รายงานวิจัยฉบับสมบูรณ์

ความสามารถในการเป็นตัวเร่งปฏิกิริยาเชิงแสงของแก้วสีสังกะสีบอโรฟอสเฟตชนิดใหม่

Photocatalytic activities of novel colored zinc borophosphate glasses

ดร.ชำนาญ ราญฎร

ธันวาคม 2559

สัญญาเลขที่ TRG5780112

รายงานวิจัยฉบับสมบูรณ์

ความสามารถในการเป็นตัวเร่งปฏิกิริยาเชิงแสงของแก้วสีสังกะสีบอโรฟอสเฟตชนิดใหม่

Photocatalytic activities of novel colored zinc borophosphate glasses

ดร.ชำนาญ ราญฎร
ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัยและ
มหาวิทยาลัยเชียงใหม่

Abstract (บทคัดย่อ)

Project Code : TRG5780112

Project Title : ความสามารถในการเป็นตัวเร่งปฏิกิริยาเชิงแสงของแก้วสีสังกะสีบอโรฟอสเฟตชนิดใหม่ (Photocatalytic activities of novel colored zinc borophosphate glasses)

Investigator : ดร.ชำนาญ ราญฎร
ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่

E-mail Address : crandorn@gmail.com, chamnan.r@cmu.ac.th

Project Period : 2 ปี

In this report, we demonstrated the catalytic activity of colored zinc borophosphate glasses, specifically their photocatalytic activity. The catalytic activity of the colored zinc borophosphate glasses was investigated using four different methods, including photooxidation reactions, photoreduction reaction, antibacterial testing, and radical polymerization. Novel colored zinc borophosphate glasses were synthesized by a conventional melt-quenching technique at 1200 C. The obtained zinc borophosphate glasses were white, purple and dark green, depending on the metal oxide colorants in the glass matrix. These colored zinc borophosphate glasses improved water dissolution, which is an inherent limitation of pure phosphate glasses. Characterization of the glasses was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and Raman and UV-Visible spectroscopy

Keywords : photocatalysts, borophosphate glasses, antibacterial, photobleaching

Executive Summary

งานวิจัยนี้สนใจในการศึกษา ปรับปรุงหรือคิดค้นแก้วสีแบบใหม่เพื่อนำไปประยุกต์ใช้เป็นตัวเร่งปฏิกิริยาเชิงแสงในกระบวนการโฟโตคะตะไลติก แก้วสีจะเป็นอีกทางเลือกหนึ่งของโฟโตคะตะลิสต์ที่มีศักยภาพ เพราะมีสีที่หลากหลายและมีไอออนของโลหะต่างๆ เนื่องจากจากการสืบค้นวรรณกรรมยังไม่ค่อยมีการศึกษาการนำไปใช้ประยุกต์ใช้ด้านนี้ แต่ก็มีการนำเสนอว่าอาจจะเกิดสารกึ่งตัวนำในเนื้อแก้วได้จากรวมตัวกันไอออนของโลหะที่เติมไป เช่น CdSe ในแก้ว ดังจะเห็นได้จากการนำสมบัติเชิงแสงของแก้วที่เปลี่ยนแปลงไปเมื่อมีไอออนของธาตุทรานสิชันหรือแลนทาไนด์แทรกอยู่ในโครงสร้างไปใช้ในด้านต่างๆเช่น หลอดฟลูออเรสซ์ laser, optical memories, solar control devices เช่นพบว่าเมื่อมี 1โมล% Ce3+ ทำให้ band gap แคบลงเป็น 3.35 eV และมี luminescence สีม่วงทั้งๆที่ไม่มี luminescence ในแก้วที่ไม่ได้โด๊ป จึงน่าสนใจที่จะศึกษาถึงความเป็นไปได้ที่จะนำแก้วสีไปใช้เป็นตัวเร่งปฏิกิริยาเชิงแสงในการสลายสารพิษภายใต้ยูวีหรือแสงมองเห็น เพราะจะทำให้แก้วสีที่ใช้ในทางสถาปัตยกรรมหรือกระจกที่ใช้ตามอาคารสามารถทำความสะอาดตัวเองได้ รวมถึงสามารถเป็นส่วนหนึ่งในการบำบัดมลภาวะบริเวณนั้นๆได้

จากการศึกษาในเบื้องต้น ผู้วิจัยได้ทำการศึกษาการหลอมแก้วสูตรต่างๆซึ่งคิดขึ้นเองและได้ลองเปลี่ยนอัตราส่วนโมลของสารที่เติมไป พบว่าได้ผลการทดลองที่น่าสนใจ และมีโอกาสที่จะนำไปสู่การประยุกต์ได้ ผู้วิจัยได้เริ่มจากการพัฒนาแก้วฟอสเฟตก่อน เนื่องจากใช้อุณหภูมิไม่สูงมากในการหลอม และทำการปรับเพิ่มคุณสมบัติให้เป็นโฟโตคะตะลิสต์โดยการเติมซิงค์ออกไซด์ (ZnO) ในอัตราส่วนระหว่างฟอสเฟตกับซิงค์ออกไซด์ต่างๆกัน เพื่อดูสีและลักษณะทางกายภาพที่เปลี่ยนไป หลังจากนั้นนำไปทดสอบความสามารถในการเป็นตัวเร่งปฏิกิริยาเชิงแสงโดยทดสอบด้วยการฟอกสีเมทิลออเรนจ์และ intelligent ink ซึ่งเป็นตัวแทนของสารพิษที่จะสลาย โดยหมึกนี้พัฒนาโดยกลุ่มของ Prof. Andrews Mills ได้รับการตีพิมพ์เป็นที่ยอมรับในการใช้ทดสอบความสามารถในการเป็นตัวเร่งปฏิกิริยาเชิงแสงของวัสดุที่เป็นแผ่นหรือแท่ง และมีการผลิตในเชิงการค้า

แก้วที่สังเคราะห์มีสีต่างกันตามอัตราส่วนโมลของซิงค์ออกไซด์กับสารให้สีต่างๆ รวมถึงความทึบแสงของแก้ว โดยพบว่าถ้ามีซิงค์ออกไซด์ปริมาณมากขึ้น แก้วที่ได้จะมีความทึบแสงมากขึ้นและมีสีเปลี่ยนไปจากใส เป็นสีขาว และสีเขียว เมื่อนำแก้วแต่ละชนิดไปทดสอบความสามารถในการสลายเมทิลออเรนจ์และ intelligent ink และเรซาซูริน นำไปฉายด้วยยูวีเอ พบว่าเมื่อมีปริมาณซิงค์ออกไซด์เพิ่มมากขึ้น แก้วมีการตอบสนองต่อแสงมากขึ้น ดังสังเกตได้จากมีการลดลงของความเข้มของสีสารละลายเมทิลออเรนจ์ การเปลี่ยนสีของ intelligent ink การเปลี่ยนสีของเรซาซูริน นอกจากนี้พบว่าเมื่อนำไปทดสอบกับการยับยั้งเชื้อแบคทีเรีย ก็ให้ผลยับยั้งการเติบโตของแบคทีเรีย ดังเห็นได้จากวงใสที่เกิดขึ้นรอบๆชิ้นงานแก้ว จึงมีความเป็นไปได้ในการนำไปพัฒนาต่อทั้งในด้านประสิทธิภาพและการนำไปประยุกต์ใช้จริง

Research Objectives

To synthesize new colored zinc borophosphate glasses e.g. blue, purple, green and yellow

To study physical properties, chemical properties and optical properties of the new colored zinc borophosphate glasses

1. Introduction

The new colored zinc borophosphate glasses are intensively attended in order to synthesize the alternative glasses that produce from uncommon glass network i.e. silica (silicon dioxide; SiO_2). Although silica glass has high performance at high temperature, it is necessary to consume high energy in producing process. The phosphate glasses are used for save the producing energy. Furthermore, the phosphate glasses enhance optical properties to suit the glasses to use in a variety of optical applications. This work synthesizes new colored zinc borophosphate glasses (e.g. white, blue, green purple and yellow glasses) and studies physical, chemical, and optical properties of the colored zinc borophosphate glasses.

1.1 General Information of Glass

Glass is a non-crystalline (amorphous) solid exhibiting glass transformation behavior and lacking of long range periodic atomic structure. Not only glasses are produced from inorganic materials, but also glasses can be produced from organic and metallic materials. A common characteristic of glasses is the presence of glass transformation behavior[1].

Traditionally, glasses are formed by high temperature melt quenching technique.

Glass formation usually takes place by rapid cooling of a molten mass. It is commonly described on the basis of either enthalpy or volume versus temperature diagrams (Fig. 1). The cooling of the molten mass to any temperature below the melting temperature (T_m) would normally result in a conversion to the crystalline state, with the formation of a long range and periodic atomic arrangement. Moreover, cooling would also continue to reduce the enthalpy due to the heat capacity of the crystal. Enthalpy would be decreased due to the decline of amplitude of atomic vibrations and structural rearrangement. However, if the melt cools without crystallization, a supercooled liquid will be obtained. As the melt continues to cool, the viscosity becomes high so that atoms cannot completely rearrange to the equilibrium structure and the enthalpy begins to deviate from the equilibrium line, following a curve of gradually decreasing slope until it becomes determined by the heat capacity of the frozen liquid i.e. the viscosity becomes so great that the structure of the liquid becomes fixed and is no longer temperature-dependent. The temperature lying between the limits where enthalpy is that of the equilibrium liquid and that of the frozen solid is known as the glass transformation region. Eventually, the frozen liquid is now a glass.

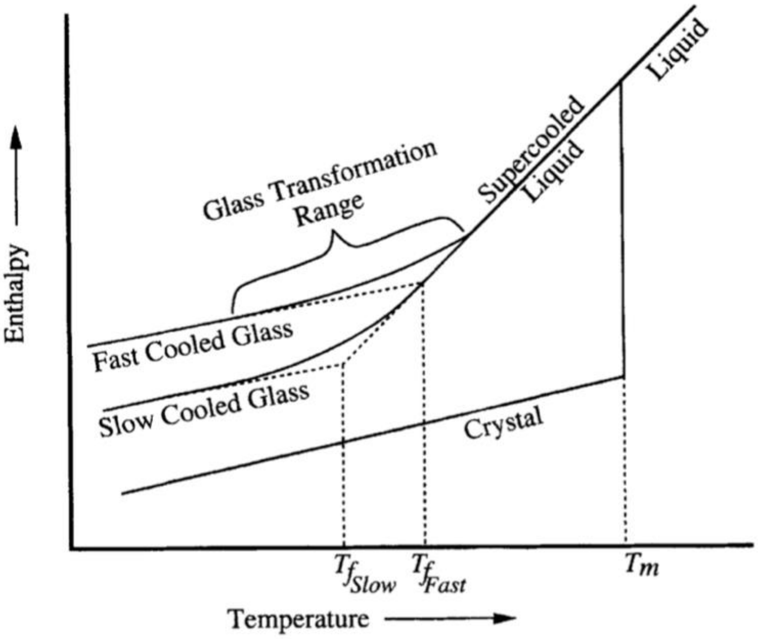


Figure 1.1 The effect of temperature on the enthalpy (or volume) of a glass forming melt.

1.2 General Information of Phosphate Glass

Phosphate glasses are inorganic polymers of the tetrahedral phosphate anions (Fig. 2) using the formation of sp^3 hybrid orbitals by the phosphorus outer electrons (3s^2 3p^3)[2-3].The charges are balanced by polymerization or the presence of metallic ions.

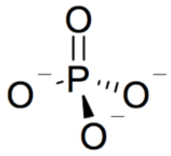


Figure 1.2 The tetrahedral phosphate anion[1]

In the absence of metallic ions, these tetrahedral link via covalent bridging oxygen to form various phosphate anions (Fig. 3)

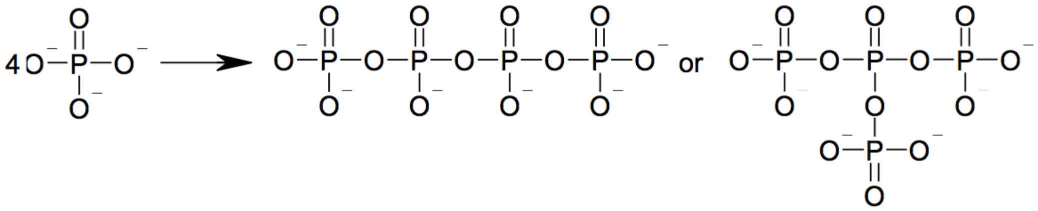


Figure 1.3 Polymerization of the phosphate anion gives rise to various polyphosphate anions linked via oxygen bridges which may be branched or linear or a combination of the two.

The melts of phosphate glasses can be formed at much lower temperature than are typically required for silicate melts. Phosphate glasses are used in optical applications such as bioactive glasses, laser and optical filters, substrates of optical devices and laser solders or glass seals. However, the main disadvantage of the phosphate glasses is poor chemical durability and water dissolution.

1.3 General Information of raw materials

Generally, glasses are either synthesized from pure components or minerals. Chemically pure chemicals usually use for low volume in any chemical laboratory because of costs; however, bulky commercial glasses use minerals as raw materials owing to saving production cost. The glass components can be classified into five categories used in production of specific glasses i.e. glassformer, flux, property modifier, colorant and fining agent. The identical compound can be categorized into different classes when used for different objective. For instance, aluminum oxide serves as a glassformer in aluminate glasses, but is considered a property modifier in most silicate glasses[1].

1.3.1 Glassformer

Glassformers are also called network formers or glass forming oxides. All type of glasses can contain one or more components. The most important component of any glass is glassformer and is assigned as primary name of the glass. For example, most of glass forming oxide is silica (SiO_2), such glass is called silicate glass. Silica, boric oxide (B_2O_3) and phosphoric oxide (P_2O_5) are commonly commercial glassformer. Moreover, a significant amount of boric oxide is also added into silica, the glass is termed borosilicate glass.

A large number of other compounds may act as glassformers under certain conditions, including germanium oxide (GeO_2), bismuth oxide (Bi_2O_3), aluminum oxide ($A1_2O_3$) and V_2O_5. Although the number of possible glass compositions is limitless, the importantly commercial glasses are based on silica as the glassformer.

1.3.2 Flux

Although silica is an excellent glass and is used in many applications, high melting temperature (>2,000˚C) for production of silicate glass is required. Addition of flux in silicate glasses can reduce melting temperature more than 400˚C. The ordinarily commercial fluxes are alkali oxides, particularly sodium oxide (Na_2O), potassium oxide (K_2O) and lead oxide (PbO). Soda (sodium oxide) and potash are extensively used for containers, windows and mirrors. Even though lead oxide is an excellent flux, glassmarkers have to concern regarding toxicity of lead oxide. The addition of flux leads to reduced cost of glass production; however, the large amount of alkali oxides in the glass matrix affect to worse effectiveness in desirable properties.

1.3.3 Property modifier

The presence of large concentrations of alkali oxides is degraded to the wide range of applications. Property modifiers including the alkaline earth and transition metal oxides are used to overcome degradation in properties of glasses, especially aluminum oxide (alumina). Use of property modifiers do not lead to excessively high processing temperatures if they are added lesser quantities due to these oxides partially act as melting temperature reducing oxides (flux). For phosphate glasses, boric oxides are used as property modifier that improve chemical durability of phosphate glasses.

1.3.4 Colorant

Colorants are used to control the color of the glasses. In most cases, colorants are metal oxides of either the 3d transition metals or the 4f rare earths (Fig. 4). Colorants are usually added in small quantities. Silver and gold are used to color glasses by the formation of colloid in the matrix of glass. Unintentional colorants in commercial glasses are iron oxides being impurity in sands. Nevertheless, the addition of *decolorants* is used for counteraction of the effect of the unintentional colorants. Some metal oxides are radioactive cause the colored glasses are decreased quality in most applications such as uranium oxides.

Common translucent glasses manufacturing is produced by sandblasting or acid etching of clear and transparent glasses. The translucence causes transmission of light through glasses decrease because of scattering of light[refa]. However, there is a production of translucent glasses i.e. addition of nanoparticles. The addition of ZnO nanoparticles in the matrix of glasses resulted in the borophosphate glasses more translucent. This zinc doped borophosphate glasses are translucently white.

Figure 1.4 The Chemistry of color glass

1.3.5 Fining agent

Fining agents are treated in very small quantities (< 1 wt%) into glass matrices to remove of bubbles from the molten mass. Fining agents include the arsenic oxides (As_2O_x), antimony oxides (Sb_2O_x), potassium nitrates (KNO_3), sodium nitrates ($NaNO_3$), sodium chloride ($NaCl$), fluorides such as CaF, NaF, and Sodium hexafluoroaluminate (Na_3AlF_6) and many sulfates. In case, glasses have only minor effects on the properties of the glasses[1]. However, prohibition of expends to produce glasses in commercial way is without the aid of fining agents. Commercially, mechanical fining process is adopted for removal content of bubbles in glass products.

1.4 General Information of Color

In explaining phenomenon of color in any material, we can divide into two categories i.e. absorbed color and complementary color. The absorbed color is a range of specific light that materials absorbed inside whereas remained light is released from them to surrounding is complementary color. For example, when visible light (containing a board spectrum in a range of 400-800 nm) pass through a material which absorbed yellow light (approximately 550 nm), the observed color is violet. Potassium permanganate

($KMnO_4$) is an example in this absorption. From Fig. 1.5, the complementary color is opposite sides of the color wheel. From reference wavelength of absorbed color and complementary color are given in Table 1.1

It is difficult to predict simply color at once from the absorption spectrum because some materials can absorb two or more absorption spectrum of intensities and energies. The predominant color is only observed after visible light is absorbed by materials.

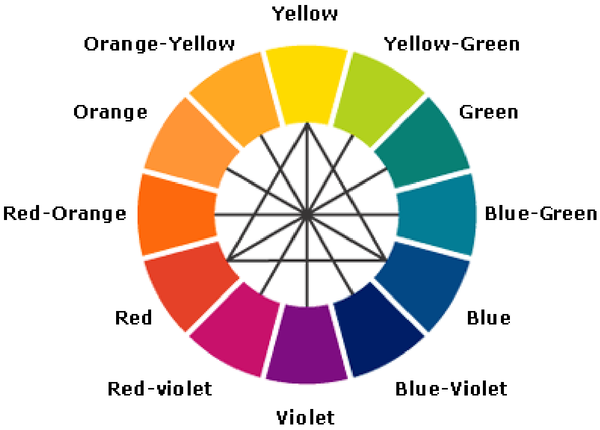


Figure 1.5 Complementary Color

Table 1.1 Visible light and complementary colors

Wavelength range (nm)	Color	Complementary color
<400	Ultraviolet	
400-450	Violet	Yellow
450-490	Blue	Orange
490-550	Green	Red
550-580	Yellow	Violet
580-650	Orange	Blue
650-700	Red	Green
>700	Infrared	

1.5 General Information of Photocatalysis

1.5.1 Band theory

http://nau.edu/cefns/labs/electron-microprobe/glg-510-class-notes/signals/

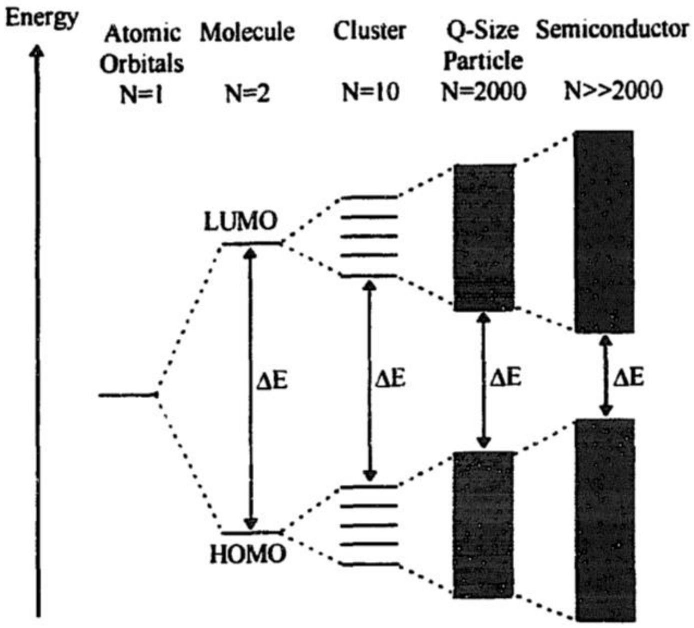


Figure 1.6 Electronic structure of semiconductor

1.5.2 Conductor, insulator and semiconductor

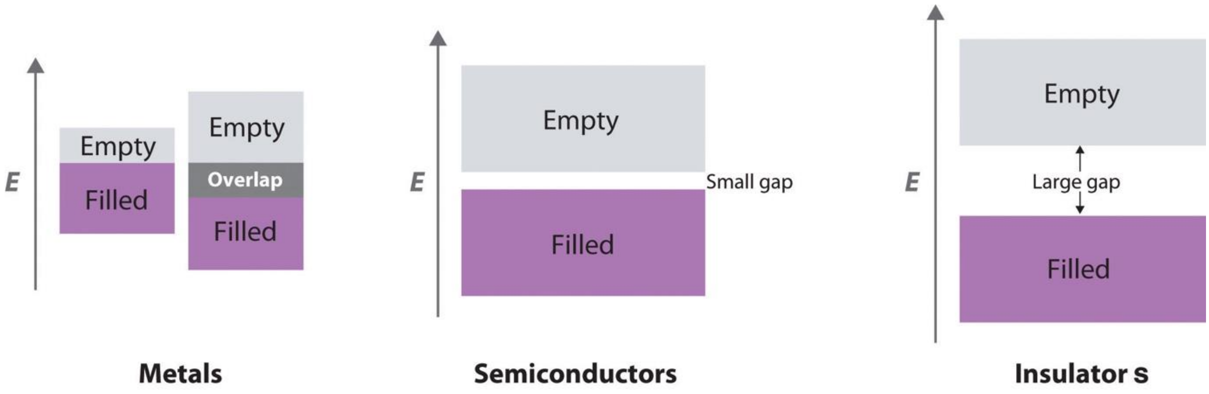


Figure 1.7 http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s16-06-bonding-in-metals-and-semicond.html

1.5.3 Photocatalyst

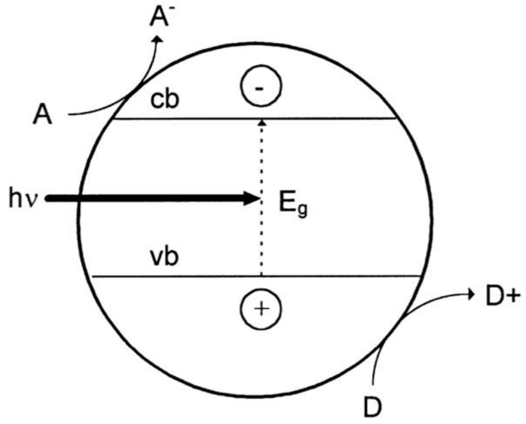


Figure 1.7 Simplified diagram of the semiconductor particle processing photocatalytic activity

1.6 General Information of Zinc Oxide

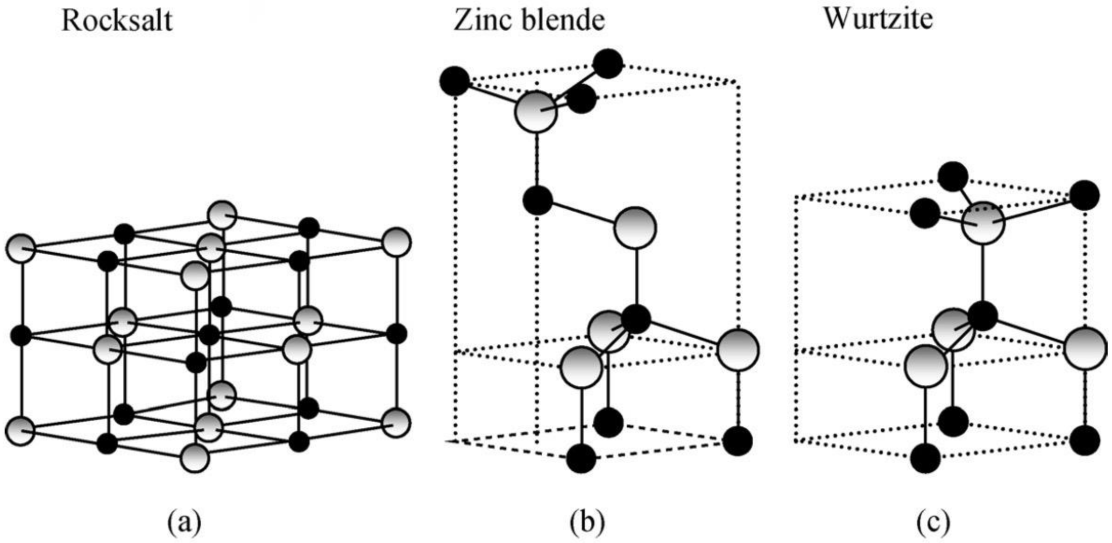


Figure 1.8 Stick-and-ball representation of ZnO crystal structure (a) Cubic rock-salt (b) cubic zinc blende and (c) hexagonal wurzite [○ : denote Zn and ●: denote O]

1.7 Literature Reviews

Commercial glasses mainly used as glassware in the kitchen and the laboratory are borosilicate glasses because of their desirable properties such as low thermal expansion coefficient, thermal shock resistance, high chemical durability and electrical resistivity. The well-known borosilicate glasses have been sold under the brand name Pyrex® and Duran®. However, the melting temperature of borosilicate glasses is quite high (above 1,500°C) so that high energy is consumed during the production. Alternative glassformer oxides have been studied such as phosphate, borate, and germinate glasses. Phosphate glasses have gained much attention in recent years. Phosphate glasses have been extensively utilized in many field because of their high thermal expansion coefficient, low melting and softening temperature, high electrical conductivity and particularly optical response. However, phosphate glasses have some restrictions to its practical utilization, for example, the pure phosphate network is hygroscopic and high thermal expansion coefficient. Water dissolution of phosphate glasses seem to be a major problem. Dissolution behavior of $ZnO–P_2O_5$ glasses in water has been studied in terms of chemical durability. It was found that ZnO could lower the water dissolution. That means the chemical durability of the phosphate glasses can be improved by ZnO addition. The stabilization of phosphate glasses has also been successively enhanced using B_2O_3 and ZnO, named borophosphate glass, because it can improve chemical durability, thermal shock resistance, higher glass transition temperatures and lower coefficients of thermal expansion. B_2O_3 is also glass forming oxides which is incorporated into phosphate glass systems and attain the desired physical and chemical properties. The 2-dimensional network of phosphate glasses formed by the connection of these tetrahedral at 3 corners has the same connectivity as that of vitreous boric oxide, although the building blocks are

4-cornered tetrahedral. As a result, ZnO and B_2O_3 composites in phosphate glasses are important topics for further activity studies of the broader applications of phosphate glasses.

Photocatalysts have gained much attention on utilizing in wastewater treatment and renewable energy. Most researches focus on seeking new effective photocatalyst powders, which need more processes e.g. coating, CVD to be suitable for using in a pilot scale. Use of photocatalyst powders in lab scale photocatalytic reaction is also quite complicated because it is necessary to separate powder and solution before evaluation of photocatalytic activity. To overcome this problem, immobilized photocatalyst on the substrate would be preferred.

To date, the addition of TiO_2 in a silicate glass-ceramics with photocatalytic ability has been studied. The network connectivity of silicate glasses and phosphate glasses is quite similar, so that phosphate glasses could have photocatalytic activity from the addition of semiconductor i.e. TiO_2. ZnO which can be use as photocatalyst for degradation of pollutants and also increases chemical durability. However, ZnO shows photoactivity under UV light, visible light activity of borophosphate glasses may be obtained by colorants. The colorants are used to control the color of the glasses. In most cases, colorants are metal oxides of either the 3d transition metals or the 4f rare earths[1].

Therefore, we proposed an idea to synthesize novel phosphate glasses to be use as photocatalysts by one step method, which can be developed further to be both glassware reactor and photocatalysts, simultaneously. As a result, complicated procedure of photoactivity test will be removed completely and easy to modified to suit pilot scale use visible light absorption of colored glasses would be providing more productive photoactivity. Metal oxide colorants have been used in our glasses for color control and photoactivity response. The chemical properties were investigated by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, IR and Raman spectroscopy and UV-Visible spectroscopy. To confirm photocatalytic activity of colored zinc borophosphate glasses, photocatalytic evaluation was performed by 3 alternative methods including to photo-oxidative reaction, photo-reductive reaction and radical polymerization. Moreover, antibacterial testing was also performed to confirm a contribution of ZnO.

2. Experimental procedure

The new colored zinc borophosphate glasses were synthesized in laboratory-scale in order to be a starting point for the development of commercial glasses. To acquire the specific properties of these colored zinc borophosphate glasses, it is necessary to characterize theses glasses and assess their photocatalytic activity. The experimental procedure for synthesis of new colored zinc borophosphate glasses was described following by:

2.1 Synthesis of colored zinc borophosphate glasses

Colored zinc borophosphate glasses were carried out by conventional melt-quenching method (Fig. 2.1) preparing from $NH_4H_2PO_4$, ZnO, $CaCO_3$ and H_3BO_3 as major compositions in the glasses (detailed in Table 2.1). The compositions of all colored zinc borophosphate glasses are in the mol% system of $39P_2O_5$–40ZnO–10CaO–$10B_2O_3$–$1MO_X$ where MO_X are metal oxide dopants, e.g., CuO, TiO_2, Cr_2O_3 and Mn_2O_3, except in the case of the translucent white zinc borophosphate glass—$30P_2O_5$–50ZnO–10CaO–$10B_2O_3$. The mixtures were calcined to remove volatile organic species at 400°C for 2 hours and were melted at 1,200°C for 4 hours. The molten mass was poured into a preheated graphite mold and suddenly followed by annealing at 550°C for 4 h to release internal stress. Colored zinc borophosphate glasses were assigned to be “colored ZBP” glasses.

Moreover, the colored ZBP glasses were specifically synthesized for proving effect of recombination center by the colorants. The compositions of colored ZBP glasses are in the mol% system of $29P_2O_5$–50ZnO–10CaO–$10B_2O_3$–$1MO_x$ where MO_x are TiO_2 and Cr_2O_3.

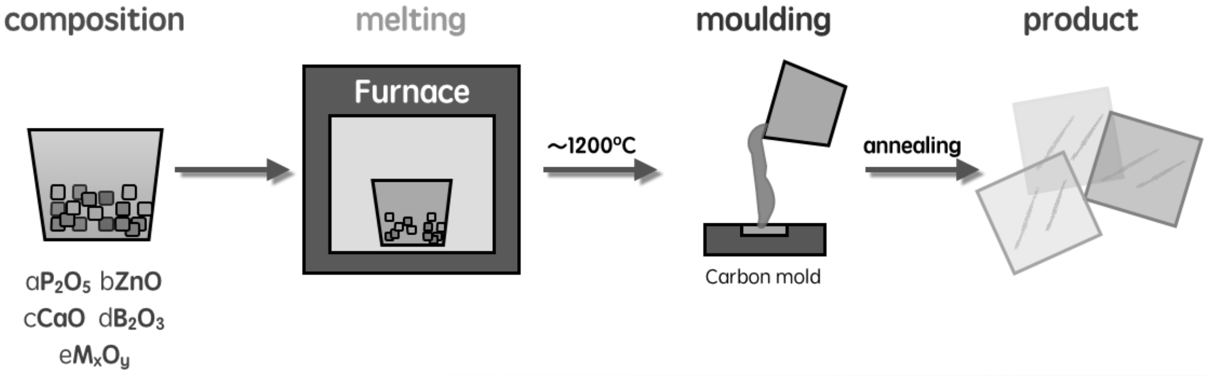


Figure 2.1 The schematic diagram of synthesis of colored zinc borophosphate glasses

Table 2.1 Chemicals used for synthesis of colored zinc borophosphate glasses

Chemicals	**Formula**	**Molecular weight (g/mol)**	**Company**	**Oxide***
Major compositions in glass				
Ammonium dihydrogen phosphate	$NH_4H_2PO_4$			P_2O_5
Zinc oxide	ZnO		Sigma Aldrich, USA	ZnO
Calcium carbonate	$CaCO_3$			CaO
Boric acid	H_3BO_3		Merck	B_2O_3
Colorants				
Copper(II) oxide	CuO			CuO
Titanium(IV) oxide	TiO_2			TiO_2
Chromium(III) oxide	Cr_2O_3			Cr_2O_3
Manganese(III) oxide	Mn_2O_3			Mn_2O_3

* Oxide compounds after calcination of entire compositions

2.2 Characterization of colored zinc borophosphate glasses

2.2.1 X-ray diffraction (XRD)

The polished colored ZBP glasses and ZBP glass powder were investigated crystal structure by Rigaku™ Miniflex 600 X-Ray Diffractometer (Japan) using Cu Kα radiation. The diffraction angle was ranged from 10^{o} (2θ) to 80^{o} (2θ) with step width of 0.05^{o} (2θ).

2.2.2 Scanning electron microscopy (SEM)

Morphology of colored ZBP glass was studied using JEOL JSM-6335F Field Emission Scanning Electron Microscope (Japan) with 15.0 kV accelerating voltages. Samples for scanning electron microscopy analysis were polished surface to show crystalline solids that embedded on surface of glasses.

2.2.3 Transmission electron microscopy (TEM)

The colored ZBP glasses were determined crystallinity within the matrix of glasses. The samples were prepared by grinding in order to scrap the colored zinc borophosphate glasses into very thin pieces and electrons could pass through samples. The grinded glass scraps were floated on ethanol and then were sieved by Cu-grid.

2.2.4 Raman spectroscopy

Functional group vibration of colored ZBP glasses was measured by DXR™ Raman microscope at room temperature with an excitation wavelength of 780 nm. The Raman spectrums collections were measured on bulky samples in 3 positions per a sample to acquire average values.

2.2.5 Infrared spectroscopy

Functional group vibration of colored ZBP glasses was measured by DXR™ Raman microscope at room temperature with an excitation wavelength of 780 nm.

2.3 Evaluation of photocatalytic activity

2.3.1 Photo-oxidative reaction

Photo-oxidation of methyl orange was observed by color bleaching of a 1.0×10^{5} M methyl orange solution. Each sample was added to 9.00 ml methyl orange solution and was kept in the dark for 12 h to ensure the complete adsorption of methyl orange on to the glass surface. As photo-oxidation reactions occur slowly and glasses generally have low photocatalytic activities, 1.00 ml of hydrogen peroxide (H_2O_2) was also added to the solution to accelerate the photobleaching of methyl orange for comparison. The solutions were irradiated with UVA light-emitting diodes and white light-emitting diodes (LEDs) for studying the behavior in the visible range. Aliquots were removed every half hour, for the UV-irradiated samples, or hour, for the visible-irradiated samples, to measure the absorbance of methyl orange by UV-Visible spectroscopy.

2.3.2 Photo-reductive reaction

Resazurin (Rz) ink tests were used to investigate reduction photocatalytic ability of the glasses. The Rz ink was prepared by dissolving 0.15 g hydroxyethyl cellulose (HEC) in 0.85 ml distilled water, followed by 1.0 g glycerol as the sacrificial electron donor. The viscous solution was stored in a refrigerator prior to use. The Rz ink was deposited on the ZBP glass surfaces. The deposited samples were irradiated by 365 nm UVA light-emitting diodes (LEDs) for 20 minutes and white LEDs for 30 minutes. The color of the Rz ink would change from blue (resazurin) to pink (resorufin) if the samples exhibited photocatalytic properties.

2.3.3 Antibacterial activity determination

The antibacterial activity of the colored ZBP glasses were observed by standard methods using *S. aureus* (Gram-positive bacterium) and *E. coli* (Gram-negative bacterium) on nutrient agar (NA) plates. The colored ZBP glasses were sterilized at 110ºC prior to antibacterial testing. Each bacterial suspension, which was adjusted to a turbidity of 0.5 McFarland, was swabbed on an NA plate using a sterilized cotton bud. Next, the samples were placed on the surfaces of NA covered with a tested bacterial strain. NA plates were incubated at room temperature (27±1ºC) for 24 h. Antibacterial activity was investigated by measuring the zone of inhibition (clear zone). The positive results were demonstrated as clear zones resulting from bacterial growth inhibition by the semiconducting materials.

2.3.4 Radical polymerization

Acrylamide was used as a monomer and N,N'-methylene-bisacrylamide (NMBA) was use as a cross-linking agent in the formation of polyacrylamide. Oxygen from air pump was used as sacrificial electron acceptor and glycerol was used as a sacrificial electron donor to accelerate gelation of the formed polyacrylamide. Polyacrylamide was prepared by dissolving of 2.0 g acrylamide, 0.05 g NMBA and 2.5 g glycerol in 5.0 ml distilled water and stirring until the solution became clear. The colored zinc borophosphate glasses were added to the solutions, followed by irradiation by UVA LEDs.

3. Results and Discussion

Selected compositions of ZnO, B_2O_3 and CaO of all synthesized colored ZBP glasses showed very low or no water dissolution compared to conventional or pure phosphate glasses. Transparent colored ZBP glasses had compositions of $39P_2O_5$–$40ZnO$–$10CaO$–$10B_2O_3$–$1MO_x$, where MO_x are metal oxide dopants. The transparent glasses were blue, purple, dark green and yellow due to addition of CuO, TiO_2, Cr_2O_3 and Mn_2O_3, respectively. The white translucent zinc borophosphate glass was obtained with higher ZnO concentrations in the composition of $30P_2O_5$–$50ZnO$–$10CaO$– $10B_2O_3$. Increase of ZnO concentration has been reported as a key to making glasses more translucent (Fig. 3.1).

Fig. 3.2 shows the XRD patterns of the synthesized colored ZBP glasses in comparison with microscope glass slide (Thermo Scientific, SiO_2 72.20%, MgO 4.30%, Na_2O 14.30%, Al_2O_3 1.20%, K_2O 1.20%, Fe_2O_3 0.03%, CaO 6.40%, SO_3 0.30%), which is at, uniform and excellent transmission. The resulting XRD patterns of all synthesized ZBP glasses and the microscope glass slide are broad peaks due to the amorphous nature of the glasses, demonstrating the formation of disordered glass. In addition to making glasses more translucent, increasing the ZnO content of the glasses resulted in the peak being shifted to higher diffraction angle (2θ) (Fig. 2b left and right). Nevertheless, no phases of the crystalline solid could be detected by XRD as the broad peak of the amorphous character was dominant.

It is difficult to obtained crystal system of crystalline particle in the glass piece by XRD. We have tried to figure out about this doubt by grinding the glass before characterization with XRD. Unfortunately, there was no any phase can be detected, sharper peak was just obtained as can be seen in Fig 3.2 (right). However, TEM image showed crystalline particles of ZnO with d-spacing close to hexagonal Wurtzite structure.

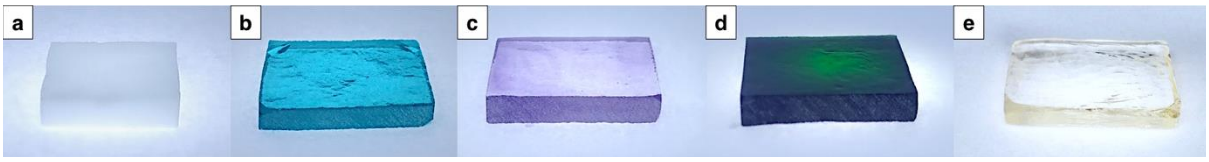


Figure 3.1. Macroscopic images of the synthesized colored ZBP glasses (a) white ZBP (b) blue ZBP, (c) purple ZBP (d) green ZBP and (e) yellow ZBP.

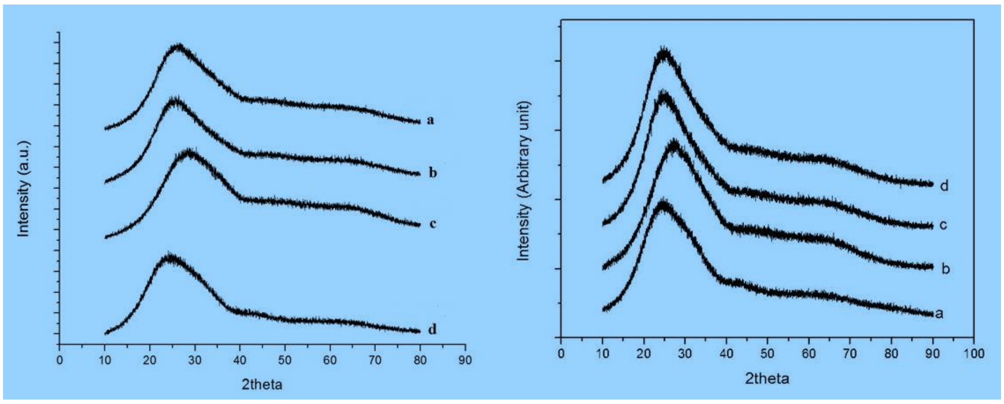


Figure 3.2. X-ray diffraction patterns of (a) microscope glass slide (b) white ZBP (c) purple ZBP and (d) green ZBP and (e) yellow ZBP glasses (left: before grinding, right: after grinding).

UV-Visible Spectroscopy

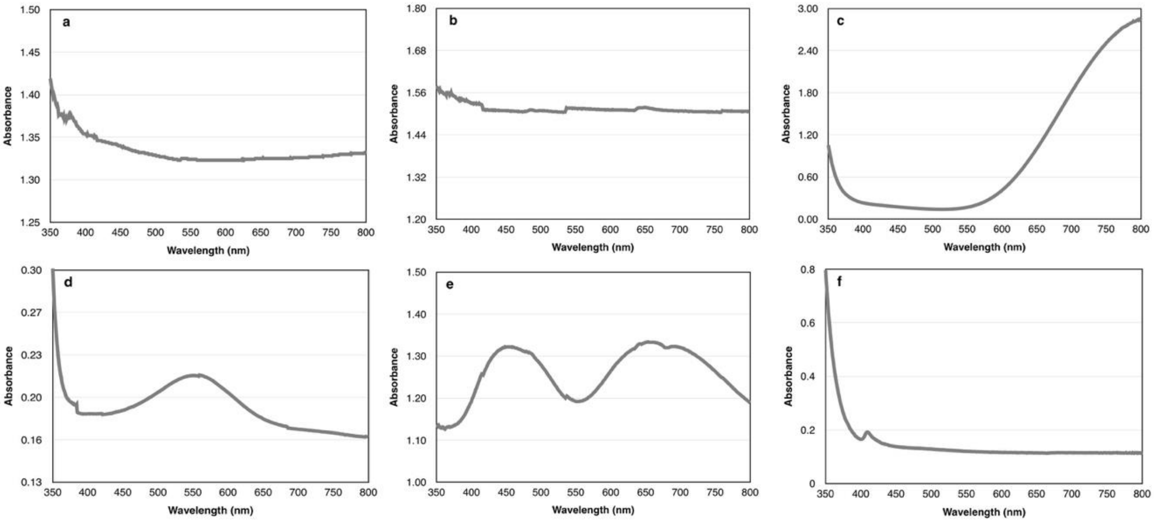


Figure 3.3. UV-Visible spectrums of the (a) microscope glass slide and the synthesized colored zinc borophosphate glasses: (b) white ZBP, (c) blue ZBP, (d) purple ZBP, (e) green ZBP and (f) yellow ZBP.

UV-visible absorption spectra of synthesized ZBP glasses and a microscope glass slide are shown in Fig. 3.3. The low absorption of the microscope glass slide correlated with the transparency and colorlessness of the sample (Fig. 3.3a). White ZBP glass exhibited no absorption of visible light, which corresponds to a white color; and a higher absorption baseline compared to the microscope glass slide suggests absorption and light scattering effects due to ZnO (Fig. 3.3b). Blue ZBP glass did not absorb light in the region of 400-600 nm Purple ZBP glass did not absorb light in the 380–400 nm region and above 700 nm characteristic of purple colored materials (Fig. 3.3d). Purple ZBP tended to absorb some UV and visible light as absorption peaks are observed at approximately 350 nm and 500–600 nm. Absorption spectrum of purple ZBP glass corresponded to the $^2T_{2g}$ to ^2E_g d–d transition of Ti^{3+} that might occur during melting. Whereas green ZBP had distinct absorption peaks in the regions of 400–500 nm and 600–800 nm (Fig. 3e). The two broad absorption peaks may be assigned to $^4A_{2g}$ to $^4T_{1g}$ and $^4A_{2g}$ to $^4T_{2g}$ d–d transition of Cr^{3+}. However, Cr^{3+} and Ti^{3+} cannot be confirmed by XPS because of a small amount addition. Yellow ZBP glass Each colored ZBP glass exhibited characteristic in the visible light region, with some UV absorption as well, which are favorable characteristics for photocatalytic applications.

Scanning electron microscopy

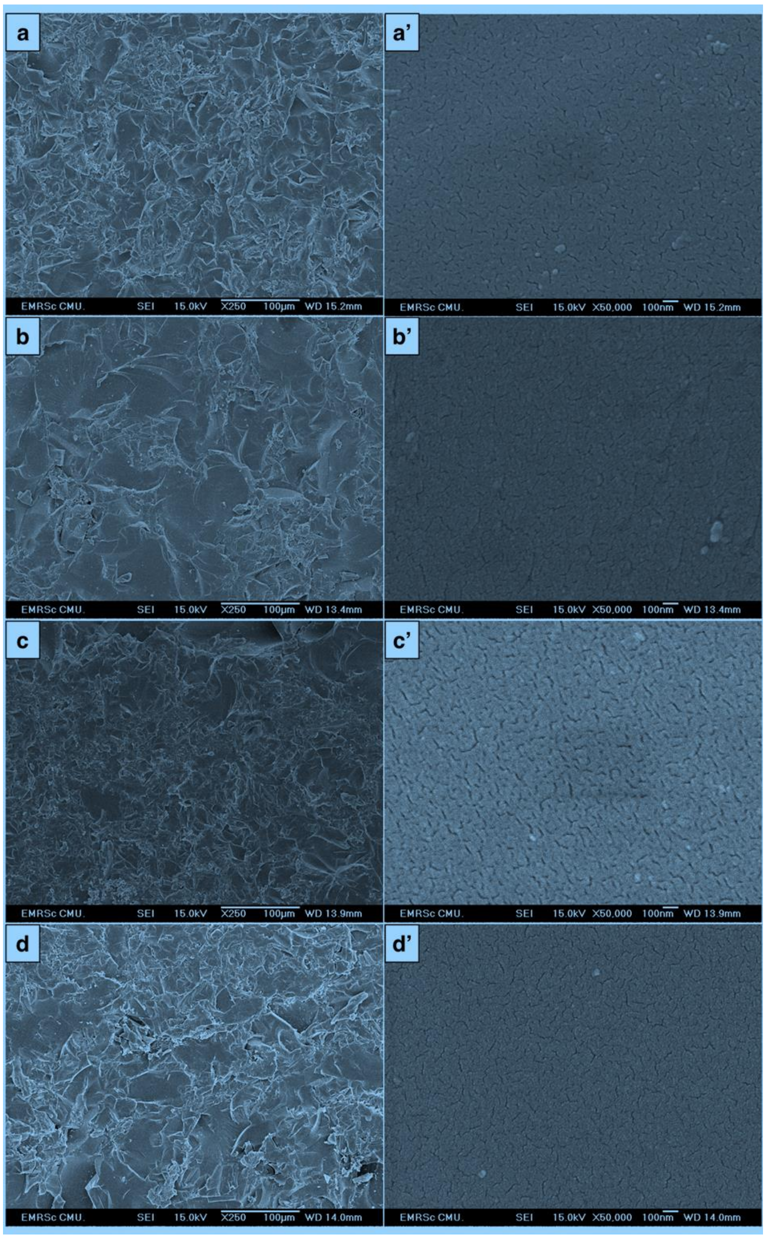


Figure 3.4. SEM images of (a) microscope glass slide and the synthesized colored zinc borophosphate glasses: (b) white ZBP, (c) blue ZBP, (d) purple ZBP, (e) green ZBP and (f) yellow ZBP in magnification of x250 (a, b, c and d) and x50,000 (a', b', c' and d')

Roughness of the glass surfaces was observed in the SEM images of all of the glasses, despite their surfaces being polished (Fig. 3.4a–e). The differences in morphology between the microscope glass slide and the colored ZBP glasses was not significantly observed. However, some embedded particles on the synthesized ZBP glass surfaces could be clearly observed. The SEM images may indicate that the colored ZBP glasses are incompletely amorphous. Narrow pores, approximately 5 nm, at the glass surface could be observed for all glasses, into which some molecules may enter and facilitate the catalytic activity of the glasses (Fig. 3.5).

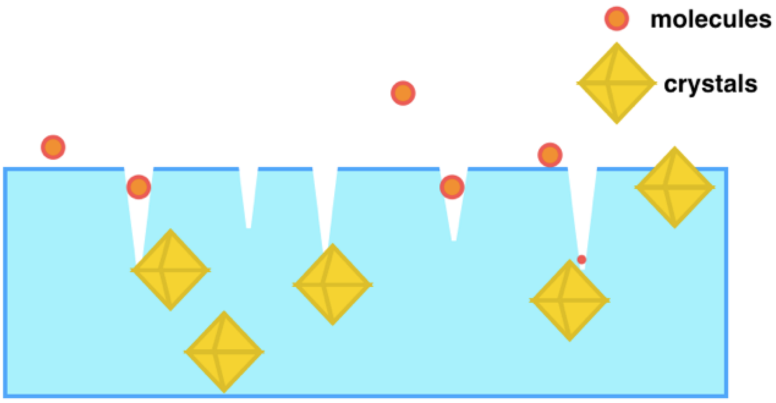


Figure 3.5. Proposed mechanism for entering of some molecules in the narrow pores of the synthesized colored ZBP glasses

Transmission electron microscopy

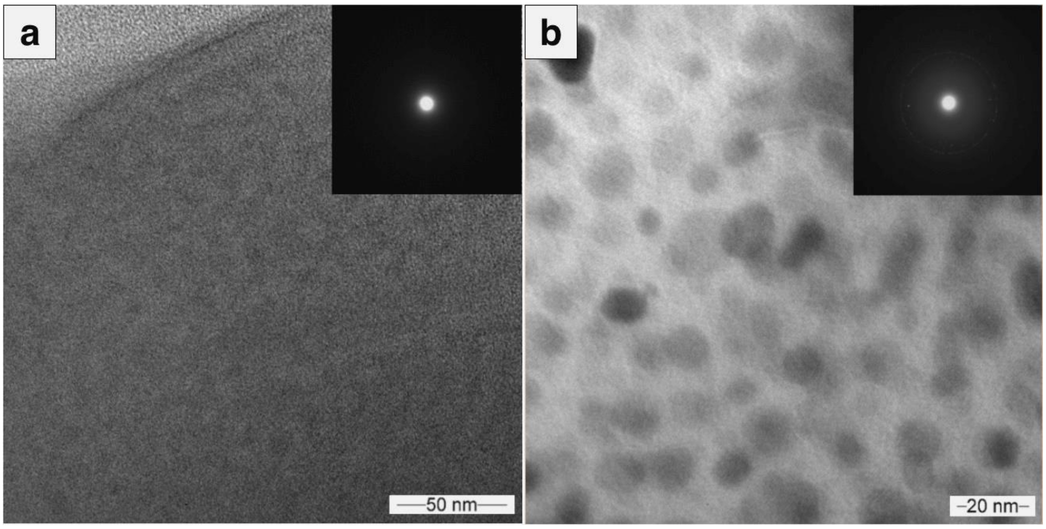
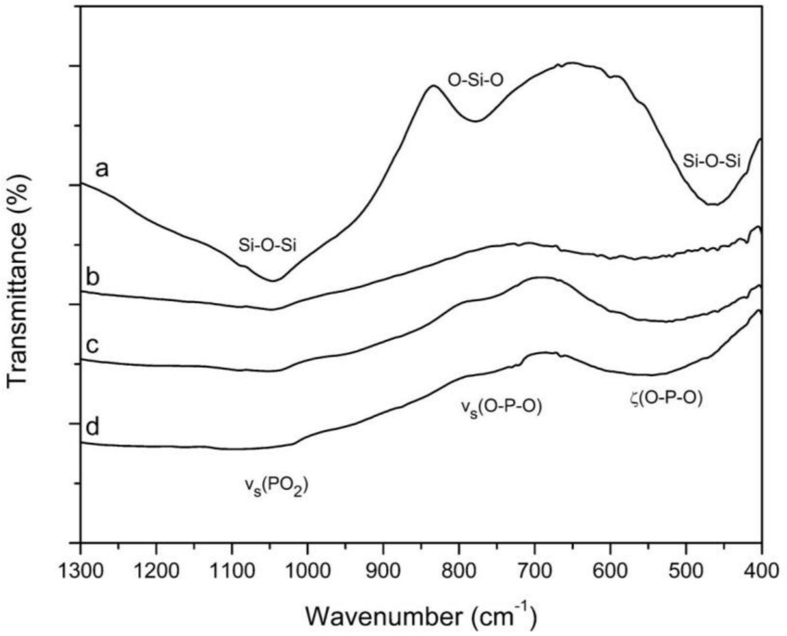


Figure 3.6. TEM images of (a) microscope glass slide and (b) white ZBP

The amorphous nature of the microscope glass slides was verified by HRTEM along with a diffraction pattern showing the absence of any crystals, confirming the non-crystallinity of the microscope glass slides (Fig. 3.6a). Surprisingly, the existence of monodisperse crystalline solids inside the glasses could be observed by HRTEM images and diffraction patterns (Fig. 3.6b) despite this process being a one-step method and not a glass- ceramic method. White ZBP revealed embedded nanoparticles of ZnO, of an approximate size of 10–15 nm as calculated by the diffraction pattern, within the glasses. The incorporation of crystalline solids in the colored ZBP glasses would be expected to play a key role in the catalytic properties of these materials.

In general, rarely crystalline particles will be found in the glass synthesized by one pot melt-quenching technique and glass matrix always showed amorphous character. XRD also showed amorphous in ZBP glasses, however, TEM images found some particles corresponding to ZnO, probably because ZnO is the main component of the ZBP glasses and XPS analysis showed Zn peak at the surface. However, no other particle can be detected by TEM, XPS and XRD, probably because of very small amount of them. Therefore, ZnO in the ZBP glasses should be a key feature of photoactivity is this work.

IR spectroscopy



IR spectra of the (a) microscope glass slide and the synthesized colored ZBP glasses: (b) white ZBP, (c) purple ZBP and (d) green ZBP.

Raman spectroscopy

The microscope glass slides exhibited a fluorescent broad band at approximately 1460 cm^{-1} (Fig. 3.7a) because of the fluorescence interference. Interpretation of the green ZBP Raman spectra was difficult due to this fluorescence interference, which exhibited a very strong band near 1800 cm^{-1} (Fig. 3.7d). However, the Raman spectra of the other colored ZBP glasses, such as the white and purple ZBPs, dis- played bands at approximately 350 cm^{-1} and 760 cm^{-1} due to O–P–O bending vibrations and the P–O–P symmetrical stretching vibration of the bridging oxygen atoms attached neighboring ^2Q and ^1Q structural units, respectively (Fig. 3.7b and c). Indeed, bending modes usually appear below 500 cm^{-1} and the purple ZBP was partly affected by the fluorescence, resulting in negligible detailed bands. The bands at 1240 cm^{-1} and 1390 cm^{-1} are due to symmetric stretching vibrations of P–O bonds. Bands at 1220 cm^{-1} and 1378 cm^{-1} of the white ZBP are also due to P–O symmetric stretching vibrations. The band at 560 cm^{-1} was assigned to the bending and torsional vibrations. However, the ZBP glasses exhibited broad bands indicating that BO_x was incorporated into the phosphate network and resulting in increased water dissolution tolerance. The presence of a broad band symmetric stretching vibration of ^1Q and ^0Q at approximately 1020 cm^{-1} (may prove why the white ZBP could over- come water dissolution. This broad band may be the result of two bands overlapping, i.e., the symmetric stretching vibration of ^1Q at 970 cm ^{1} and ^0Q at 1046 cm^{-1}. The incorporation of B_2O_3 was confirmed by the symmetric stretching vibration of the B–O–P bonds at approximately 660 cm^{-1} (Fig. 3.7b). Moreover, an increase in ZnO content also affected the increase of ^1Q and ^0Q. The ^1Q and ^0Q species could not be observed for green ZBP due to the disturbance from the fluorescence.

IR spectra of microscope glass slide and colored ZBP glasses are shown in Fig. 3.8. IR spectrum of microscope glass slide, which consists of silicate network former, showed Si–O vibra- tional bands (Fig. 3.8a). The colored ZBP glasses (Fig. 3.8b–d) showed IR spectra at 1050–1100 cm^{-1} of the symmetrical stretching vibration PO_2 or phosphorous non-bridging oxygen. Whereas bands around 720 cm^{-1} are assigned to symmetric stretching vibrations P–O–P of bridging oxygen atoms. The broad band at 500–550 cm^{-1} are assigned to bending vibrations of P–O–P or may due to deformation mode of PO group. However, white ZBP (Fig. 3.8b) exhibited a broader band compared to purple ZBP and green ZBP (Fig. 3.8c and d), probably because a high amount of ZnO contribute the formation of bridging oxygen atoms attached neighboring ^2Q and also Zn ion act as a network former.

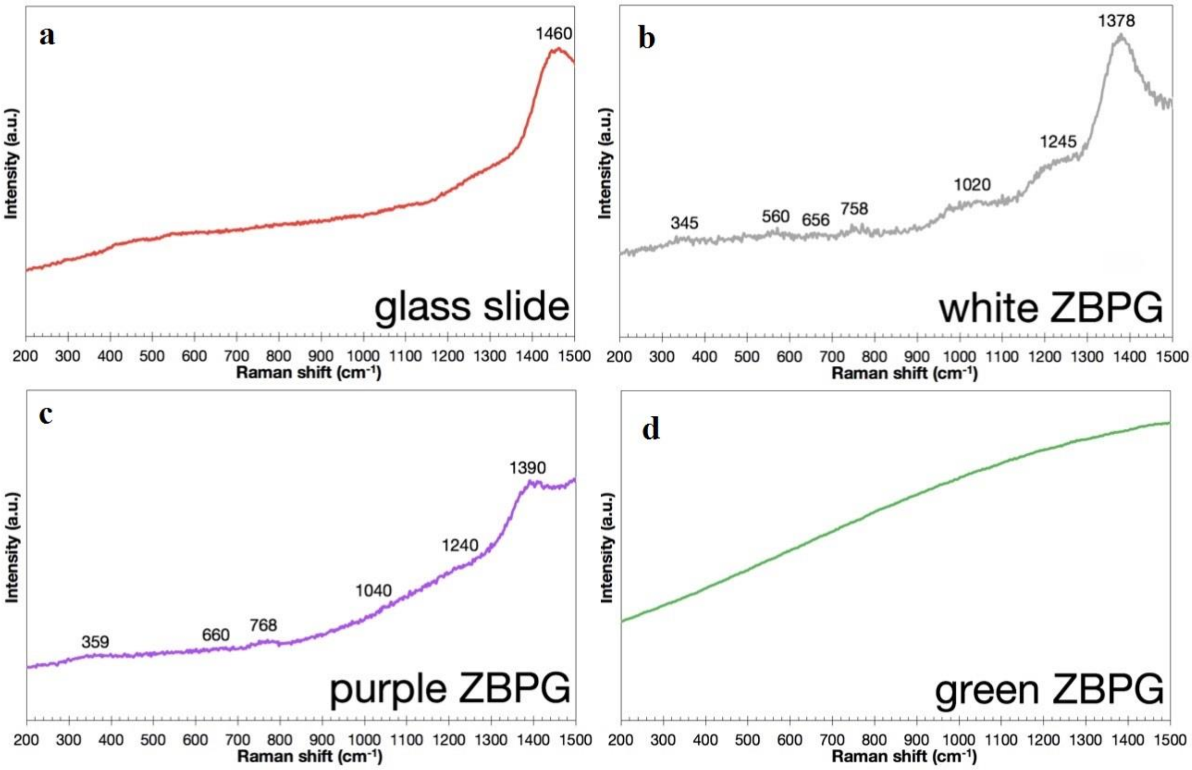


Figure 3.7. Individual Raman spectrums of the glass slide (a) and the synthesized colored ZBP glasses: (b) white ZBP, (c) purple ZBP, (d) green ZBP

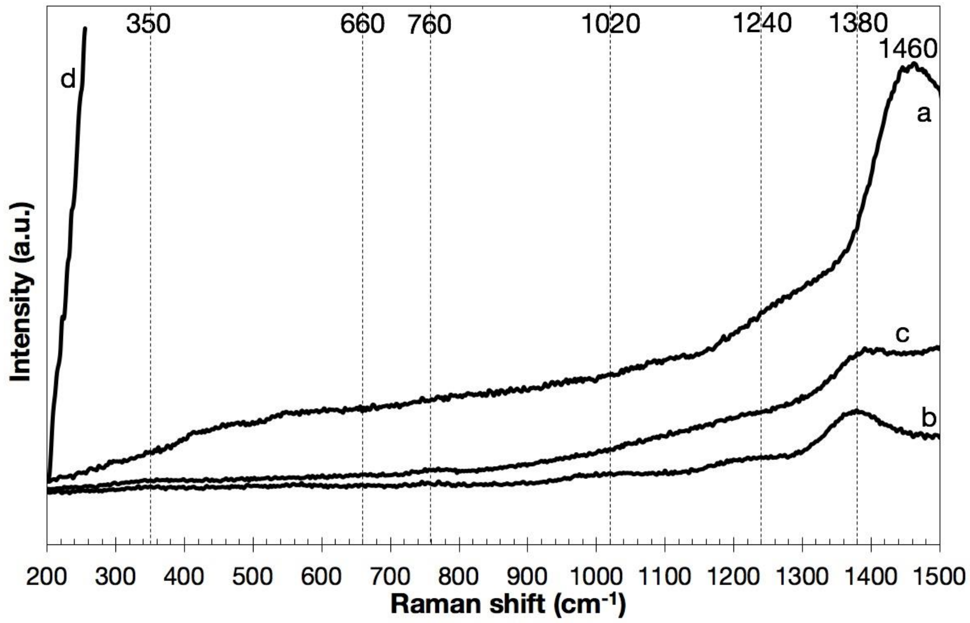


Figure 3.8. Raman spectrums of the (a) glass slide and the synthesized colored ZBP glasses: (b) white ZBP, (c) purple ZBP and (d) green ZBP

Photo-oxidative reaction

Photooxidation reactions of the colored ZBP glasses were per- formed by photobleaching methyl orange (MO) dye. As ZnO is a UV active semiconductor and additional metal oxide colorants were added to the glass matrix, the photoactivity of these glasses were evaluated under both UV and visible light. The photo- activity of glasses with added TiO_2 has been reported and compared between TiO_2 coated glass (amorphous solid) and TiO_2 embedded into the glass as prepared by a glass-ceramic method (crystalline solid). It was found that the crystallinity of TiO_2 in the glass-ceramics significantly enhanced the photocatalytic ability in the degradation of methylene blue compared to TiO_2 coated glass. However, the colored ZBP glasses are different from the glass-ceramics in both preparation and connection to the semiconductor in the matrix of the glass. In general, the photoactivity of the immobilized semi- conductor is slower compared to the powders due to their lower surface area. As a result, H_2O_2 addition was also tested for the colored ZBP glasses, which contain nanoparticles within the glass matrix by one pot synthesis. These colored ZBP glasses may exhibit lower photocatalytic activity due to their very low surface area and lack of semiconductor particles at the surface. The presence of H_2O_2 was ascribed to increased hydroxyl radicals.

The photobleaching of MO in the presence of H_2O_2 under dark conditions was negligible (Fig. 3.9a), confirming that H_2O_2 had no direct effect. Photobleaching of MO using the colored ZBP glasses was better than the control MO and the microscope glass slide experiments. The control MO experiment was per- formed in H_2O_2 solution under UV irradiation without any catalysts present. Microscope glass slides were used to confirm that the photocatalytic activity only occurred using the colored ZBP glasses and that the activity was not due to the commercial glass or the decomposition of H_2O_2 on the rough surface of glass. A slight decrease in MO concentration was observed in the control MO under UV light, as well as in the microscope glass slide experiment due to the hydroxyl radicals generated by dissociation of H_2O_2 under UV (Fig. 3.9b and c). Purple ZBP and green ZBP exhibited similar activities and could accelerate the degradation of MO as the photobleaching activity observed was significantly higher compared to the controls (Fig. 9d and e). It can be confirmed that the degradation of MO was promoted by the photocatalytic properties of purple ZBP and green ZBP, however, white ZBP had the best photocatalytic activity of all of the glasses in this work. These results correlated to the HRTEM that found ZnO nanoparticles in the colored ZBP glasses, and the photoactivity increased with increased ZnO concentration (white ZBP [purple, green ZBP). It should be noted that the photoactivity in the presence of H_2O_2 under UV light was greater than in the absence of H_2O_2.

It is also reassuring that the photobleaching of MO obtained via photocatalytic activity of ZBP glasses, not due to H_2O_2 decomposition, the photobleaching of MO under UV without the addition of H_2O_2 was evaluated. It was found that the degradation of MO was observed even without any H_2O_2 addition and the white ZBP glass had higher activity compared to the green ZBP and purple ZBP glass. However, the photoactivity of the ZBP glasses without H_2O_2 was slow.

The photobleaching of MO in the presence of H_2O_2 under visible light was also performed, however, the control experiments showed negative results. No degradation of MO was observed, but the MO concentration increased upon irradiation with visible light. We ascribe this result to the evaporation of the MO solution due to the heat from the white LED lamp. This negative result can be proved as the concentration of MO in the dark control was kept at room temperature and was constant because there wasn't any heat from the LED lamp. The MO concentration tested using photoactive purple ZBP and green ZBP could overcome complications due to evaporation of the MO aqueous solution, resulting in a slight decrease in MO concentration. The white ZBP still exhibited the best photo- catalytic activity. The trend of the photoactivity under visible light is similar to the photoactivity under UV light and depends on the concentration of ZnO. It can be confirmed that the colored ZBP glasses exhibit photoactivity under both UV and visible light, although it was hard to observe the visible light results as ZnO is less active under visible light, and the evaporation of the solution due to the heat from the LED lamps.

However, the coloring agents may act as a recombination centers in the glass, to be absolutely sure that ZnO is the key feature of the photoactivity, not due to the recombination center of the coloring agent, new composition of ZBP glasses were fabricated by fixing the ZnO concentration. The white, green and purple ZBP glasses with new composition (30 x) P_2O_5–50ZnO–10CaO–10B_2O_3–xMO_x, where xMO_x are 1Cr_2O_3 and 1TiO_2, respectively, were used for coloring agent effect investigation. The photobleaching of MO under UV in the presence H_2O_2 addition were similar among the three ZBP glasses (S3). As a result, it can be confirmed that the effect of coloring agent to be recombination centers in the glasses is negligible and ZnO is a key factor for the photoactivity.

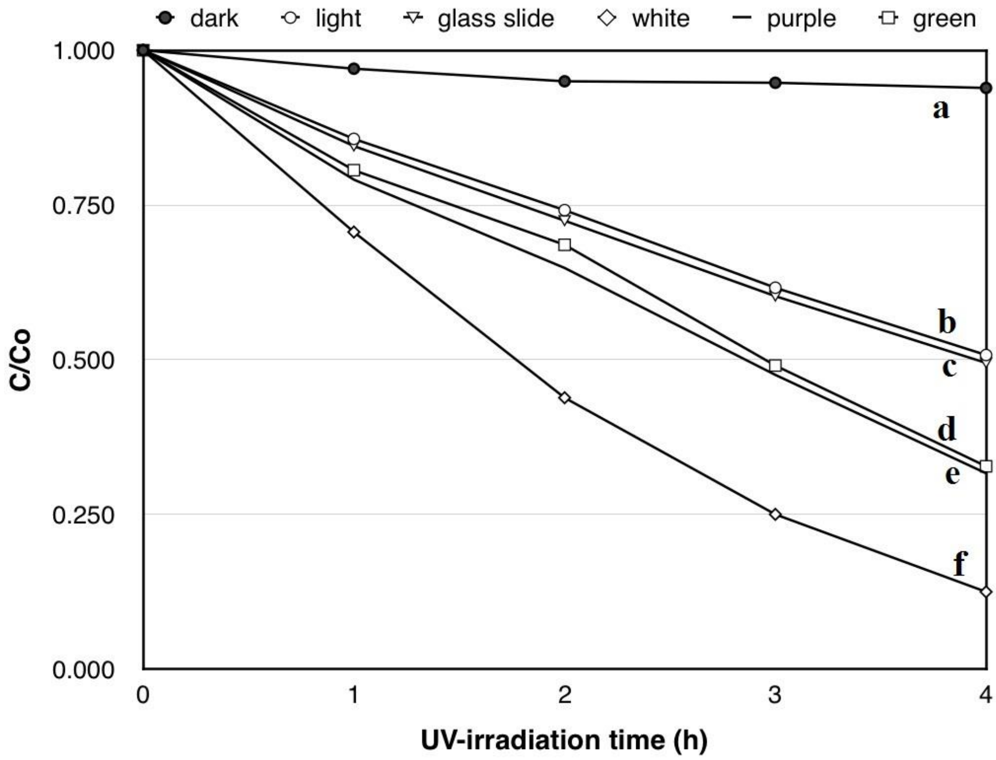


Figure 3.9. Photobleaching of methyl orange in the presence of H_2O_2 with UV irradiation under various conditions: (a) dark, (b) light, (c) microscope glass slide + light, (d) green ZBP + light, (e) purple + light and (f) white ZBP + light

The photobleaching of MO in this work have been carefully investigated as can be seen in Fig 3.9. It was found that the MO concentration decrease slightly under decomposition of H_2O_2 under UV and no effect of rough surface of glass to H_2O_2 decomposition because MO concentration decrease in the same amount for the control experiment (H_2O_2+UV+MO) and the microscope glass slide experiment (H_2O_2+UV+microscope glass slide+MO) as shown in Fig. 3.9b,c (which no ZBP glasses were tested). Moreover, it is clearly seen that MO concentration decrease significantly faster when there are ZBP glasses as the photocatalysts (Fig.3.9d, e, f).

Photoactivity without H_2O_2 under UV

The photoactivity after equilibrium adsorption have been done under UV without H_2O_2 and found that the trend of photoactivity is still similar to H_2O_2 addition, which is the white ZBP glass showed higher activity compared to purple and green. However, the photoactivity is significantly slower than using H_2O_2.

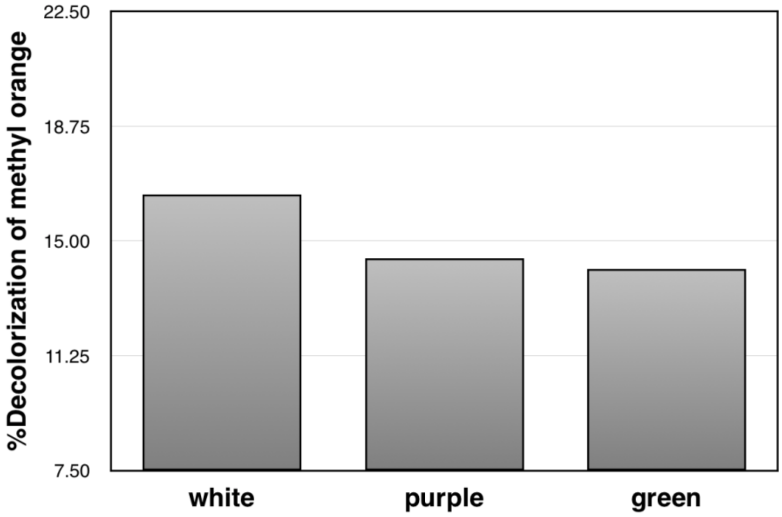


Figure 3.10 : Photobleaching of methyl orange under UV irradiation for 24 hours, without H_2O_2 addition

Photoactivity with H_2O_2 under visible

The photoactivity after equilibrium adsorption have been done under visible light (white LED bulb) with H_2O_2, which is no decomposition of H_2O_2. It was found that the trend of photoactivity is similar to H_2O_2 addition under UV, which is the white ZBP glass showed higher activity compared to purple and green. However, the photoactivity is slighly slower than UV irradiation.

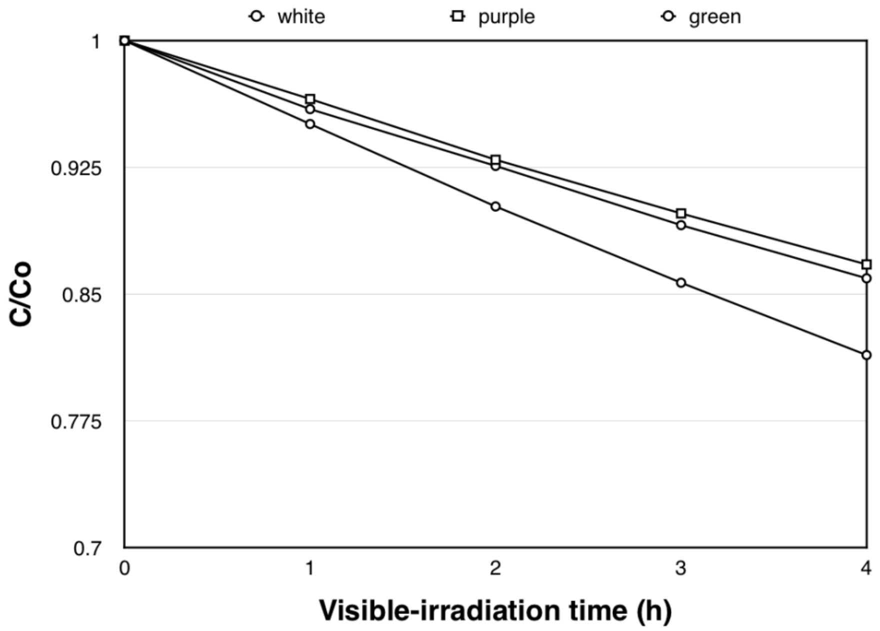
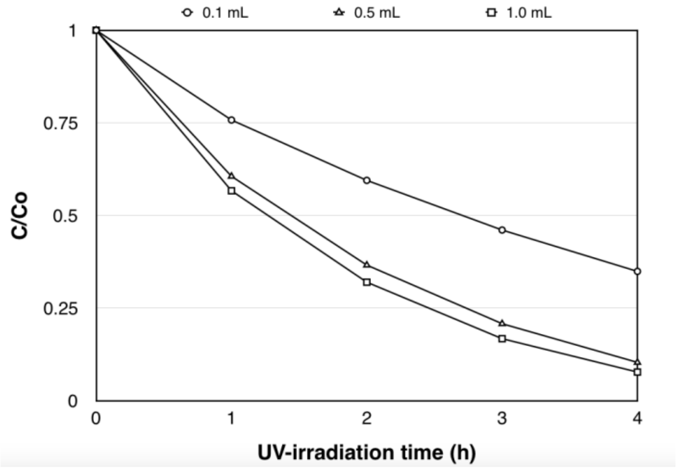


Figure 3.11 : Photobleaching of methyl orange in the presence of H_2O_2 under visible light irradiation

Photoactivity under UV with various amount of H_2O_2

It was found that various amount of H_2O_2 affected to the photobleaching of MO confirming that photocatalytic activity of ZBP glass responsible for the photobleaching of MO.



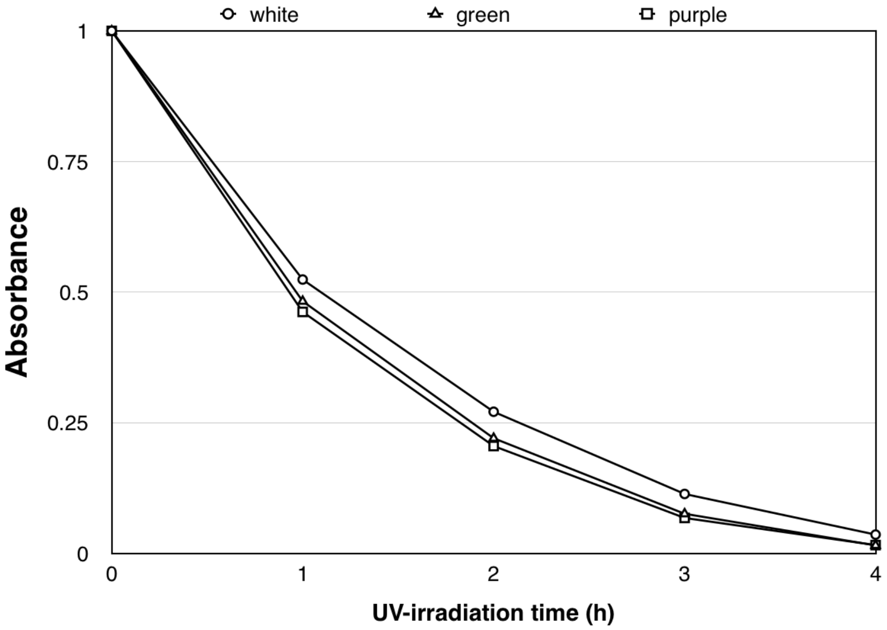


Figure 3.12 : Photobleaching of methyl orange in the presence of H_2O_2 with UV irradiation of new composition coloured ZBP glasses (50 mol% ZnO concentration)

Our results showed that photoactivity, antibacteria and polymerization of white ZBP > green ~ purple ZBP so that ZnO content would be a key role for activities. An effect of recombination center from colorant might be negligible because activities increase with increasing ZnO content.

However, to answer the question from referee, we have synthesized the new white, green and purple ZBP with same amount of ZnO and investigated their photooxidation activities. It was found that the photobleaching of MO of the new colored ZBP glasses is similar. Purple and green ZBP has a little bit higher photoactivity than white ZBP probably because of actual weigh of ZnO is slightly different : white = 9.243g ZnO, green = 9.298g ZnO, purple = 9.349 g ZnO.

Photo-reductive reaction

In general, the main drawback of organic dye photoreduction is the slow rate that was observed. Photocatalytic activity ink indicators were developed for rapidly assessing the photo- catalytic activity via photoreducing reaction. The ink was degraded in a few minutes due to the presence of a sacrificial electron donor (SED) donating electrons to generated hole in the valence band of the semiconductor. This results in the suppression of the combining of electron–hole pairs in semiconductors.

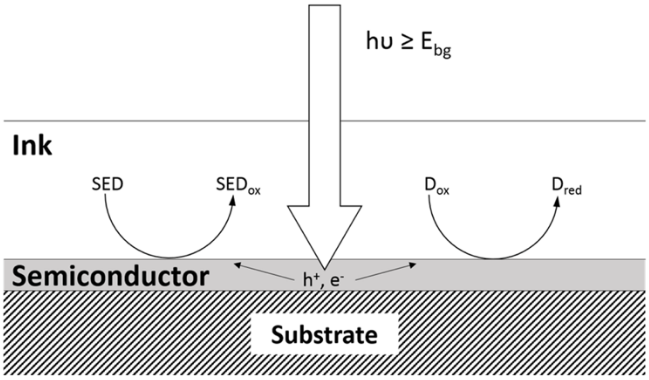


Figure 3.12 Proposed reaction scheme of photoreductive activity of zinc borophosphate glasses

Resazurin (Rz) ink was prepared in the presence of glycerol, which acts as the sacrificial electron donor. The results of the photoreduction reaction of the colored ZBP glasses are tabulated in Table 1. The control sample, Rz ink under dark and light, were used to ensure that the Rz ink was stable under UV irradiation. After the Rz ink was exposed to UV light, the color of the Rz ink was still constant which demonstrated the stability of the ink. No color change of Rz ink deposited onto a microscope glass slide under UV irradiation was observed. All of the colored ZBP glasses could convert the color of Rz ink from blue to pink. This finding may confirm that the photocatalytic reducing activity only occurred due to the ZnO nanoparticles embedded within the colored ZBP glasses. The microscope glass slide was unable to change the color of the Rz ink as expected as it did not contain a semiconductor in its matrix. Photogenerated electrons from the excitation by UV in the ZBP glasses reduced resazurin (blue) to resorufin (pink).

The photoreduction reaction of colored ZBP glasses under visible irradiation was also performed. Similar to UV, photoreduction of resazurin was observed for the ZBP glasses but at a faster rate, which we ascribe to the heat of the visible LED light source.

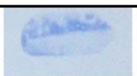
	Resazurin	Glass			
		glass slide	white	purple	green
Dark					
Light					

Table 1. Changing color of resazurin ink with UV irradiation for 20 minutes

Antibacterial activity

Antibacterial testing is another standard method for activity assessment of ZnO nanoparticles[26]. The bactericidal activity of the colored ZBP glasses was investigated using an observation of clear zones occurring due to growth inhibition of bacteria. In this study, *S. aureus* and *E. coli* were used as representations of Gram-positive and Gram-negative bacteria, respectively. *S. aureus* is a Gram-positive bacterium that has a thick peptidoglycan layer and a plasma membrane. *E. coli* is a Gram-negative bacterium that has a more complex cell wall consisting of an outer membrane and a plasma membrane.

Microscope glass slides were used as the control glass for both of *S. aureus* and *E. coli* to confirm that no clear zones were observed when using commercial glass. The clear zones could be observed when using the colored ZBP glasses for both gram-positive and gram negative bacteria. The clear zone of *S. aureus* of the colored ZBP glasses was larger than the clear zone of *E. coli*. Gram-negative bacteria are generally more resistant compared to Gram-positive bacteria because of their highly complex cell wall.27 White and purple ZBP had similar photocatalytic bactericidal activities on S. aureus and were greater than the activity of green ZBP (Fig. 10b– d). The antibacterial activity on *E. coli* of the white and purple ZBP were similar to the observed activity on *S. aureus*.

Antibacterial activity of colored ZBP is almost consistent with ZnO concentration, and complements the contributions of ZnO to the photoactivity of the glasses.

Interestingly, the antibacterial activity of the colored ZBP glasses can occur over several days. The colored ZBP glasses could be used as productive construction materials. There are two possible mechanisms that are suggested to describe annihilation of the bacterial cell; (1) penetration of nanoparticles through the cell membrane results in bacteria not surviving and (2) generation of reactive oxygen species as oxidizing agents. However, the ZBP glasses may not be properly categorized by either mechanism (1) or (2) because ZnO nanocrystals are immobilized in the glass matrix and no reactive species may be produced from UV irradiation and water dissolution during the antibacterial tests. A tentative proposed mechanism for the antibacterial activity of the ZBP glasses may involve (1) generation of room light photogenerated radicals passing through the bacterial cell membrane and (2) generation of reactive species at the surfaces of the colored ZBP glasses. These reactive species may be generated at the embedded ZnO nanoparticles due to localized electrons from dangling bonds of the amorphous character of the phosphate network. A P–O–Zn network was found by XPS in zinc borophosphate glasses with different compositions, and it is reported that increasing the ZnO content depolymerizes the glass structure by replacing bridging P–O–P sites with non-bridging P–O–Zn sites. However, a further comprehensive and careful investigation is required to clarify the mechanism.

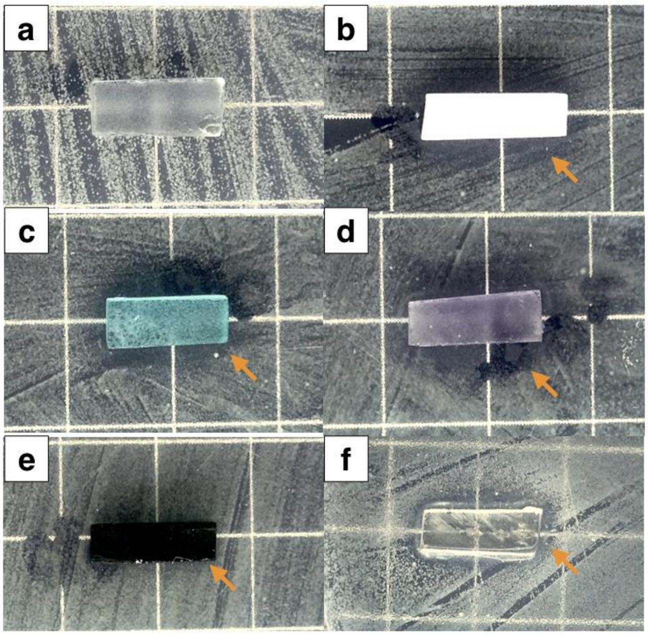


Figure 3.13. Antibacterial testing of using *S.aureus* consists of (a) microscope glass slide (b) white ZBP (c) purple ZBP (d) green ZBP and (f) yellow ZBP for a day.

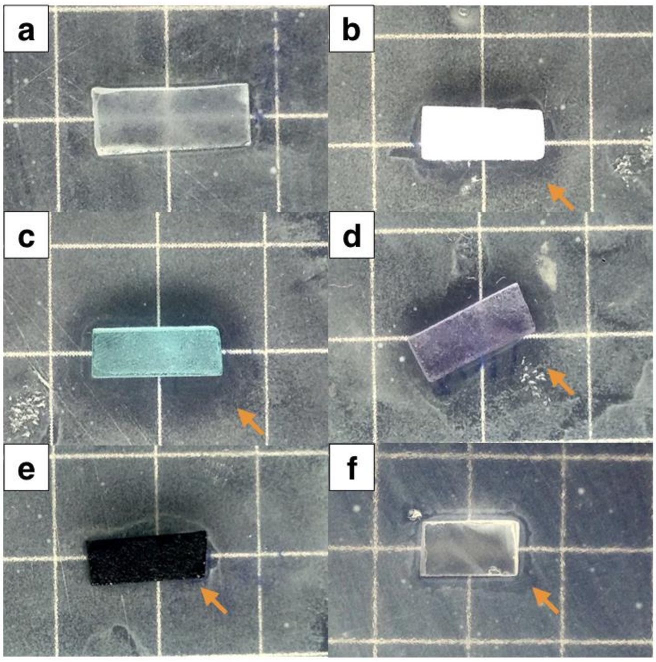


Figure 3.14. Antibacterial testing of using *E.coli* consists of (a) microscope glass slide (b) white ZBP (c) purple ZBP (d) green ZBP and (f) yellow ZBP for a day.

Radical polymerization

Polyacrylamide is conventionally synthesized via radical polymerization using acrylamide as the monomers and ammonium persulfate as the radical initiator. Recently, radicals from photocatalytic reactions at valence band and conduction band were found that could initiate polymerization. However, photo- catalyst powders used in these reactions will be buried within the polymer because polymerization occurred at a radical generated on the surface of the photocatalyst. The colored ZBP glasses might be an alternative way to generate radicals for polymerization without having to worry about excess radicals or incorporation of the catalyst into the polymer. Polymerizations using colored ZBP glasses were examined by placing the glasses into acrylamide solutions containing acrylamide, N,N'-methylene-bisacrylamide and water. It was found that the colored ZBP glasses could initiate polymerization of acrylamide but reaction was rather slow. Therefore, glycerol was added to accelerate the radical polymerization because glycerol can act as sacrificial electron donor and can be decomposed by photocatalytic process to increase active intermediate species capable of initiating polymerization of acrylamide. Nevertheless, clarification of the mechanism is still required. The radical polymerization occurred within 4 hours in the presence of the colored ZBP glasses compared to no polymerization in the original acrylamide solution or acrylamide solution with a microscope glass slide added. This finding should be intriguing for clean radical polymerizations because the colored ZBP glasses can be easily separated from the polymer. Polyacrylamide hydrogels produced using colored ZBP glasses as initiators can be observed. The hydrogels are considerably similar in features, that are, translucent and flexible. Moreover, the amount of produced hydrogels correlated to ZnO concentration because white ZBP produced larger hydro- gels compared to the purple ZBP and green ZBP. It can be concluded that the photocatalytic activity of the colored ZBP glasses attributed in initiation of acrylamide polymerization.

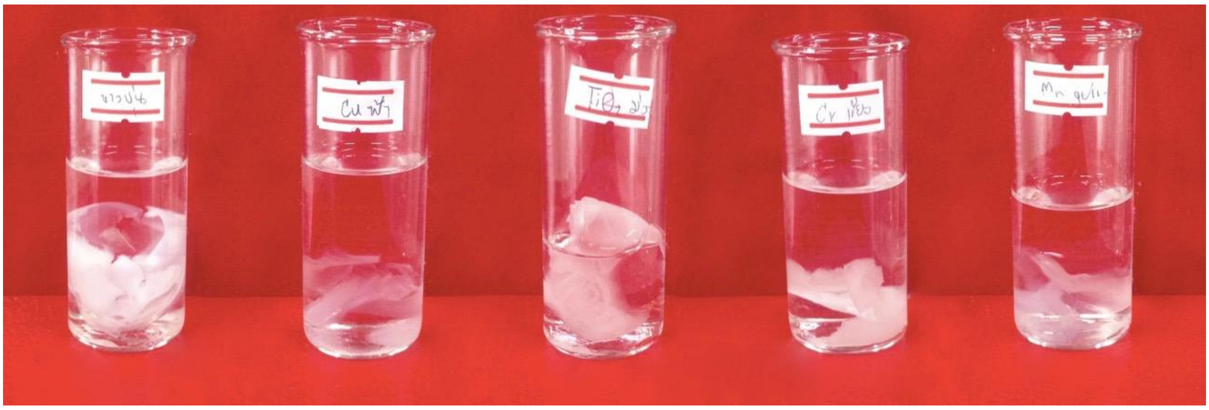


Figure 3.15. Polyacrylamide occurred from radical polymerization initiating by the synthesized colored ZBP glasses; white ZBP, blue ZBP, purple ZBP, green ZBP and yellow ZBP (from left to right).

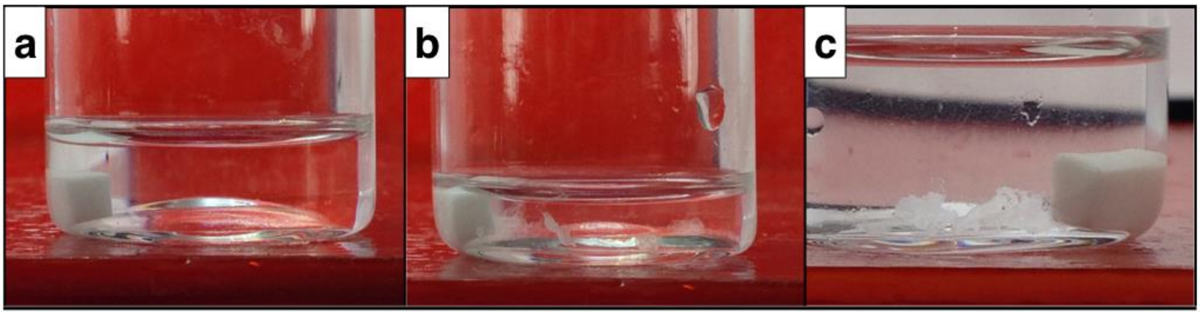


Figure 3.16. Polyacrylamide prepared by radical polymerization initiating using the synthesized white ZBP glass irradiating with UV in 24 h (a) without air pump and (b, c) with air pump.

Since the traditional polymerization of acrylamide photocatalyzing by ZBP glasses occurs very slowly, air pump could accelerate the process. The addition of oxygen affected to the reaction which oxygen would capture generated electrons from conduction band of ZBP glasses. The electron capture contributed to the decrease recombination of electron-hole. The polyacrylamide hydrogel slightly occurred after 24 hours (Fig. 3.16). The imperfection of the polymerization resulted from decreasing of acrylamide solution concentration because of vaporization of acrylamide solution during the reaction proceed in the presence of air pump. However, we could assume that the colored zinc borophosphate glasses could be use as photoinitiator in polymerization of acrylamide.

Various butanol amounts were added to the acrylamide solution, without any glycerol, to be absolutely sure that photogenerated radicals are the species responsible for the polymerization process. However, we have tried with the ZnO powder, which is a key photocatalyst in all colored zinc borophosphate glasses to reduce reaction time. It was found that the amount of butanol affected to acrylamide polymerization as can be seen in Fig. 3.17. Polyacrylamide was completely obtained from photocatalytic process using ZnO as photocatalyst without butanol (Fig. 3.17a). Whereas, incomplete polymerization was clearly observed after addition of butanol (Fig. 14b-c). It was attributed to confirm that photogenerated radical species from ZBP glass response to the polymerization.

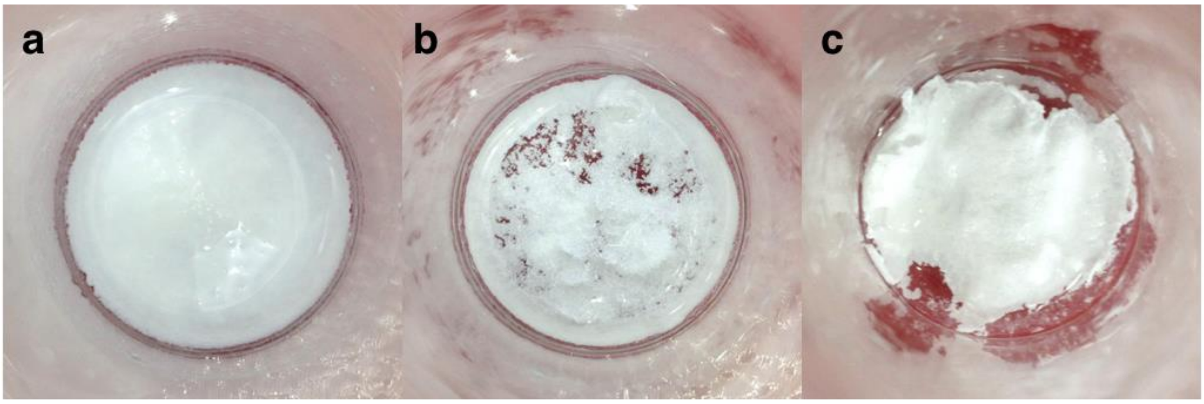


Figure 3.17. Polyacrylamide using the ZnO powder for photoinitiation of polymerization with UV-irradiation (a) in the absence of butanol and in the presence of butanol (b) 5 %v/v and (c) 10 %v/v.

4. Conclusions

The colored zinc borophosphate (ZBP) glasses have been successfully synthesized by a one-step melt-quenching technique. XRD patterns only indicated amorphousity of the colored ZBP glasses because of amorphous nature of glasses. HRTEM and electron diffraction patterns demonstrated the colored ZBP glasses are incompletely amorphous owing to the presence of monodisperse nanocrystalline ZnO embedded within the glass matrix. Furthermore, surface morphology of colored ZBP glasses showed the crystalline particles by SEM. IR and Raman spectrum revealed the different network structure of colored ZBPglass from microscope glass slide. The distinction could explain water dissolution of the colored ZBP glasses. The catalytic ability of the colored ZBP glasses was performed by four different methods. The photobleaching of methyl orange of the colored ZBP glasses in the presence of H_2O_2 and in the absence of H_2O_2 proved their photoactivity. Rapid photo-reduction was carried out by the resazurin ink test showed that all colored ZBP glasses demonstrated photocatalytic activity changing blue (resazarin) to pink (resorufin) in UV irradiation. Antibacterial testing proved the effect of ZnO in the colored ZBP glasses on the inhibition of bacterial growth for both of Gram-positive and Gram-negative bacterium i.e. *S.aureus* and *E.coli*, respectively. Interestingly, the colored ZBP glasses could be used as photoinitiators for polyacrylamide polymerization. It can be concluded that the novel colored ZBP glasses exhibit catalytic properties due to the embedded nanocrystalline ZnO as the observed activity increases with increased ZnO concentration. The colored ZBP glasses may be a productive catalytic material for outdoor applications.

Colored ZBP glasses with multiple catalytic properties have been successfully synthesized using a one-step melt-quenching technique. Monodisperse nanocrystalline ZnO embedded within the glass matrix can be confirmed by HRTEM and electron diffraction patterns. The catalytic properties of the colored ZBP glasses were tested by four different methods. The photo- bleaching of methyl orange using the colored ZBP glasses proved their photoactivity. Rapid photoreduction of resazurin ink showed that all of the colored zinc borophosphate glasses demonstrated photocatalytic activities. Antibacterial testing proved the effect of ZnO in the colored ZBP glasses on the inhibition of bacterial growth for both Gram-positive and Gram- negative bacteria S. aureus and E. coli, respectively. Interestingly, the colored ZBP glasses could be used as photoinitiators for polyacrylamide polymerization. It can be concluded that the novel colored ZBP glasses exhibit catalytic properties due to the embedded nanocrystalline ZnO as the observed activity increases with increased ZnO concentration. The colored ZBP glasses may be a productive catalytic material for outdoor applications.

Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

   Chayopas Tupberg, Nopakarn Chandet, Kamjad Wattanavichan, Chamnan Randorn, Catalytic and Antibacterial Activities of Novel Colored Zinc Borophosphate Glasses , RSC Advances, 6(2016), 79602–79611. DOI:10.1039/c6ra17232f. IF2015=3.289.