Physical and Optical Properties of CuO doped in Glasses Prepared from Rice Husk Ash in Suphan Buri Province, Thailand

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Abstract. Glasses were prepared by rice husk ash (RHA) from Suphan Buri Province, Thailand. RHA was composed of SiO$_2$ (95.932%), can be used instead of sand in the glass production. The glasses doped with CuO and composition of (40-x)SiO$_2$ (used RHA as SiO$_2$): 20B$_2$O$_3$: 25Na$_2$O: 15CaO: xCuO where x is 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 mol%. The density and refractive index of the glasses trend increases, while the molar volume trend decreases with the increasing of CuO concentration. The absorption bands were showed with the peaks around 774 nm ($^2$B$_{1g}$ → $^2$B$_{2g}$). The color coordinate in CIE L*a*b* system confirmed the blue color in glasses was obtained by adding the CuO.

1. Introduction

Rice is an important agriculture in many countries across Asia. Rice husk is the outer cover of rice with less nutritional value, consequently, it is removed from the milling process of rice [1]. In Thailand, rice was an important export agricultural product. Many rice husks were obtained from mill in Suphanburi province. Moreover, many rice husks from rice milling can be an agricultural waste, therefore, it should be changed for the benefit. From the research found that when rice husk is burnt rice husk ash is generated, the rice husk ash contains silica [2]. The rice husk ash is mainly composed of silica (87% to 97%). Thus, possibility of using RHA instead of SiO$_2$ in a glass production by reason of their properties such as high silica content and low transition oxide contamination [3]. Glass materials can be added other element in glass composition because of their properties for instance transparency, ease for making, flexibility in size and shape and low cost [4]. Sodium Borate glasses have interest as host material due to their many special properties such as high transparency, high thermal stability and low melting point. Furthermore, the adding sodium oxide (Na$_2$O) to glass production for increase the homogenization and reduce the melting point [5]. While, calcium oxide (CaO) has been added to improve their properties such as reduces the glass transition temperature and glass crystallization [6]. Color of glasses obtain by addition of transition metal elements [7]. Cu$^+$-doped glasses are interesting due to copper ion create color centers with absorption bands in visible spectrum, thus producing a blue
color for the materials [8]. In this work, the glasses were prepared from RHA used instead of sand and add content of CuO in the glass composition of (40-\(x\))SiO\(_2\) (use RHA as SiO\(_2\)): 20B\(_2\)O\(_3\): 25Na\(_2\)O: 15CaO: xCuO (where: \(x\) is 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 mol\%). The RHA glasses were investigated in several physical and optical properties, density, refractive index, UV-Visible absorption and color coordinate in CIE L*a*b* system.

2. Experiment
Rice husk ash (RHA) from Suphan Buri Province, Thailand was sintered at 1000°C and used instead of sand in the glass composition. The glasses doped with CuO and composition of (40-x)SiO\(_2\) (use RHA as SiO\(_2\)): 20B\(_2\)O\(_3\): 25Na\(_2\)O: 15CaO: xCuO where \(x\) is 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 mol\%. Each batch weighs about 30 g was melted in alumina crucibles in the electrical furnace at 1,200 °C for 3 hours. The melts were quenched at room temperature air by pouring onto graphite plate. Afterwards, the glass sample were annealed at 500°C for 3 hours. All glass samples were cut and polished in a dimension of 30 mm x 50 mm x 3 mm as show in Fig. 1.

![Fig. 1 The RHA glasses doped with CuO](image)

The Archimedes principle have been used for measured the densities of the glasses by using a 4-digit sensitive microbalance. The density was computed by equation:

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

where \(W_{\text{air}}\) , \(W_{\text{water}}\) is the weight of each sample measured in the air and water, respectively, and \(\rho_w\) is the water density.

The molar volume of glasses was computed by 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, \(\rho\) is the density of glasses [9]. The refractive index for the glasses were investigate by using an Abbe’ refractometer (ATAGO-3 T) with mono-bromonaphthalene at room temperature. The absorption spectra and color coordinate system of the glass samples were confirmed by a UV-Visible spectrophotometer in wavelength 200-1100 nm. The color of all glass samples was confirmed by using the method of CIE L*a*b* color coordinate.

3. Results and discussion
The chemical compositions of rice husk ash (RHA) sintered at other temperature were measured by XRF as present in Table 1. The major composition of RHA is SiO\(_2\) and low transition oxide contaminations. As a result, the RHA can be used instead of sand in the glass composition [2].
Table 1. The chemical compositions of RHA.

| Sintering condition | % by weight |
|---------------------|-------------|
|                     | SiO₂   | K₂O   | CaO   | MnO   | Fe₂O₃ | CuO   | ZnO   |
| Sintered at 200 °C  | 94.515 | 4.074 | 1.024 | 0.193 | 0.193 | 0.007 | 0.021 |
| Sintered at 400 °C  | 94.486 | 4.055 | 1.033 | 0.197 | 0.187 | 0.012 | 0.030 |
| Sintered at 600 °C  | 94.609 | 3.990 | 1.017 | 0.192 | 0.155 | 0.009 | 0.028 |
| Sintered at 800 °C  | 95.247 | 3.387 | 0.977 | 0.193 | 0.151 | 0.011 | 0.033 |
| Sintered at 1,000 °C| 95.932 | 2.711 | 0.968 | 0.186 | 0.161 | 0.009 | 0.032 |

The density of the glasses was shown in Fig. 2. The result was show that the density tended to increases with increasing CuO contents owing to the molecular mass of CuO is heavier than SiO₂. As a result, replacing SiO₂ with CuO helps in improving the compactness of the glass structure, while the molar volume trend decreases with the increasing of CuO concentration because Cu²⁺ ions enter the gap of the glass structure acting as network modifier and producing BO (bridging oxygen) in the glass construction [10]. The refractive index tended to increase with increasing content of CuO (Fig. 4). It was found that as the density is increased, the refractive index also increased owing to the refractive index depends on the density and on polarizabilities of the atom in a given material [2].
The molar volume of RHA glasses doped with CuO was calculated using the following linear equation:

\[ y = -0.0065x + 22.017 \]

The refractive index of RHA glasses doped with CuO was determined with the following equation:

\[ y = 0.0007x + 1.5565 \]

The optical absorption spectra of the glass samples were recorded in the wavelength of 200-1100 nm at room temperature as presented in Fig. 5. The absorption bands were showed with the peaks around 774 nm (\( ^3B_{1g} \rightarrow ^2B_{2g} \)), due to Cu\(^{2+}\) ion in octahedral coordination with a strong tetragonal distortion [11]. In addition, the other peaks can be seen from the absorption band between 200-400 nm (\( ^3B_{1g} \rightarrow ^2E_g \)) owing to the d–d transition of Cu\(^{3+}\) ion in the glasses [12]. The color of all glass samples was confirmed by using the method of CIE L*\(a^*b^*\) color coordinate is shown in (Fig. 6). The glasses show blue color was obtained from Cu\(^{2+}\) ions. While, the CuO content increases from 0.1 to 0.5 mol%, intensity of these absorption bands also increased [13]. Which, this increase is due to the visible absorption band originating adding Cu\(^{3+}\) in the glass extends into the visible spectrum region [8].
Fig. 5. The absorption spectra of RHA glasses doped with CuO.

Fig. 6. The CIE 1931 chromaticity diagram of RHA glasses doped with CuO.
4. Conclusions
The glasses were prepared by Rice Husk Ash form Suphan Buri Province, Thailand, after sinter at 1000ºC. Form the result, the major of RHA is SiO$_2$. The glasses doped with CuO was showed physical properties of the density increases with increasing content of CuO, while the molar volume trend decreases with the increasing of CuO concentration. The refractive index decreases with increasing content of CuO. The absorption bands were showed with the peaks around 774 nm ($^2$B$_{1g}$ $→$ $^2$B$_{2g}$). The color coordinate in CIE L*a*b* system confirmed the blue color in glasses doped with CuO content. Therefore, the glasses from RHA can be used instead of sand in glass composition and blue color of the glasses sample was obtain by adding the CuO in to glass composition.

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