a). It is related to the compactness of the sample. The density of the glass samples increases with adding Sm^{3+} ion concentration from 0.1 mol% to 2.5 mol %. It shows that the networks of borate glasses have a large number of empty interstices. Subsequently, the Sm^{3+} ion will fill in the empty interstices. Therefore, the mass of a substance will increase and effect in increasing of the glass sample density [40]. The data of glass sample density can generate molar volume. Fig. 2(b) is the molar volume of the glass sample. It shows that there are two behaviors of the sample glass. Firstly, the glass samples doped with Sm^{3+} ion concentration from 0.1 mol% to 0.3 mol% decrease with increasing the Sm^{3+} ion concentration. The behavior determines that non-bridging oxygen bond had not been occurred. Meanwhile, the second behavior of molar volume increases from 0.5 mol% to 2.5 mol% Sm^{3+} ion concentration due to the presence of non-bridging oxygen bond. It implies that they force the interstices and increase in the volume of the glass structure [6,40].

3.2. Absorption spectra

The absorption spectra of the glass sample are shown in Fig. 3. The absorption spectra were measured from 500 nm to 1800 nm. It shows that electrons are excited from $^6H_{5/2}$ to $^4P_{7/2}$, $^4I_{13/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6F_{1/2}$ and $^6H_{13/2}$, and it is similar to other literature [6,9,14]. The transition corresponded to the wavelength of 398 nm, 477 nm, 947 nm, 1080 nm, 1227 nm, 1375 nm, 1477 nm, 1526 nm and 1584 nm, respectively. The highest intensity of absorption spectra is the $^6H_{15/2} \rightarrow {}^6F_{7/2}$ transition with 1227 nm wavelength. The intensity of absorption spectra increases with the addition of Sm^{3+} ion concentration. That occurs due to the 4f-4f transition of the rare earth ions and generates the light in the visible region [40].

3.3. Photoluminescence spectra

Fig. 4 presents the photoluminescence spectra including the excitation and emission spectra of the glass sample. The excitation spectra were measured in the range of 325 nm to 575 nm, monitored at λ_{em} = 598 nm. All states originate from $^6H_{5/2}$ to $^4I_{9/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^4L_{13/2}$, $^6P_{5/2}$, $^4M_{17/2}$ and $^4I_{13/2} + {}^4M_{15/2} + {}^4I_{11/2}$ and centered at 344 nm, 361 nm, 374 nm, 401 nm, 416 nm, 439 nm and 476–561 nm, respectively. The highest intensity of excitation spectra is the $^6H_{5/2} \rightarrow {}^4L_{13/2}$ transition centered at 401 nm. Meanwhile, the emission spectra were measured from 525 nm to 750 nm, excited at λ_{ex} = 402 nm, and resulted 4 energy levels that are $^6H_{5/2}$ (561 nm), $^6H_{7/2}$ (597 nm), $^6H_{9/2}$ (644 nm) and $^6H_{11/12}$(706 nm) originated from $^4G_{5/2}$ transition. The energy levels were compared and found to be very similar [5,9,41]. The intensity of the emission spectra increases with increasing the Sm^{3+} ion concentration from 0.1 mol% to 0.3 mol%.

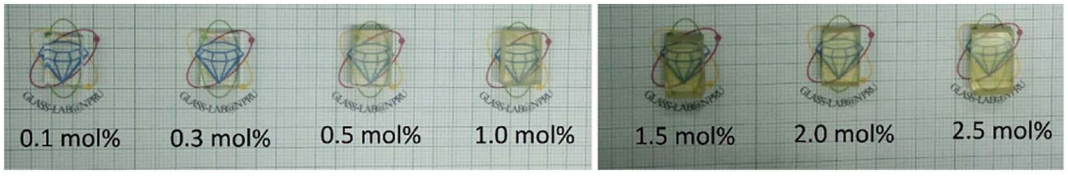

Fig. 1. Prepared sample of glass doped with Sm^{3+}.