Development of Imitation Black Spinel from Coconut Shell Ash as a Glass Modifier

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Abstract. The aims of this research, Study the effect of using ashes from coconut shell ash as a Glass Modifier in glass composition to develop imitation black spinel. From the analysis of main components of coconut shell ash, both before and after burning. It was found that before burning, coconut shell ash has main element is K$_2$O SiO$_2$ and CaO. In proportion equal to 60.83, 14.64 and 14.11 (wt\%) and also found that the elements of the additives that affect the color including MnO, Fe$_2$O$_3$ and CuO. After sintering at a temperature of 400, 600, 800 and 1,000 °C. Found that quantity K$_2$O and CaO has decreased proportion. On the other hand, SiO$_2$ has increased proportion. Then Use the ashes from the burnt coconut shell ash as a chemical replace K$_2$O in glass formula (45-x)B$_2$O$_3$: 20SiO$_2$: 15Bi$_2$O$_3$: 20K$_2$O: xCoO (where x was 8, 10, 12, 14 and 16 mol\%). Found that the glass is opaque. The density of the glass was between 4.1338 ± 0.0004 and 4.1587 ± 0.0019 g/cm$^3$, which is greater than the density of black spinel. Glass had a hardness value of 6.5 Mohs scale which is comparable to the felspar, but it is less than the hardness of the real black spinel, which is 7.5 Mohs scale.

1. Introduction
The coconut is a plant that originated in Southeast Asia and is cultivated in many countries [1]. Coconut can be used in all parts such as leaves are used to make brooms and roofs, fruit is used to extract oil or use as an ingredient in the food [2]. Some studies have made use of coconuts by combining them with ceramic matrices composites to develop an environmentally friendly product. Thai coconuts are a popular fruit product from the world market, with an annual export of 370 million or more than 8 billion baht, even in 2020 that Thailand and the world have to face. With the epidemic of COVID-19, exports of fragrant coconut continued to expand by 30%. Coconut shells are part of the process leftover and there is no value-creation process yet, which is one of the main contributing factors to air pollution as it accounts for approximately 3.18 million tons per year, which is more than 60% of the amount of waste in the country [3]. Coconut shell waste is found in large quantities in the local coconut industries [4]. Coconut shells are biological wastes, as are bamboo, hemp, oil palm shell and rice husk, which have the potential to reinforce thermoplastics [5-7]. On the other hand, coconut shells have useful properties such as low density, low cost, good thermal properties and high toughness. Developing a process to make use of coconut shells is also thought to help minimize the harm to health [8]. Glass is a popular material used in a number of applications such as building structures, containers, decorations, and research. Glass is classified as an amorphous solid, formed by the cooling of the liquid phase at an optimum rate without producing a crystalline structure. There are different types of glass depending on the glass former, each of which is suitable for different applications. One of the very popular glasses is borate glass. Borate
glass is a glass whose primary structure is formed from boron oxide. It has the advantage of being more resistant to chemical reactions than other types of glass. Borate glass differs from silicate glass, that is, when alkali oxide is added to the borate glass cause a decrease in glass transition temperature, an increase in liquidus temperature, an increase in thermal expansion coefficient and can also cause an increase in viscosity. In this research to the development of imitation black spinel from coconut shell ash as a glass modifier.

2. Materials and Methods
Coconut shell ash was selected from the cultivated areas in Nakhon Pathom Province. Selected ash was sintered at 1,000 °C. The glass samples were prepared in formula \( (45-x)B_2O_3 : 20SiO_2 : 20Bi_2O_3 : 15K_2O : xCoO \) where \( x \) is a concentration of CoO (\( x = 8, 10, 12, 14, \text{and} 16 \text{ mol%} \)) and use coconut shell ash replace \( K_2O \). After preparing the ingredients according to the above recipe, all the ingredients are mixed together until homogeneous in the porcelain crucible, then the mixed substances are then heated in an electric furnace at 1,200 °C for 3 hours, where the heating rate was 10 °C/min, then melted glasses is placed on a graphite base and then annealed sample at 500 °C for 3 hours to reduce the stress on the sample. The samples were annealed, cut and polished in width 10 mm and length 15 mm, thickness 3 mm dimensions for further properties studies. The physical properties of glasses were determined using conventional methods. The density was measured by the Archimedes method. Hardness of glass was measured by Mohs scale for compare with real black spinel stone.

3. Results
The CoO doped glasses have been found to be Opaque. Figure 1. presents the photographs of CoO doped glass samples in this work.

![Figure 1. different concentration of CoO doped glass samples](image)

3.1. Chemical composition
This research has been conducted in laboratory test on coconut shell ash samples using X-Ray Fluorescence (XRF). From the results, it was found that before sinter coconut shell ash contained \( K_2O \), \( SiO_2 \) and \( CaO \) as the main elements with the proportion of 60.83, 14.64 and 14.11 wt%, and also found that the elements of the color additives were \( MnO \), \( Fe_2O_3 \) and \( CuO \). After sintering at 400, 600, 800 and 1,000 °C, the proportion of \( K_2O \) and \( CaO \) decreased, on the other hand, \( SiO_2 \) increased as shown in Table 1. In this experiment, coconut shell ash after calcination at 1,000 °C was used as an element in the glass. The high-temperature calcination will reduce the contaminated coloring agent.
Table 1. The results measurement of the Chemical composition of coconut shell ash samples

| Chemical composition | Before sinter (wt%) | After sinter | 400 °C (wt%) | 600 °C (wt%) | 800 °C (wt%) | 1,000 °C (wt%) |
|----------------------|--------------------|-------------|-------------|-------------|-------------|---------------|
| SiO₂                 | 14.64              |             | 17.49       | 21.70       | 26.90       | 30.21         |
| P₂O₅                 | 6.41               |             | 6.27        | 5.91        | 4.71        | 4.30          |
| K₂O                  | 60.83              |             | 59.62       | 57.91       | 56.03       | 55.35         |
| CaO                  | 14.11              |             | 12.95       | 11.11       | 9.38        | 7.52          |
| TiO₂                 | 0.34               |             | 0.24        | 0.22        | 0.20        | 0.17          |
| MnO                  | 0.21               |             | 0.18        | 0.17        | 0.17        | 0.16          |
| Fe₂O₃                | 2.83               |             | 2.68        | 2.45        | 2.12        | 1.90          |
| CuO                  | 0.30               |             | 0.28        | 0.28        | 0.28        | 0.27          |
| ZnO                  | 0.33               |             | 0.29        | 0.25        | 0.21        | 0.12          |

3.2 Density and molar volume

Density is a significant and instructive tool that substantiates variation in the geometrical configuration of glass networks [9]. The densities of the glasses were measured based on the Archimedes principle using a 4-digit sensitive microbalance (AND, HR-200). The density was calculated using the formula:

\[
\rho = \left( \frac{W_{\text{air}}}{W_{\text{air}} - W_{\text{water}}} \right) \times \rho_w \quad \text{(g/cm}^3) \tag{1}
\]

where \(W_{\text{air}}\) and \(W_{\text{water}}\) is the weight of the sample in air and distilled water, respectively. \(\rho\) represents the density of glasses and \(\rho_w\) is the density of distilled water. The density of water is 1.0000 g/cm³ [10].

The molar volume of glasses was obtain using:

\[
V_M = \frac{M}{\rho} \quad \text{(cm}^3/\text{mol)} \tag{2}
\]

Where M is the total molecular weight of the glasses sample.

Figure 2 Density of glass sample
From the results, it was found that the density of the glass samples increases with increasing the CoO concentration because CoO with a molecular weight greater than B$_2$O$_3$, it is replacing B$_2$O$_3$ in the glass structure. By replacing B$_2$O$_3$ by CoO, it is predicted that the inter atomic spacing is increased. CoO also acts as a modifier in the glass network and produces more non-bridging oxygen (NBO), which is observed in molecular volume increase with increasing CoO concentration. The density and molar volume are shown in Figures 2-3, respectively. The density and molar volume are between 3.9704 ± 0.0217 to 4.2015 ± 0.0066 g/cm$^3$ and 30.1075 to 30.3499 cm$^3$/mol, respectively. It was found that the density of all glass samples was greater than that of the real black spinel. (The average density of real spinel is 3.64 g/cm$^3$).

3.3 Hardness
Hardness is the ability to bear loads while stressing occurs within a material, another important property of a material that can be used as information for resistance to changes in size and shape. The hardness has many characteristics: abrasion resistance, scratch resistance and pressing resistance. For the hardness of coated materials such as ceramics, coated metals, and other putty materials, hardness refers to the ability of a coating to be applied or coated on a surface that is resistant to scratching, pressed or scratched with a solid. In the jewellery business, the difference between diamonds, gems and minerals can be measured using Mohs measurement standards. A harder gemstone is able to scratch a gem with a lower hardness, but a less hard gem cannot scratch a more solid gem, while a gem with a higher hardness will scratch each other. The hardness examination of the cut gem should, if possible, should not be performed except as a final test. Because the gem can be flawed, most of the gemstones that have been cut have been cut. Hardness is not used as a test. In addition to being in the form of a gem. Mohs’ scale might easily confuse the jeweller as well as the public. The Mohs scale was measured for all glass samples dope CoO at concentrations of 8, 10, 12, 14 and 16 mol%, with moles found to be 6.5 Mohs’ scale, which is comparable to the felspar, but it is less than the hardness of the real black spinel, which is 7.5 Mohs scale.

3.4 Commercial
Consider commercial, the cost of imitation black spinel includes electricity, furnace depreciation, the crucible, and chemical costs. Production of 1 kg at a time would cost about $100, but manufacturing on an industrial scale could reduce costs. One-kilogram of glass can be made into more then 1000 imitation black spinel tablets (1 carat = 0.2 g), which costs an average of $0.02 per carat, which the average price of real black spinel is about $ 20 per carat. Therefore, imitated black spinel is a hundred times cheaper than real black spinel, although its hardness is slightly less than real black spinel, but can be used as an ornament or decoration.
4. Conclusions

In this research, the glasses were produced by coconut shell ash were selected from the cultivated areas in Nakhon Pathom Province, Thailand. Coconut shell ash after calcination at 1,000 °C was used as an element in the glass (use replace K2O). The glasses doped with CoO, the results show the density and molar volume increases with increasing concentration of CoO, density of all glass samples was greater than that of the real black spinel. The Mohs scale of all glass samples less than the hardness of the real black spinel. Therefore, imitated black spinel was developed can be used as an ornament or decoration.

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6. References

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