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Invited Paper

Development of Borate Glass Doped Dy^{3+} for X-ray Scintillator-Crystal

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Abstract. X-ray detector is the important tools in the medical applications because it is used in the several instruments such as surgery, treatment and imaging process of diseases. In this research, we have been developed x-ray detector material based on borate glass doped Dy^{3+} ion by melt quenching technique. The composition of developed glass medium was $10ZnO:10Al_2O_3:20BaO:(60-x)B_2O_3:xDy_2O_3$ where x was 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, and 2.5 mol%. The quenching concentration effect occur at 1.0 mol% of Dy^{3+} ion concentration both optical and x-ray luminescence. The density and molar volume of glass medium in the quenching concentration were 3.06 g/cm^3 and 25.67 cm^3/mol. The energy of x-ray source was arranged in 50 kV and 20 mA. The highest intensity of x-ray luminescence was centered at 574 nm due to $^4F_{9/2}\rightarrow{}^6H_{7/2}$ transition. For emission spectra, the glass medium was excited by λ_{ex}=350 nm and showed similar emission light to x-ray luminescence that was 482, 574, 660, and 754 nm. The developed glass medium is the potential candidate for x-ray scintillator-crystal with the low-energy photon.

1. Introduction

X-ray is the electromagnetic wave which has the range of wavelength, energy, and frequency from 0.01 to 10 nm, 100 eV to 100 kV, and $3x10^{16}$ to $3x10^{19}$ Hz, respectively. In the medical field, an x-ray is used by medical personnel to observe inside the human body without damaging the body. In general, x-ray for the medical applications have the range of energy between 30 to 120 kV [1]. Several benefits of x-ray are to make sure the injured human body and observe the development of disease, operation result, and side effect of the treatment. The medical instruments which use x-ray as the light source are CT-Scan, mammography, PET/CT, and LINAC. These instruments need the device which can detect the presence of x-ray after passing the human body. One of the devices that are used for x-ray detection is scintillator. Photomultiplier tube will be connected to the scintillator to change the intensity of emission light to electrical signal. So that, the imaging and analysis can be investigated in the personal computer.

The scintillator is the device which absorbs high energy photon and emits visible light. There are several kinds of scintillators, depend on the applications, to detect the exposure of radiation such as single crystals, polycrystalline ceramics, glasses, etc [1]. The optical characterization of ceramic crystal garnet has been developed by Fujimoto, Y et al. However, the x-ray luminescence showed which developed scintillator absorbed x-ray energy in 80 kV [2]. Struebing, C. et al. and Beckert, M.B. et al. have been investigated glass-ceramics doped rare earth and boro germanate glasses. The scintillator still absorbed high-energy photon in the range 60-65 kV [3, 4]. It is well known that x-ray in the medical application should have low-energy photon considering of safety radiation of patients. Several methods have been developed to observe x-ray scintillator [5, 6]. Meanwhile, these methods have disadvantages such as long sample preparation and high temperature of manufacture.

In this research, we proposed glass medium doped rare earth ion by the melt-quenching method. This developed method was fast, simple sample preparation and low-cost fabrication. Borate oxide was chosen as host matrix due to good heat stability, lower melting point, lower thermal expansion coefficient, and higher density than other oxide glass [7, 8]. The addition of heavy metal oxide on glass medium will increase the rare earth solubility and decrease the phonon energy [9]. Meanwhile, Dy^{3+} ion as activator is the promising candidate for luminescence material in the yellow region (570-600 nm) and blue region (470-500 nm) due to the intense transition of $^4F_{9/2}\rightarrow{}^6H_{13/2}$ and $^4F_{9/2}\rightarrow{}^6H_{15/2}$ respectively [10].

2. Experiment

In this paper, the prepared glass medium doped Dy^{3+} ion has been developed by melt-quenching method [11–13]. The formula of the glass medium was $10ZnO:10Al_2O_3:20BaO:(60-x)B_2O_3:xDy_2O_3$ where x was 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, and 2.5 mol%. All raw materials were powder and have purity 99.99% from Sigma-Aldrich. The composition of material was calculated by batch calculation to fill the stoichiometry. Subsequently, the materials were mixed in the alumina crucible and melted in the electric furnace at 1100^0C for 3h. The glass medium was moulded at stainless steel and annealed at 500^0C for 3h. The glass was cut and polished with the dimension of 2.0 x 1.0 x 0.031 cm^3 for characterization. Figure 1 shows the cut and polished glass medium doped Dy^{3+} ion from 0.1 to 2.5 mol%. The characterization of glass medium consist of physical, optical properties, and x-ray induced luminescence. The physical properties come under density, and molar volume, while the optical properties which were measured were absorption, excitation, and emission spectrum [14]. The glass medium absorption was measured by UV-Vis-NIR Spectrometer (UV-3600 Shimadzu) under wavelength from 300 to 2000 nm. The light source of the spectrometer is 50-watt halogen lamp and a deuterium lamp. The excitation and emission spectra were measured by Cary Eclipse Fluorescence Spectrophotometer (Agilent Technology Inc.). The detector of this instrument is a photomultiplier tube (PMT) and the light source is flash xenon lamp. All measurements were observed at room temperature.

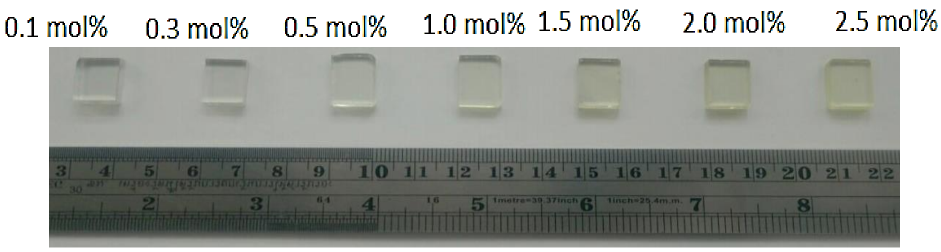


Fig 1. The prepared glass medium after cut and polished based on melt quenching technique [14]

3. Results and Discussion

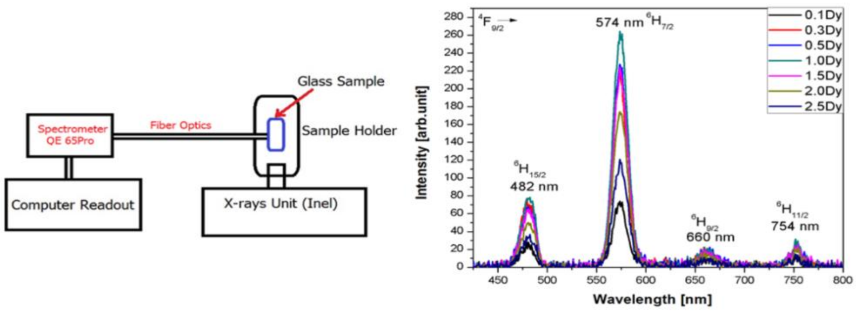
The glass weight was measured in the air and liquid by 4 digits digital microbalance and the density was calculated by Archimedes law. The weight of glass in the air and water were measured and calculated by following Eq. (1). The molar volume of the glass medium can be calculated from the density of glass medium and expressed as Eq. (2).

$$\rho = \left(\frac{W_u}{W_u - W_c}\right)\rho_c \tag{1}$$

$$V_m = \frac{M_W}{\rho} \qquad (2)$$

where $M_w = x_1 z_1 + x_2 y_2 + x_3 y_3 + \cdots + x_n z_n$. Mole fraction and molecular weighted of each compound are denoted by x_1, x_2, x_3, …, x_n and z_1, z_2, z_3, …, z_n, respectively. The prepared glass medium was quenching at 1.0 mol% of Dy^{3+} ion concentration, while the density and molar volume at quenching concentration were 3.06 g/cm^3 and 25.67 cm^3/mol respectively. Excitation spectra were measured by selecting λ_{em}=575 nm and emission spectra were measured under excitation of λ_{ex}=350 nm [14].

Figure 2(a) shows the experimental setup of x-ray induced optical luminescence spectrometer. Cu target x-ray generator (Inel,XRG3D-E: X-Ray generator) was used to measure x-ray induced optical luminescence spectra. X-ray source was arranged at 50 kV and 20 mA for all samples. Emission spectra were detected by the spectrometer (QE65 Pro, Ocean Optics) with optical fibre.



(a) (b)

Figure 2. (a) Diagram for measuring the x-ray induced optical luminescence at Nakhon PathomRajabhat University, (b) Near-infrared emission spectra of glass medium doped 0.1 to 2.5 mol% of Dy^{3+} ion

Near-infrared emission spectra of the glass medium are shown in Figure 2(b). The intensity of x-ray luminescence increased with adding the concentration of Dy^{3+} ion from 0.1 to 1.0 mol%. Furthermore, the addition of Dy^{3+} concentration from 1.0 to 2.5 mol% decrease the intensity of x-ray luminescence. It shows that the quenching concentration of x-ray luminescence was identical with optical luminescence. Figure 2(b) presents 4 transition states from $^4F_{9/2}$ to another energy level such us $^6H_{15/2}$, $^6H_{7/2}$, $^6H_{9/2}$, $^6H_{9/12}$, and $^6H_{11/2}$ [15]. These transitions are corresponded by several wavelengths which are 482, 574, 660, and 754 nm and compared with other literature [16]. The highest peak of 574 nm in the yellow region occur due to $^4F_{9/2} \rightarrow {}^6H_{7/2}$ transition that is similar to emission spectra [14].

3. Conclusion

Glass medium doped Dy^{3+} ion based on melt quenching method has been successfully developed. The density of glass medium from 0.5 to 2.5 mol% increased because the mass molecular of Dy_2O_3 is heavier than B_2O_3. The increasing molar volume and decreasing emission intensity of glass medium from 0.5 to 2.5 mol% is affected by the presence of Non-Bridging oxygen. The x-ray induced optical luminescence show the transitions from $^4F_{9/2}$ to $^6H_{15/2}$, $^6H_{7/2}$, $^6H_{9/2}$, $^6H_{9/12}$, and $^6H_{11/2}$ when excited by λ_{ex}=350 nm. That are corresponded by the wavelength of 482, 574, 660, and 754 nm.The x-ray source was arranged in 50 kV and 20 mA. From the results, it can be concluded that glass medium doped Dy^{3+} is the promising material for x-ray scintillator-crystal with the low-energy photon.

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