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Soda-based glass fabricated from Thailand quartz sands doped with silver compound

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ABSTRACT

Yellow colored glass which used for luxury art glass in ancient time was fabricated by the addition of silver compound into the molten glass. It was proved that it was actually silver nanoparticle technology. In this work, the SiO_2–(Na_2O,K_2O)–CaO–B_2O_3–Al_2O_3–MgO glass system was prepared in the laboratory scale based on local quartz sands from Trat Province, eastern area of Thailand as the silica raw material. Various concentrations of silver nitrate were added. After the complete conventional melting process, the bubble-free yellow glasses were yielded. Physical and optical properties such as density, refractive index and optical absorption spectra were measured. Scanning electron microscope coupled with energy dispersive spectroscopy was carried out to study their morphology. The refractive indices and densities were increased as the increase of the silver contents. Electron micrographs showed the presence of silver nanoparticle in the glass matrix. UV–VIS spectra were in good agreement with that found from SEM measurements and corresponded with the universally accepted. It was also showed that the more brilliance on the surface of the glass products was obtained after firing with a gas torch.

1. Introduction

It was reported along the last twenty years that the coloration of commercial glass by incorporation of noble metal nanoparticles such as Cu, Ag and Au, has found considerable interest in advanced materials research due to their electronic, optical and thermal properties as well as catalytic properties for potential applications in the fields of physics, chemistry, biology, medicine and materials science [1–4].

In fact, the exploitations with nanotechnology were not new. Historical evidences showed that gold and silver nanoparticles were used in the deep red colored Roman glass [5,6]. It is well known that the Lycurgus cup (4th century A.D.), which can be seen at the British Museum, is a striking example of the early (artistic) use of metal nanoparticles embedded in glass: the vessel appears green in daylight (reflected light), but red when it is shown from the inside (transmitted light). This peculiar color display is due to the presence of metal nanoparticles (~70 nm) containing silver and gold [7].

Oxide glasses containing silver inclusions have been the subject of intense investigations during the last decade. These materials have potential applications in fields such as non-linear optics [8], electrochemical devices [9], electro-optical devices [10] and dosimeters [11]. The SiO_2 based glasses provide an optically transparent matrix in which atoms, molecules and/or small particles can be physically trapped. The method used to incorporate the Ag into SiO_2 based glasses depends of the process used to prepare them [12–15]. The glass is prepared from the melting process; the Ag is introduced in the form of a metallic oxide, which is diluted in the melted silica at high temperature [16–18]. This method produces dense glasses with low degree of porosity. The optical spectrum of silver-doped glasses shows different features depending on the aggregation state of the metal. It was found that spherical silver particles (~10 nm) produces an absorption band around 410 nm, while spherical particles split this absorption in two bands located at shorter and longer wavelengths [19]. These bands have been associated with the plasmon absorption band in nanometric Ag colloidal particles [20–22].

In this work, the soda-based glass samples were fabricated using Thailand quartz sand and various concentrations of silver nitrate. Their physical and optical properties were determined and discussed.

2. Experimental

Glass samples were prepared in the laboratory scale over the matrix of SiO_2–(Na_2O, K_2O)–CaO–B_2O_3–Al_2O_3–MgO, labeled as SE0. Local quartz sands from Trat site (eastern province of Thailand) was used as the source of silica raw material. It was the surface-to-near surface glass sand deposit which contained more than 98.0 wt% SiO_2 and low iron content (0.05 wt%). It

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Table 1
The values of density and refractive index of the glass samples.

Sample no.	$AgNO_3$ Conc. (wt%)	n_D at 589 nm	ρ (g cm^{-3}) at 25 °C
SE0	0	1.500	2.4871
SE1-2	0.01	1.500	2.4908
SE2-2	0.1	1.500	2.4993
SE3-2	0.5	1.505	2.5057
SE4-2	1.0	1.510	2.5089
SE5-2	2.0	1.515	2.5125
SE6-2	5.0	1.520	2.5361

showed in pink–gray color. Its grain was mostly angular and fine. The values of grain size, grain concentration and specific area were 250 ± 100 μm, 0.166 %vol and 0.046 m^2/g, respectively [23,24]. Various concentrations of $AgNO_3$ were added from 0.01 to 5.0 wt%, labeled as SE1-2, SE2-2, SE3-2, SE4-2, SE5-2 and SE6-2, respectively. The well-mixed and dried powders mixture of 150 g each was contained in a ceramic crucible for each composition. They were melted using an electric furnace at maximum temperature of 1100 ± 50 °C for 4 h and then cooled down to room temperature.

Refractive index (n_D) of these glass samples was measured at room temperature using a Rayner Duplex II refractometer with a refractometer fluid $n_D \leqslant 1.79$ and 589-nm sodium light. The uncertainty was ± 0.005.

By applying Archimedean buoyancy method, the density of the prepared glass samples was measured with distilled water as the immersion liquid. All weight measurements were done using an analytical balance, Meltler Toledo AG 104 at 25 °C.

The absorption spectra were recorded by Perkin Elmer Lambda 900 UV–VIS-NIR spectrometer at room temperature in a spectrum range of 300–800 nm with an accuracy of ±0.8 nm in the visible range.

Sample SE6-2 which contained 5.0 wt% $AgNO_3$ was fired using a gas torch at temperatures around 600 ± 100 °C. Structures and composition of the glass samples were analyzed using a Jeol JSM 5410 LV scanning electron microscope coupled with an Oxford Instruments INCA Penta FETx3 analytical system. Prior to characterize, its surface was coated with gold using Jeol JFC-1200 Fine Coater. Field emission scanning electron microscope; Hitachi FE SEM S-4800, coupled with Horiba Emax X-act EDX analysis system were carried to confirm the presence of Ag both before and after firing. Its surface was also coated with platinum using Hitachi E1010 Ion Sputter.

3. Results and discussion

Results from the measurements, the refractive indices and the densities of the glass samples were 1.500–1.520 and 2.4871–2.5361 g cm^{-3}, respectively, as shown in Table 1. They were increased linearly as the increase of $AgNO_3$.

The colors of all samples were shown in Fig. 1. It can be seen that the glass samples were homogenous and free of bubbles. The color of the based glass was colorless while it changed to pale, bright and almost opaque colors with increasing concentration of $AgNO_3$. SE4-2 was light brownish-yellow. With maximum doping,

Fig. 1. Macroscopic appearance of the glass samples.

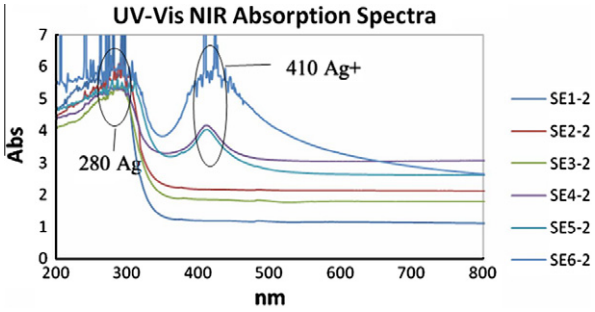

Fig. 2. UV–VIS spectra of the glass samples.

SE6-2 became opaque brownish-yellow and loosed visible transmittance.

The appearance of brownish-yellow color was a clear indication of the formation of silver nanoparticles. This color exhibited by metallic nanoparticles was due to the coherent excitation of al the free electrons within the conduction band, leading to an in-phase oscillation which was known as the surface plasmon resonance (SPR) [25–27].

The UV–VIS absorption spectra of the glass samples containing as-prepared silver nanoparticles were shown in Fig. 2. The spectra exhibited a strong SPR absorption band of the glass samples centered at 410 nm and certainly increased in absorbance as a function of silver contents without any shift in the peak wavelength. The increase of absorbance was observed when the rate of silver nanoparticles formation has increased and more clusters of silver nanoparticles were formed during the same time. It was corre-

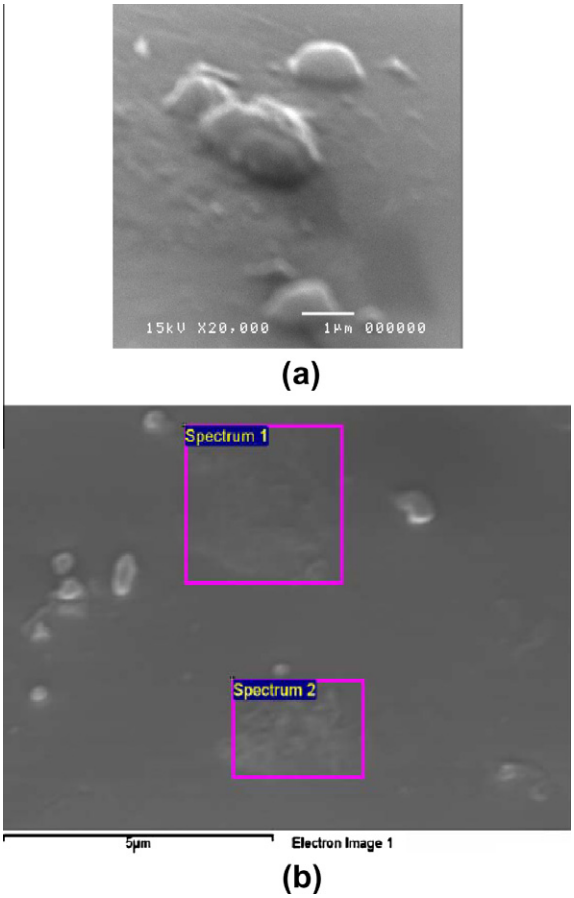

Fig. 3. SEM micrograph of SE6-2: (a) using SEM Jeol JSM 5410 LV and (b) using FE-SEM Hitachi S-4800.