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The effect of addition of PTFE or urea on luminescence response of copper-doped lithium tetraborate

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Abstract

Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) is a promising material for application in personal dosimetry due to its tissue equivalent properties. The addition of copper as a dopant in $\text{Li}_2\text{B}_4\text{O}_7$ is known to increase the sensitivity for both photoluminescent (PL) and thermoluminescent (TL) emission. Therefore, in this paper, synthesis of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ is reported. The optimum synthesis condition was achieved using the solution-assisted method, followed by calcination at 700°C for 2 h. The addition of 0.1 wt% Cu resulted in the highest PL and TL emissions. Further investigation of the influence of polytetrafluoroethylene (PTFE) or urea addition on the luminescence response of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ is described. All samples were characterized by x-ray diffraction (XRD), attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrometry, photoluminescence spectrofluorophotometer, thermoluminescence reader, scanning electron microscopy (SEM), and energy dispersive x-ray (EDX) spectroscopy. The addition of PTFE decreased the PL emission of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ but slightly increased its TL emission. Meanwhile, the addition of urea increased the luminescence emission for both PL and TL of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$.

1. Introduction

Ionizing radiation, including UV light, x-rays, gamma rays and particle radiation (α , β , and neutron), are widely used in medical, energy, and nuclear applications. People working in such areas are at a high risk of being exposed to ionizing radiation and need to monitor their radiation doses [1]. These individuals constantly have to be aware of the threshold dose of ionizing radiation for the human body to avoid the damage it can cause. The personal dosimeter is a device that is used as an ionizing radiation detector for workers in these fields [2]. A commonly used dosimeter is the thermoluminescence dosimeter (TLD) [1–3]. Materials with thermoluminescent (TL) properties were first introduced by Daniel *et al* [4]. Since then, the research on its synthesis and applications has been developing continuously. TL materials display luminescence when the energy stored by prior irradiation in the materials is exposed to heat [5]. Research results on materials with TL properties for application in personal dosimeters have been reported previously [1–3, 5]. TL materials are required to have tissue equivalent features when used for TLDs.

Among the reported TL materials, lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) is the most promising candidate for use in TLDs. Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) has an effective atomic number for photoelectric absorption (Z_{eff}) of 7.4, which is similar to that of human tissue (7.3) [6]. $\text{Li}_2\text{B}_4\text{O}_7$ exhibits perfect linearity when high doses of irradiation ($\sim 10^3$ Gy) are applied [5]. Moreover, $\text{Li}_2\text{B}_4\text{O}_7$ has a slow fading rate, only 10% in the first three months, and can

be produced using a simple technique [7, 8]. Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) can be prepared via several methods. The first method is by heating at $600\text{ }^\circ\text{C}$ using a hydrated precursor of lithium tetraborate ($\text{LiB}_5\text{O}_6(\text{OH})_4\cdot\text{H}_2\text{O}$) or a mixture of lithium borates ($\text{LiB}_2\text{O}_3(\text{OH})\cdot 3\text{H}_2\text{O}$ and $2\text{LiB}_5\text{O}_6(\text{OH})_4\cdot 3\text{H}_2\text{O}$ or $\text{LiB}_2\text{O}_3(\text{OH})\cdot 3\text{H}_2\text{O}$ and H_3BO_3) [9]. The second method is by solution-assisted synthesis using a stoichiometric amount of Li_2CO_3 and H_3BO_3 [7, 10]. The third method is solid state synthesis by milling and homogenizing of Li_2CO_3 and H_3BO_3 powders and sintering at $400\text{ }^\circ\text{C}$ for 3 h and then continued heating at $750\text{ }^\circ\text{C}$ for 2 h [11]. The fourth method is by solution combustion synthesis (SCS), using LiNO_3 , H_3BO_3 , glycine, and urea as combustion fuel [12]. Among these techniques, the solution-assisted procedure is the most straightforward and economic method. Hence, in this study, we used the solution-assisted method.

There have been several research effort towards improving the TL properties $\text{Li}_2\text{B}_4\text{O}_7$, mainly by addition of different dopants. Schulman first introduced Mn as a dopant for $\text{Li}_2\text{B}_4\text{O}_7$ using the melting zone technique. However, this resulted in low sensitivity and a TL emission in the range of red light (600 nm), which is uncomplimentary for the photomultipliers in TL readout equipment [6]. The effect of other dopant and co-dopant, such as Mn, Cu, Mg, Ag, Ce, Dy, (Cu, Ag), (Cu, In, Ag), Ni, or Cr, on the TL properties of $\text{Li}_2\text{B}_4\text{O}_7$ have been reported [8, 12–18]. Among these dopants, Cu showed the most promising results in improvement of TL properties. The use of copper as a dopant resulted in better TL properties, higher TL sensitivity and an emission spectrum at $\sim 360\text{ nm}$, which is within the detection wavelength of photomultipliers [7]. A comparison study on the sensitivity of $\text{Li}_2\text{B}_4\text{O}_7$ and lithium tetraborate doped with Cu ($\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$) to gamma and neutron irradiation has been performed [6]. The report showed that $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ was 50 times more sensitive to gamma radiation compared to $\text{Li}_2\text{B}_4\text{O}_7$ and 5 times more sensitive compared to commercially available dosimeters (LiF: Mg, Ti). On the other hand, $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ was about 5 times less sensitive to thermal neutrons than $\text{Li}_2\text{B}_4\text{O}_7$. Therefore, more research on how to further improve the TL properties of $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ still needs to be performed, as we know that $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ has the most tissue equivalent properties among other TL materials.

In this research, we investigated the photoluminescence (PL) and TL properties of $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ with polytetrafluoroethylene (PTFE) as the binder or urea as the combustion agent. To the best of our knowledge, there are no reports on the synthesis and study of PL and TL properties of $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ with the addition of PTFE or urea. We also investigated the optimal synthesis conditions by varying the calcination temperature and concentration of Cu. Subsequently, the optimal calcination temperature was used for the synthesis of $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ with various concentrations of PTFE or urea. Hence, we could determine the synthesis conditions to produce $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ with the addition of PTFE or urea that result in the best PL and TL properties.

2. Materials and methods

2.1. Materials

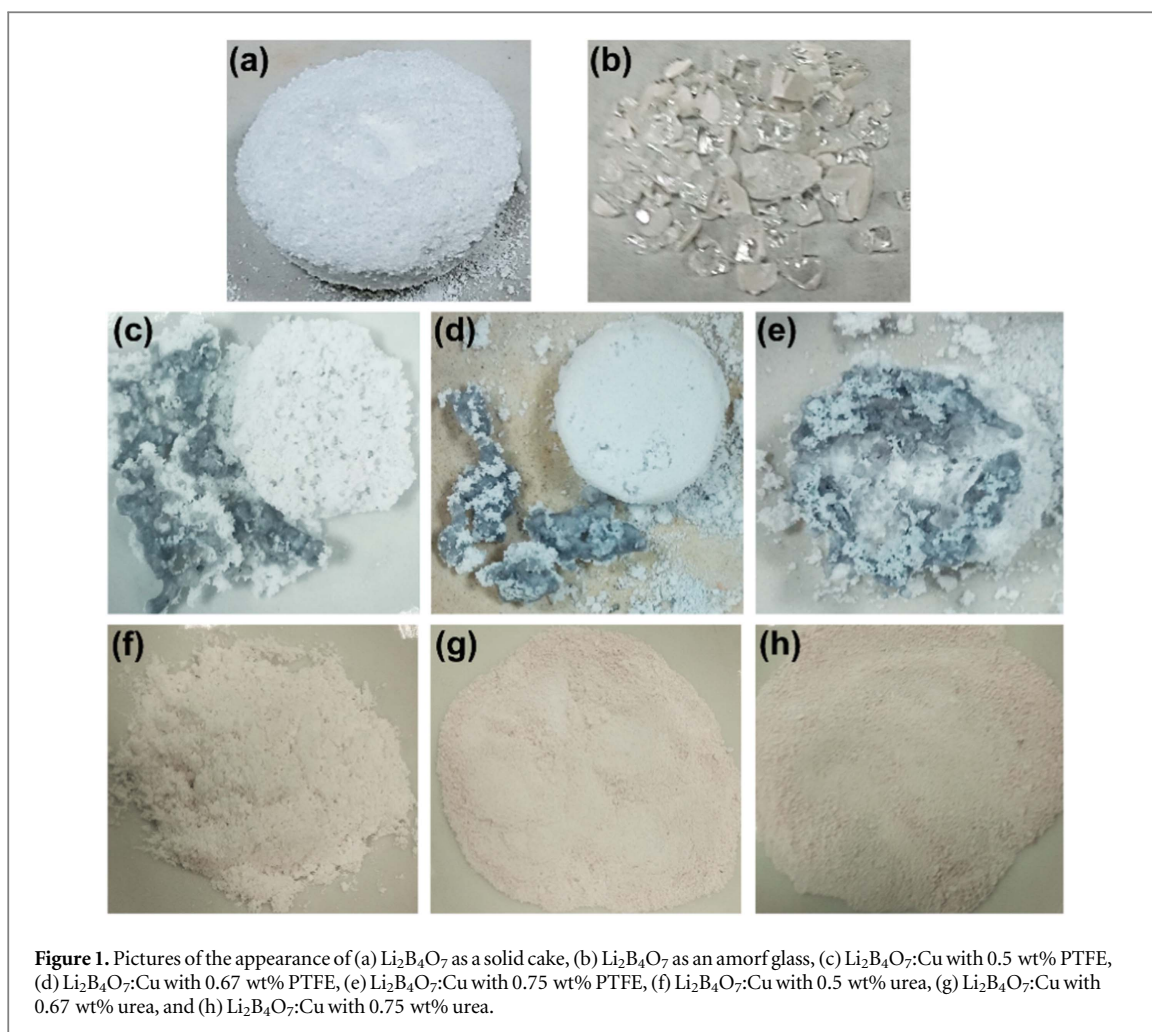
Lithium carbonate (Li_2CO_3), boric acid (H_3BO_3), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$), lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), and urea $\text{CO}(\text{NH}_2)_2$ were purchased from Merck, Indonesia. Polytetrafluoroethylene (PTFE) was bought from Sigma-Aldrich, Germany. DI water was obtained from the Chemistry Department of ITB, Bandung, Indonesia.

2.2. Synthesis methods

Lithium carbonate (0.0059 mol) and boric acid (0.024 mol) were dissolved in 40 ml DI water using 600 rpm magnetic stirring at $60\text{ }^\circ\text{C}$ for 30 min. The precursor solution was then dried in the oven at $150\text{ }^\circ\text{C}$ for 3 h. The dried precursor was milled, and subsequently, calcination was carried out in a furnace for 2 h at various temperatures (500, 700, or $900\text{ }^\circ\text{C}$). The sample was cooled and removed from the furnace when the temperature was at most $100\text{ }^\circ\text{C}$. The dried samples were milled by mortar and then characterized. In order to investigate the effect of (i) dopant concentration and (ii) PTFE, or (iii) urea, on the TL performance of the sample, copper nitrate trihydrate (0.05, 0.1, or 0.3 wt%), PTFE (0.5, 0.67, or 0.75 wt%), or urea (0.5, 0.67, or 0.75 wt%) were varied in the precursor, respectively. In the case of the experiment with additional of urea, the reaction mixture was heated in a microwave oven (Panasonic Microwave, 2.45 MHz, 800 W) at medium mode for 10 min, so all solvent evaporated, instead of drying in the oven at $150\text{ }^\circ\text{C}$ for 3 h. Subsequently, the same procedures we conducted for the milled and calcination treatment.

2.3. Characterization methods

The resulting samples of $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$, $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ with the addition of PTFE or urea were characterized using the following instrumental methods. Attenuated total reflectance-Fourier transform infrared spectrometry (ATR-FTIR) measurements were carried out using an Alpha FTIR spectrometer Bruker 1 176 397. X-ray diffraction (XRD) measurements were performed on a Phillips Analytical PW 1710 BASED. Scanning electron microscopy (SEM) operated at 15 kV was done using a Hitachi 3500. Energy dispersive x-ray

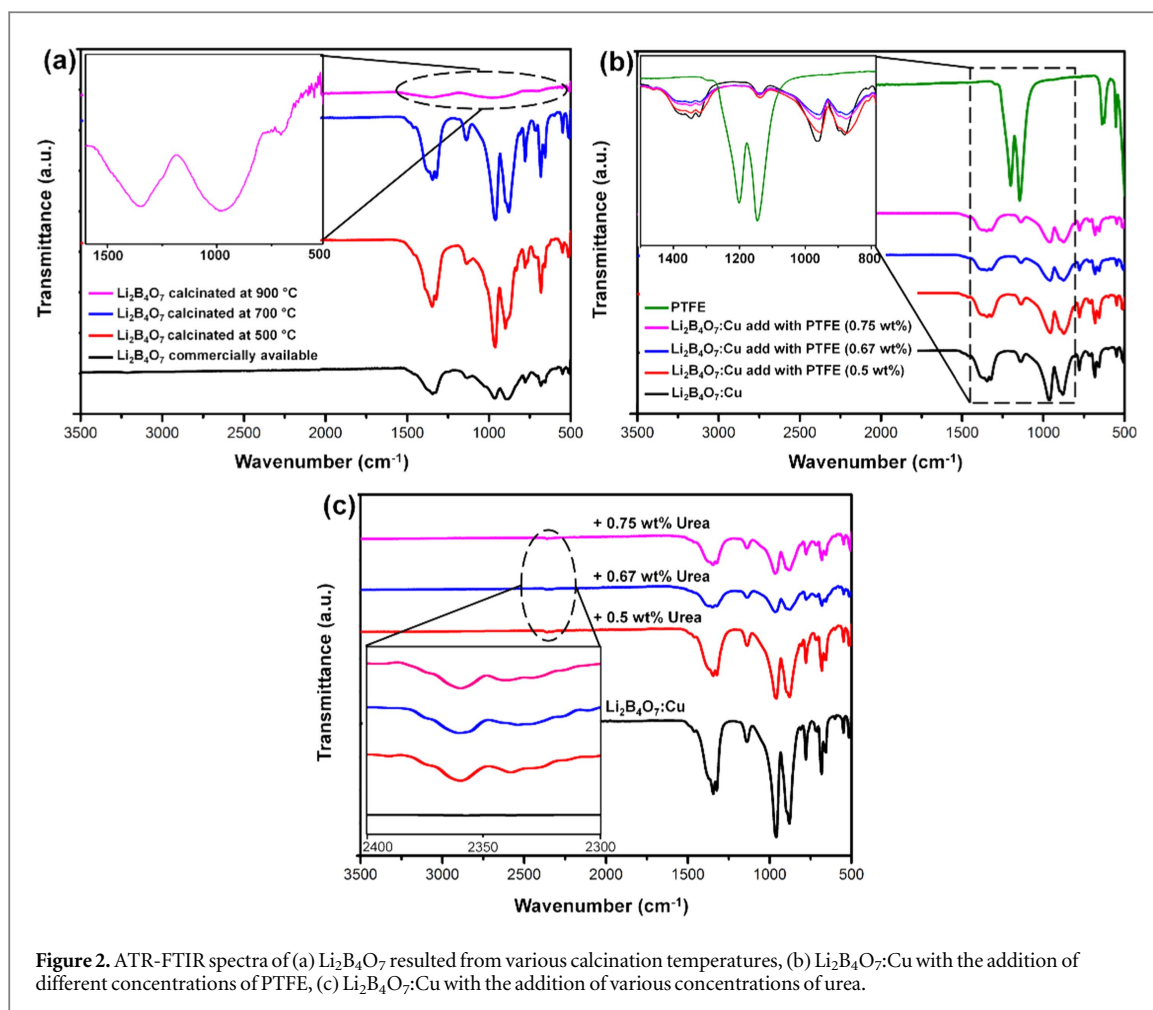


spectrometry (EDX) measurements were performed using a JEOL-JSN-6510LV. Photoluminescence measurements at an excitation wavelength of 265 nm were conducted using an RF-5300PC spectrofluorophotometer, Shimadzu Corp. Thermoluminescence (TL) measurements were accomplished using a TL reader Harshaw 3500. Before the measurements, the samples were irradiated with gamma rays using Cesium-137 at doses of 10 mGy under normal atmospheric conditions at room temperature. Subsequently, the emission of the sample (0.055 g) was measured with a heating rate of 10 °C/s in a temperature range of 50 °C–350 °C. Measurement of the emission was performed twice per sample.

3. Results and discussion

The $\text{Li}_2\text{B}_4\text{O}_7$ obtained after calcination had a different appearance depending on the calcination temperature. In figure 1(a), the product appears as a solid cake after calcination at 500 or 700 °C for 2 h. On the other hand, the sample looked like glass when the calcination temperature was at 900 °C for 2 h and slow cooling in the furnace until 100 °C and outside the furnace to room temperature afterward, as shown in figure 1(b). $\text{Li}_2\text{B}_4\text{O}_7$ has a relatively low melting temperature (~917 °C) and ability to form a glass material [19]. Therefore, by applying a calcination temperature at 900 °C for 2 h, which near its melting temperature, resulted in the formation of an amorphous glass of $\text{Li}_2\text{B}_4\text{O}_7$.

The synthesis of $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ was conducted with a similar solution-assisted method as in the synthesis of $\text{Li}_2\text{B}_4\text{O}_7$. However, copper nitrate trihydrate ($(\text{CuNO}_3)_2 \cdot 3\text{H}_2\text{O}$) was added as the Cu dopant source. The resulted $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ after the calcination process, showed a form similar to the solid cake form of $\text{Li}_2\text{B}_4\text{O}_7$. The appearance of the $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ samples with the addition of various concentrations of PTFE are shown in figures 1(c)–(e). After the calcination process, the resulted product appeared as nonhomogeneous powders (white powder and gray ashes). The gray ashes belong to the decomposition of PTFE (decomposition temperature at 470 °C–600 °C), as we did the calcination at 700 °C. However, the samples of $\text{Li}_2\text{B}_4\text{O}_7\text{:Cu}$ with the addition of various concentrations of urea resulted in homogenous powders, see figures 1(f)–(h). After



calcination at 700 °C for 2 h, the samples showed changes in coloration from a white powder after microwave heating to a slightly pink powder.

3.1. Structure analysis

Structure analysis of the samples was carried out by ATR-FTIR and XRD measurements. Analysis of the functional groups of the samples was done based on the ATR-FTIR measurements results, as shown in figure 2. Commercially available $\text{Li}_2\text{B}_4\text{O}_7$ was used as reference for comparison with our synthesized $\text{Li}_2\text{B}_4\text{O}_7$. Figure 2(a) displays the spectra of the synthesized $\text{Li}_2\text{B}_4\text{O}_7$ with various calcination temperatures and of the commercially available $\text{Li}_2\text{B}_4\text{O}_7$. The spectra of synthesized $\text{Li}_2\text{B}_4\text{O}_7$ with calcination temperatures at 500 or 700 °C resulted in the same pattern as the commercially available $\text{Li}_2\text{B}_4\text{O}_7$. The characteristic peaks at 1600–1200 cm^{-1} (asymmetric stretching of B–O from BO_3), 1500–700 cm^{-1} (plane bending of O–B–O from BO_4), 950–870 cm^{-1} (stretching of BO_4), 870–500 cm^{-1} (deformation of O–B–O from BO_4) were present in the spectra of the synthesized $\text{Li}_2\text{B}_4\text{O}_7$ (with calcination temperature at 500 or 700 °C) as in the commercially available $\text{Li}_2\text{B}_4\text{O}_7$ [20]. However, a different result was observed for the $\text{Li}_2\text{B}_4\text{O}_7$ after calcination at 900 °C. Only two broad and low-intensity peaks appeared in this sample, at 1576–1189 cm^{-1} (asymmetric stretching of B–O from BO_3) and at 1189–775 cm^{-1} (plane bending of O–B–O from BO_4) [20]. The different forms of the samples, from solid cake to glass, resulted in different ATR-FTIR spectra. The narrowness and low intensity of the peaks from the amorphous glass of $\text{Li}_2\text{B}_4\text{O}_7$ result from the rigidity of the glass limiting the vibration of the atoms and molecules in the chemical bonds. Further functional group characterizations were performed on the $\text{Li}_2\text{B}_4\text{O}_7$ samples with the addition of various concentrations of copper as a dopant. Similar results as the spectra observed from the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ samples were observed. No new peaks were present because of the addition of copper as a dopant (see figure S1 is available online at stacks.iop.org/MRX/5/044003/mmedia in the Supplementary Information).

Based on the synthesis of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$, a concentration of 0.1 wt% copper was used in the further synthesis of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of PTFE or urea. This amount of copper concentration was chosen because it displayed high PL and TL intensity, which will be discussed in the next section. The ATR-FTIR results from the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of various concentrations of PTFE are shown in figure 2(b). Compared to the

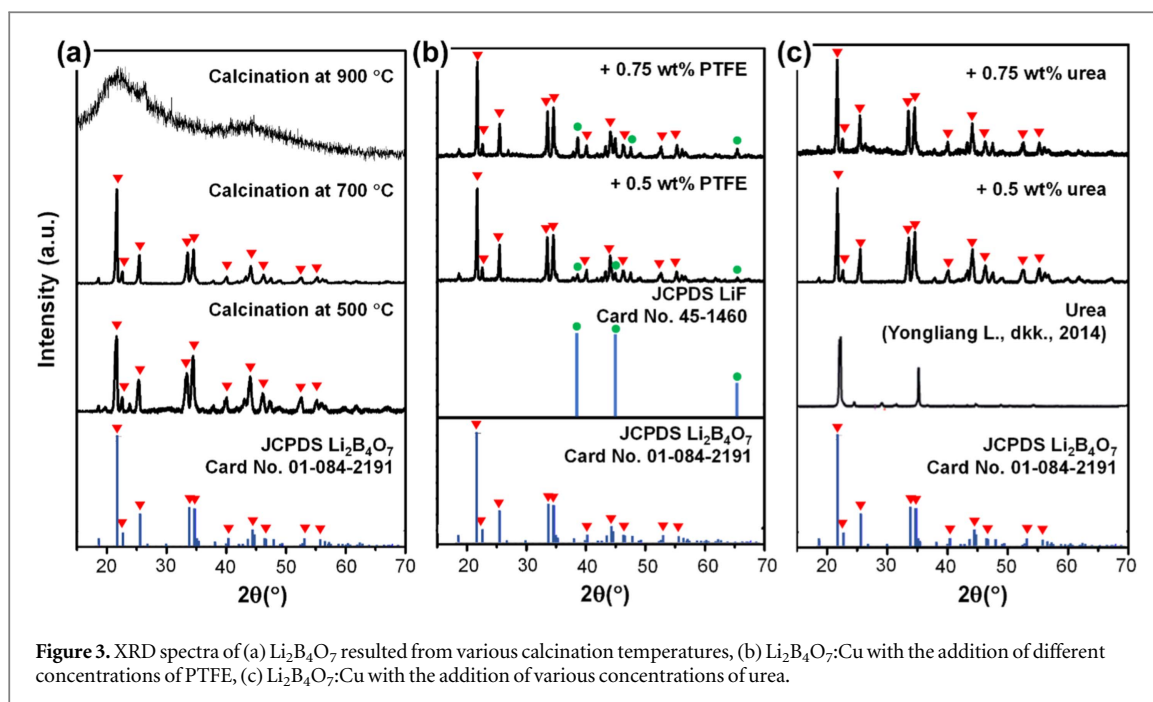


Figure 3. XRD spectra of (a) $\text{Li}_2\text{B}_4\text{O}_7$ resulted from various calcination temperatures, (b) $\text{Li}_2\text{B}_4\text{O}_7$:Cu with the addition of different concentrations of PTFE, (c) $\text{Li}_2\text{B}_4\text{O}_7$:Cu with the addition of various concentrations of urea.

spectrum of PTFE and $\text{Li}_2\text{B}_4\text{O}_7$:Cu, no new peaks appeared with the addition of PTFE. Similar characteristic peaks were observed as in the $\text{Li}_2\text{B}_4\text{O}_7$ sample. From this we can conclude that most of the PTFE decomposed; thus there are no peaks to indicate the presence of PTFE in the $\text{Li}_2\text{B}_4\text{O}_7$:Cu. However, the EDX result of $\text{Li}_2\text{B}_4\text{O}_7$:Cu with the addition of 0.5 wt% PTFE showed the existence of fluorine and carbon elements in the samples, as shown in figure S2 in the Supplementary Information.

In the synthesis of $\text{Li}_2\text{B}_4\text{O}_7$:Cu with the addition of urea, the resulted product after calcination at 700 °C for 2 h was characterized by ATR-FTIR measurement, as shown in figure 2(c). The characteristic peaks of $\text{Li}_2\text{B}_4\text{O}_7$ are prominently visible. Nevertheless, a new broad peak with low intensity appeared at $\sim 2300\text{ cm}^{-1}$, which is attributed to the vibration of the isocyanate functional group ($\text{N}=\text{C}=\text{O}$). This result is in agreement with previously reported research, which explains that heating urea at higher temperature leads to the formation of $(\text{HNCO})_3$ trimer [21]. The formation of $(\text{HNCO})_3$ trimer consisting of the isocyanate functional group resulted in the pinkish color of the powder sample after calcination at 700 °C for 2 h. This color appearance is in agreement with the previously reported result that the pink color is characteristic for O-polyisocyanates [22]. Further EDX analysis confirmed the presence of nitrogen and carbon elements in the sample of $\text{Li}_2\text{B}_4\text{O}_7$:Cu with the addition of urea, see figure S3 in the Supplementary Information.

Characterization using XRD measurement was performed to verify the structure and the crystallinity of the samples. The XRD spectra of the samples are depicted in figure 3. The synthesis of $\text{Li}_2\text{B}_4\text{O}_7$ with various calcination temperatures is shown in figure 3(a). The products of $\text{Li}_2\text{B}_4\text{O}_7$ treated with calcination at 500 or 700 °C show diffraction peaks that are in agreement with JCPDS $\text{Li}_2\text{B}_4\text{O}_7$ Card No. 01-084-2191. By increasing the calcination temperature to 700 °C, the resulted $\text{Li}_2\text{B}_4\text{O}_7$ displayed better crystallinity. The crystallite size of $\text{Li}_2\text{B}_4\text{O}_7$ can be calculated using the Scherrer equation from the plane (112). The sample of $\text{Li}_2\text{B}_4\text{O}_7$ treated with calcination at 700 °C had a bigger crystallite size of 25.86 nm compared to the $\text{Li}_2\text{B}_4\text{O}_7$ treated with calcination at 500 °C, which was 18.56 nm. However, increasing the temperature to 900 °C resulted in an amorphous material. Hence, for the synthesis of $\text{Li}_2\text{B}_4\text{O}_7$:Cu and $\text{Li}_2\text{B}_4\text{O}_7$:Cu with the addition of PTFE or urea, calcination was carried out at 700 °C for 2 h. The same XRD spectrum was observed from the $\text{Li}_2\text{B}_4\text{O}_7$:Cu (with the addition of 0.1 wt% of Cu) as from the $\text{Li}_2\text{B}_4\text{O}_7$, as shown in figure S4 in the Supplementary Information. The calculated crystallite size of $\text{Li}_2\text{B}_4\text{O}_7$:Cu was 25.85 nm. There were no new peaks present from the copper, which indicates that the existence of Cu as a dopant does not interfere with the crystal structure of $\text{Li}_2\text{B}_4\text{O}_7$.

The XRD spectra of the $\text{Li}_2\text{B}_4\text{O}_7$:Cu with the addition of PTFE are displayed in figure 3(b). The XRD spectra belong to the $\text{Li}_2\text{B}_4\text{O}_7$:Cu with the addition of 0.5 wt% and 0.75 wt% of PTFE. The spectra from these samples were compared with JCPDS $\text{Li}_2\text{B}_4\text{O}_7$ Card No. 01-084-2191 and JCPDS LiF Card No. 45-1460 as reference spectra. Three new diffraction peaks were observed at 2θ of 38.63°, 44.90° and 65.40° from the sample spectra. The three new peaks belong to LiF, based on JCPDS LiF Card No. 45-1460. Decomposition of PTFE during the annealing process at 700 °C resulted in the formation of LiF. This result is also confirmed by the EDX result, as shown in figure S2 in the Supplementary Information. By increasing the amount of PTFE in the $\text{Li}_2\text{B}_4\text{O}_7$:Cu, the intensity of the three new peaks increased. The calculated crystallite size of the $\text{Li}_2\text{B}_4\text{O}_7$:Cu with the addition of

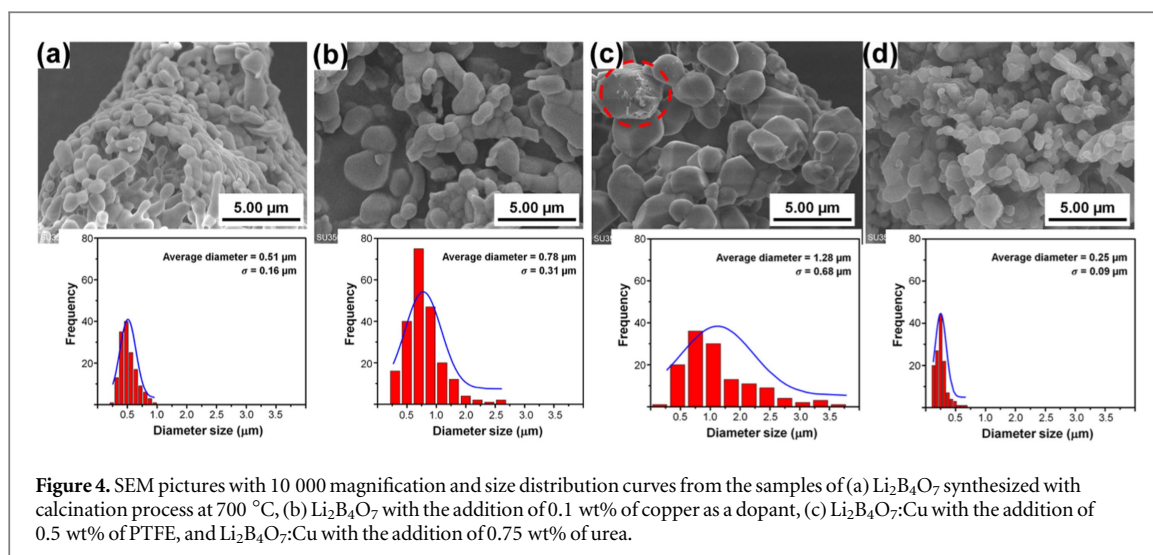


Figure 4. SEM pictures with 10 000 magnification and size distribution curves from the samples of (a) $\text{Li}_2\text{B}_4\text{O}_7$ synthesized with calcination process at 700°C , (b) $\text{Li}_2\text{B}_4\text{O}_7$ with the addition of 0.1 wt% of copper as a dopant, (c) $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of 0.5 wt% of PTFE, and $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of 0.75 wt% of urea.

0.5 wt% and 0.75 wt% of PTFE were 37.98 and 39.16 nm, respectively. From this information, we conclude that the addition of PTFE in the synthesis of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ increases the crystallinity of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ and the formation of LiF.

In figure 3(c), the XRD spectra of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of urea are shown. JCPDS $\text{Li}_2\text{B}_4\text{O}_7$ Card No. 01-084-2191 and urea were used as the reference spectra [23]. No new peaks were observed from the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ samples with the addition of urea (0.5 and 0.75 wt%). However, a similar pattern of crystallite size was found as in the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ samples with the addition of PTFE. The crystallite of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ increased with a higher amount of urea added to the system during synthesis. The calculated crystallite size was 29.56 and 31.32 nm for the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of urea at 0.5 and 0.75 wt%, respectively. The parameters for crystallite size calculation of $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$, $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of PTFE, and $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of urea are summarized in table S1 in the Supplementary Information.

3.2. Morphology analysis

The morphology of the samples was characterized by SEM measurement. SEM pictures and particle size distributions of $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$, $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of PTFE, and $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of urea are shown in figure 4. The particle diameters of the samples were calculated from ≥ 100 particles diameter data using the imageJ program. In the SEM pictures of the samples, agglomerations were observed in all the samples. Moreover, coalescence occurred due to calcination at 700°C , resulting in bigger particles. The average particle diameter of $0.51\ \mu\text{m}$ (with a diameter range of $0.2\text{--}1.0\ \mu\text{m}$) was calculated from the $\text{Li}_2\text{B}_4\text{O}_7$ sample, as shown in figure 4(a). By adding 0.1 wt% of copper, the average diameter of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ increased up to $0.78\ \mu\text{m}$ with a diameter range of $0.2\text{--}2.6\ \mu\text{m}$, see figure 4(b).

In figure 4(c), a small trace of decomposed PTFE was observed in the SEM pictures (area marked by a red circle). Moreover, a similar result was observed in the sample of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of PTFE 0.5 wt%. By adding PTFE to the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$, the average particle diameter increased to $1.28\ \mu\text{m}$, which subsequently led to a decrease in the uniformity of the particles size (with diameter range $0.1\text{--}3.7\ \mu\text{m}$). The bigger particles size resulted because of the increase in the coalescent process, which occurs more effortlessly because of the presence of PTFE as a binder agent. On the other hand, the average diameter of the particles decreased to $0.25\ \mu\text{m}$ (with diameter range $0.1\text{--}0.7\ \mu\text{m}$) when urea was added to the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$, which led to an increase of the uniformity of the particle size.

3.3. Photoluminescence (PL) properties

PL emission intensity was measured using a PL spectrofluorophotometer with an excitation wavelength of 265 nm. The PL emission spectra of the $\text{Li}_2\text{B}_4\text{O}_7$ with the addition of various concentrations of copper compared to the PL emission spectra of synthesized and commercially available $\text{Li}_2\text{B}_4\text{O}_7$ are shown in figure 5(a). The PL emission spectra of $\text{Li}_2\text{B}_4\text{O}_7$ (synthesized and commercially available) display the same three peaks at wavelengths 361, 420, and 493 nm. These three peaks indicate the three-level energy that causes luminescence in the $\text{Li}_2\text{B}_4\text{O}_7$. After the addition of copper as a dopant, the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ samples showed the same PL emission spectrum, which means no new peaks appeared due to the addition of the copper, although the intensity of the PL emission increased with the increasing of the copper concentration to 0.1 wt%. This result occurred in the presence of copper as dopant because it fills in defects caused by a vacancy in the $\text{Li}_2\text{B}_4\text{O}_7$ crystal structure [24].

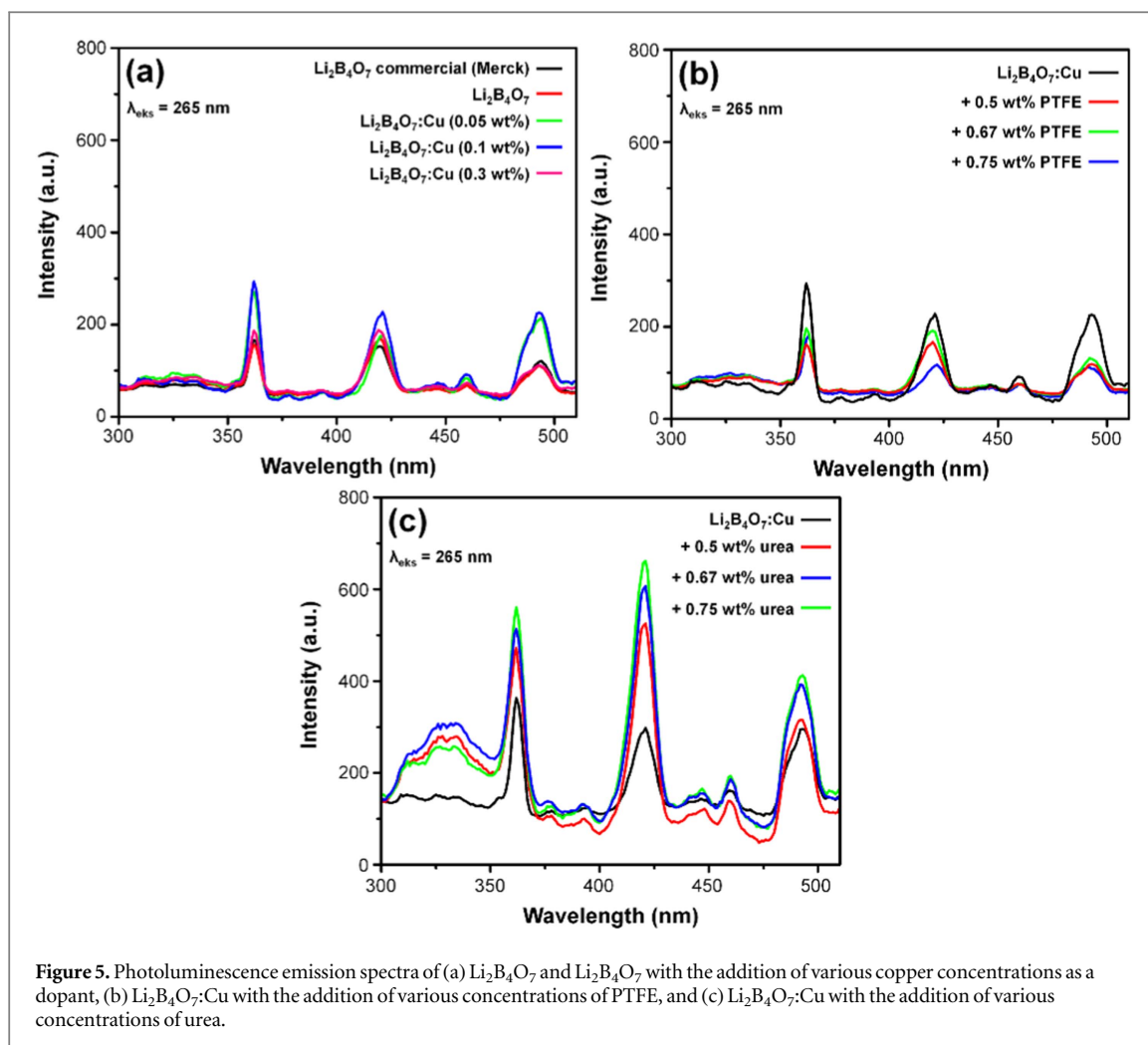


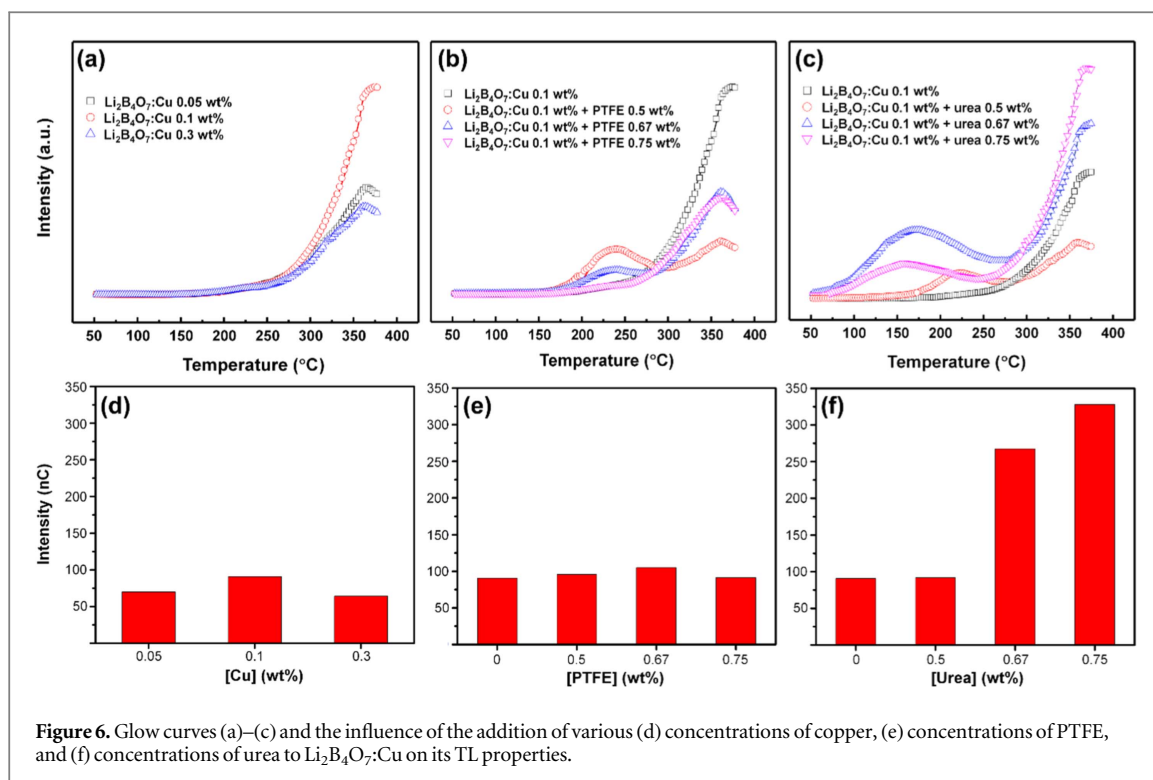
Figure 5. Photoluminescence emission spectra of (a) $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{Li}_2\text{B}_4\text{O}_7$ with the addition of various copper concentrations as a dopant, (b) $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of various concentrations of PTFE, and (c) $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of various concentrations of urea.

The emission peaks at 361 and 420 nm can be attributed to the transition of Cu^+ from triplet to singlet state [25]. Furthermore, the PL emission peak at 492 nm belongs to the electron transition from the conduction band to the energy level caused by the presence of Cu^{2+} in the $\text{Li}_2\text{B}_4\text{O}_7$ crystal. The Cu^{2+} ion acts as an electron trap, following the recombination mechanism of $\text{Cu}^{2+} + \text{electron} \rightarrow \text{Cu}^{+*} \rightarrow \text{Cu}^+ + h\nu$ (492 nm) [24].

The PL emission spectra of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the various additions of PTFE are depicted in figure 5(b). The intensity of PL emission decreased due to the addition of the PTFE. This result occurred due to the existence of fluorine in the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$, which acts as a new trap in the energy level. The presence of this trap causes a decrease in radiative transition, and thus, the intensity of PL emission also decreases. In figure 4(c), the PL emission spectra of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the various additions of urea are shown. A new PL emission peak appeared at 320 nm as a result of the addition of urea. By adding urea, the intensity of the PL emission increased with the increase in the concentration of urea. The highest PL emission intensity was shown by the sample with the addition of 0.75 wt% urea. The increasing of intensity is due to the presence of a conjugated system of the isocyanate ($\text{N}=\text{C}=\text{O}$) functional group in the sample. From the morphology analysis of the sample, adding urea during synthesis of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ resulted in more uniform and smaller particle sizes of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$, which led to an increase of surface area and consequently increased the PL emission intensity.

3.4. Thermoluminescence (TL) properties

The thermoluminescence emission of $\text{Li}_2\text{B}_4\text{O}_7$ doped with various concentrations of copper was investigated using TL reader. The influence of the copper concentration, the addition of PTFE, or urea in the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ on the Glow curves and TL emission are summarized in figure 6. From figure 6(a), the highest emission intensity detected at 350 °C, which belongs to the sample of $\text{Li}_2\text{B}_4\text{O}_7$ with the addition of 0.1 wt% copper. The new peak observed at the curve profile of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of PTFE at 240 °C, as shown in figure 6(b). This new peak is attributed to the formation of LiF in the sample, as reported by Singh and Sahare [26]. Furthermore, the shift of glow curve also observed in the samples of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of urea, as depicted in figure 6(c). The new peak identified at 220 °C for the sample of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of 0.5 wt% urea. This new peak shifted to the temperature at 160 °C for the samples of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of 0.67 or



0.75 wt% urea. This shifting of glow curve is probably due to different trap energy occurred with the addition of different concentration of urea.

From the glow curves of each sample, the area under the curve was used to determine the TL emission properties as shown in figures 6(d)–(f). Based on the analysis of the influence of the copper concentration on the TL emission, the addition of 0.1 wt% Cu showed the highest TL emission, see figure 6(d), which is in line with previously reported results [5]. Based on this result, the addition of 0.1 wt% copper was used for the further synthesis of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of various concentrations of PTFE or urea.

In figure 6(e), the results of the influence of the addition of various PTFE concentrations are shown. By adding the concentration of PTFE, increased the TL emission of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ but only slightly. The concentration of 0.67 wt% showed the highest TL emission for $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of PTFE. This result is in agreement with the result previously reported by our group [27]. On the other hand, by adding urea during synthesis of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$, increased the TL emission intensity with the increase of the urea concentration. The TL emission intensity was three times higher compared to that of the sample without addition of urea, as shown in figure 6(f).

By adding urea during the synthesis of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ led to improvement of TL emission of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$. There are three possible explanations regarding the increase of TL emission from $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ due to the addition of urea during synthesis. Firstly, as reported by Kingsley *et al* [21], heating urea at high temperature leads to the formation of isocyanate $(\text{HNCO})_3$ trimer, which contains nitrogen bonding atoms. The nitrogen atom in the trimer isocyanate can act as an energy trap, which makes radiative transition work more efficiently in the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$. Secondly, as shown by the SEM result, the addition of urea causes a decrease in particle diameter and an increase in uniformity, which leads to the formation of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with high crystallinity. The decrease in particle diameter can increase the surface area of the sample. These phenomena lead to a higher absorptivity of radiative beams, which occur more effectively on the surface of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ particles. The larger surface area results in better absorption of radiative beams and as a result the TL emission will be higher. Thirdly, the presence of trimer isocyanate as a new conjugated system in the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ crystal not only may increase the PL emission but may also increase TL emission of $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$. However, the mechanism of how trimer isocyanate conjugates with $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ crystal is still unknown. More studies have to be performed to investigate the position of trimer isocyanate in the $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ crystal to understand its mechanism accurately.

4. Conclusions

Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) has been successfully synthesized via the solution-assisted method and subsequent calcination at 500 or 700 °C. Calcination temperature at 700 °C produced better crystallinity of

$\text{Li}_2\text{B}_4\text{O}_7$. By performing calcination at 900°C for 2 h, resulted in an amorphous glass $\text{Li}_2\text{B}_4\text{O}_7$. Thus, the calcination temperature influences the structure and crystallinity of lithium tetraborate. During the calcination process, Cu was inserted in $\text{Li}_2\text{B}_4\text{O}_7$ lattice crystal. This insertion of Cu in $\text{Li}_2\text{B}_4\text{O}_7$ lattice crystal acts as a dopant, which results in the defect in $\text{Li}_2\text{B}_4\text{O}_7$ lattice crystal. This defect further caused the electron trap in the $\text{Li}_2\text{B}_4\text{O}_7$ material that results in increased PL and TL properties of $\text{Li}_2\text{B}_4\text{O}_7$. Furthermore, the structure and morphology of $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$, $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ with the addition of PTFE or urea were confirmed by ATR-FTIR, XRD, EDX, and SEM results. The addition of PTFE in $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ decreased particle size uniformity. In contrast, the addition of urea to $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ increased particle size uniformity. The addition of copper as a dopant led to an increase of luminescence emission intensity of $\text{Li}_2\text{B}_4\text{O}_7$ for both photoluminescence (PL) and thermoluminescence (TL). The highest emission intensity resulted from $\text{Li}_2\text{B}_4\text{O}_7$ with 0.1 wt% of Cu. Furthermore, the addition of PTFE in $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ decreased the PL emission intensity but slightly increased the TL emission intensity. On the other hand, the addition of urea increased both PL and TL emission intensity.

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