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Study properties of Cr_2O_3 doped in glasses prepared from sugar cane ash

Nattapon Srisittipokakun[1,3], Nakarin Singkiburin[3], and Jakrapong Kaewkhao[2,3]

[1] Industrial Physics Program, Faculty of Science, Nakhon Pathom Rajabath University Nakhon Pathom, Thailand
[2] Physics Program, Faculty of Science, Nakhon Pathom Rajabath University Nakhon Pathom, Thailand
[3] Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom, Thailand

Abstract

The physical and optical properties of glass samples which manufactured using sugar cane ash were investigated. The chemical composition of the sugar cane ash was first analyzed using an X-Ray fluorescence Spectrometer (XRF). The sugar cane ash samples were sintered at different temperatures (400 °C, 600 °C, 800 °C and 1000 °C) under the same background conditions. Samples were produced with increasing concentrations of Cr_2O_3. It was found that the density and refractive index of the glass samples was found to increase as a result of increasing the concentration of Cr_2O_3 in the sample. The absorption spectra of the samples was measured using a UV-visible light spectrometer. The absorption peak was found to be at 640 nm. This was thought to be due to the transition $^4A_{2g}$ (F) $\rightarrow ^4T_{2g}$ (F). This was in turn thought to be due to the Cr^{3+} ion in octahedral coordination with strong tetragonal distortion. There was another absorption band that was observed at approximately 460 nm. This was thought to be due to the split components of the $^6A_{1g}$(S) $\rightarrow$ $^4T_{2g}$ (G) transition. Iron, in the Fe^{2+} state, exists in the glass in equilibrium with the yellow ferric ion (Fe^{3+}). The color coordinate in the glass samples were measured and showed good agreement with the absorption spectra that was observed

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1. Introduction

Sugarcane production is an important industry for Thailand's economy. Thailand is the second largest exporter of sugar in the world. All parts of the sugarcane plant are used in Thailand. Juice is extracted for refining into sugar and the remaining plant, know as bagasse, is burnt for energy production or for use in making biological materials. Sugar cane bagasse is an important biomass source for heat and power generation in Thailand [1]. Sugar Cane Bagasse Ash (SCBA) is an advanced cementitious material that contains significant amounts of poz-zolanic minerals such as silica and alumina [2]. N. Srisittipokakun et al. reported the effect of adding CuO, MnO_2 and Fe_2O_3 to glass mixtures. They reported on the physical, structural and optical properties of glasses that were made from rice husk ash. In another paper it was found that, the addition of CuO, MnO_2 and Fe_2O_3 affected most of the properties of the glass samples that were produced [3]. Y. Ruangtaweep, reported the composition and structure of rice husk ash, RHA, at different sintering temperatures. The optical and physical properties of glass from RHA were studied and compared with glasses made from SiO2 from a purer source [4]. Adding transition metals to glass affects its color and physical properties. The atomic number and atomic weight of chromium are 24 and 51.996 g/mol, respectively. The chromium 3d54s1 electron configuration is a paramagnetic transition ion. It is known that the chromium has various oxidation states; Cr^{3+}, Cr^{4+}, Cr^{5+}, Cr^{6+}. The most stable chromium ions are Cr^{3+} and Cr^{6+} ions [5]. When these are added to glass they create glass which is green, Cr^{3+}, and yellow, Cr^{6+}. This can be observed in the UV-VIS spectrum.

In this work the physical and optical properties of glass samples produced from sugar cane ash with varying concentrations of Cr_2O_3 were investigated.

2. Materials and Methods

SiO_2 composition measurements in the sugar cane ash were performed using a PANalytical MiniPal 4 EDXRF spectrometer, equipped with a 30 kV rhodium anode tube with a heliumpurge facility. A high-resolution silicon drift detector was used to measure

*Corresponding author; email: cena_nuk@hotmail.com

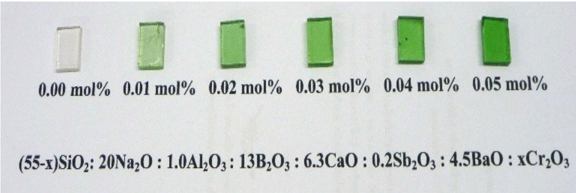

Figure 1: Digital photograph of Cr_2O_3 doped in glasses.

Table 1: **Table 1.** Chemical analysis of sugar cane ash following burning at 1000 °C.

Compound	1000 °C
MgO	2.50
Al_2O_3	1.70
SiO2	67.91
P_2O_5	2.71
SO_3	1.08
Cl	1.33
K_2O	1.74
CaO	20.06
TiO_2	0.09
MnO	0.10
Fe_2	O3 0.73
CuO	0.04
ZnO	0.02
Total	100.00

the intensity of the x-rays. Matrix corrections were made by using either a ratio to the Compton peak or theoretical alpha coefficients, using minipal 4 software. Details of these corrections can be seen later in the paper. Samples were prepared a melt quenched technique. The composition and loss on ignition results for all SCBA samples. Examination of the sugar cane ash revealed that the concentration of SiO_2 was at a level of over 70%. The SCBA +212 samples gave the two highest concentrations. This was in agreement with other findings reported in the literature [6]. The composition ratios of the mixtures used to produce the glass samples were as follows: (55-x)SiO_2: 20Na_2O: 1.0Al_2O_3: 13B_2O_3: 6.3CaO: 0.2Sb_2O_3: 4.5BaO: xCr_2O_3 where x = 0.00, 0.01, 0.02, 0.03, 0.04 and 0.05 mol%

The chemical composition of the sugar cane bagasse ash that was used for this research, SCBA, was analyzed using an X-Ray fluorescence Spectrometer (XRF). The main component was found to be SiO_2 which indicated it could be used in the production of glass. All of the chemicals that were used to produce the glass samples were weighed and thoroughly mixed in the proportions shown above. The mixed powder was loaded in a porcelain crucible and melted at 1200 °C for 3 hrs using a furnace. The glass samples were obtained by pouring the heated mixture onto a graphite mould. The transparent glass samples that were obtained were annealed at 500 °C for 3 h.

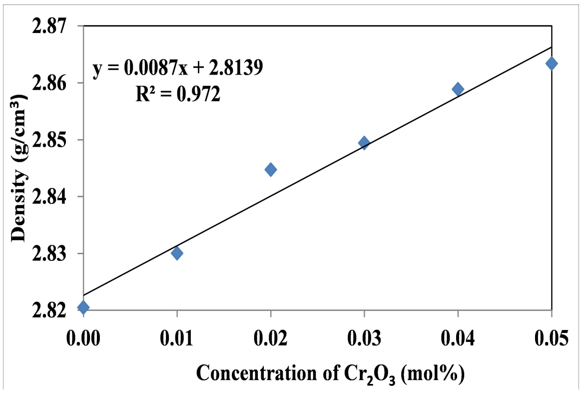

Figure 2: Density of glass samples

The temperature of the annealing furnace was gradually reduced to room temperature with a cooling rate of 10 °C/min. This was done to reduce thermal stress in the samples and to cool them down to the room temperature so that they would become solid. As a result of this process clear and transparent glass samples were formed. The samples were cut and polishedusing diamond clay for 30 min for each sample. Fig.1. shows the cut and polished glass samples.

The densities of the glass samples were determined using Archimedes' method. This equation for this can be seen in Eq. (1). Water was selected as an immersive fluid. For all samples, the measurement was done at room temperature and repeated three times in order to reduce error.

$$\rho = \frac{W_A}{W_A - W_B} \times \rho_{\text{ref}} \quad (1)$$

where W_A is the weight of the glass sample in air, W_B is the weight of the glass sample in water and ρ_{ref} is the density of water at room temperature (27 °C). Following the density calculations the molar volumes of the glass samples were calculated using the following equation:

$$V_M = \frac{M_T}{\rho} \quad (2)$$

where, V_M is the molar volume, M_T is the total molecular weight and ρ is the density of the glass sample. The absorption spectra and color coordinates system (CIE L*a*b*) of the glass samples were measured using a UV – visible spectrophotometer (cary-50). The refractive indices were measured using an Abbe refractometer (ATAGO) with a sodium vapor lamp as a light source. This produces light with a wavelength of 589.3 nm (D line). Monobromonaphthalene was used as a contact layer between the sample and prism of the refractometer [4, 5].

3. Results and Discussion

The composition of the sugar cane bagasse ash samples that were produced for this research are shown in

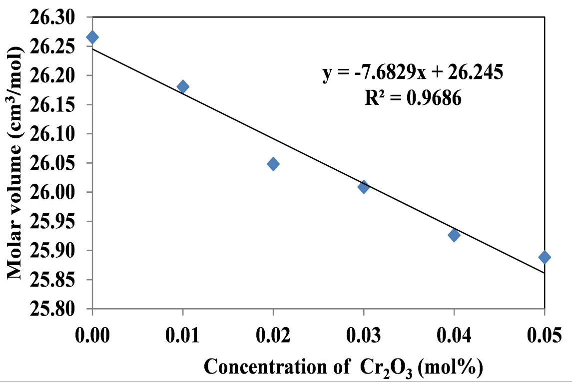

Figure 3: Molar volume of glass samples

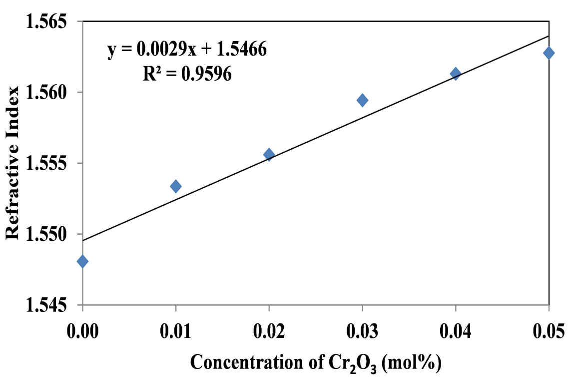

Figure 4: Refractive index of glass samples

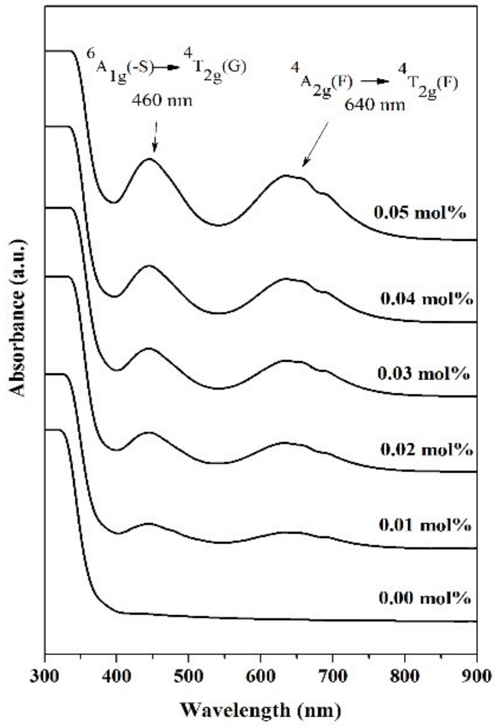

Figure 5: Absorption spectra of glass samples

table 1. This ash was produced by burning the sugar cane bagasse at a temperature of 1,000 °C [3].

3.1. Physical properties

Measuring the density of materials is an important tool which can be used to determine any changes of the structural softening/ compactness of a sample. It can also be used to detect changes in geometrical configuration, coordination number, cross-link density and the dimension of interstitial spaces in a material. The density of glass samples was found to increase with increasing Cr^{3+} concentration. This is shown in fig.2. This was thought to be due to the molecular weight of the Cr2O3 being larger than SiO_2 that it displaces in the mixture.

It was found that as the as Cr^{3+} ion content increases the molar volume of the glass samples decreases and the density of the samples increases (fig.3.). This finding agrees with the definition of density and is an expected result. It is though that some of this effect may be due to Cr^{3+} ion substitutions inside the glass network. It is thought that these could decrease the intermolecular spacing and decrease the molar volume leading to an increase in density.

The refractive index of the glass samples was found to increase with increasing concentrations of Cr^{3+} ions. This was thought to be due to the increased density of the glass samples with higher concentrations of Cr^{3+} ions. This is shown in fig.4. As the density of the glass samples increases the structure of the glass will become more compact. This will have the effect of slowing the velocity of light in the sample which will in turn cause the refractive index to increase.

3.2. Absorption spectral analysis

The absorption spectra of glass samples containing Cr_2O_3 are shown in figure 5. It can be seen that the absorption peaks were found to be at 640 nm and 460nm. It was thought that the 460nm absorption peak is due to the split components of the $^6A_{1g}$ (S) $\rightarrow$ $^4T_{2g}$ (G) transition iron in the glass. This exists in equilibrium with the yellow ferric ion (Fe^{3+}). It was though that the peak at 640nm was due to the $^4A_{2g}$ (F)$\rightarrow$ $^4T_{2g}$ (F) transition. This was thought to be caused by Cr^3+ ions in octahedral coordination with a strong tetragonal distortion. The color of all of the glass samples was measured using CIE L*a*b* color coordinates. The glass sample without Cr_2O_3 was found to be colorless while those with increasing concentrations of Cr_2O_3 were found to be green. The brightness of each sample, L*, was found to decrease with increasing Cr_2O_3 concentrations. This finding corresponds with the absorption spectra. The colour coordinates of the samples can be seen in fig.6.

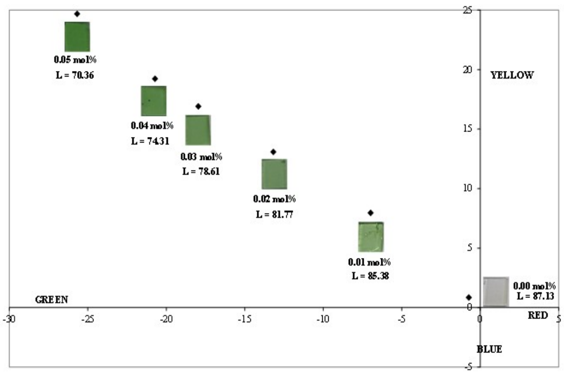

Figure 6: The CIE L*a*b* color scale of Cr_2O_3 doped in glass samples

4. Conclusions

Glass produced from sugar cane bagasse ash with the addition of Cr_2O_3 shows various interesting properties. The density and refractive index of the glass was found to increase with increasing Cr_2O_3 concentration. The molar volume was found to decrease and the density was found to increase. This effect was mainly thought to be due to the definition of density however it is although thought that Cr^{3+} ion substitution inside the glass network may have caused dome of this effect. Peaks in absorption spectra of Cr_2O_3 doped glasses were found at 640nm and 460nm. The peak at 640nm was thought to be due to the $^4A_{2g}$ (F) $\rightarrow$ $^4T_{2g}$ (F) transition caused by Cr^{3+} ions and the peak at 460 nm was thought to be due to to the split components of the $^6A_{1g}$ (S) $\rightarrow$ $^4T_{2g}$ (G) transition. This exists in equilibrium in the glass with the yellow ferric ion (Fe^{3+}).

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