

Selenium ruby lead-free high refractive index glass prepared from local sand

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Most of high refractive index glasses are lead containing glasses. Because of its toxicity and considering the environmental issues as well as the human beings, lead becomes less favorable for utilization in glass production and lead free or leadless glasses have been produced by using other elements such as barium (Ba) and bismuth (Bi) to replace lead. In this work, the colorless lead-free high refractive index glasses were prepared in the laboratory scale, using the main compositions of local sand from Tak site and barium carbonate that used for replacing lead oxide. Prior to melt, selenium powder (Se) and cadmium sulfide (CdS) can be added in order to produce red colored glasses. Well-mixed and dried powders mixtures were melted in a ceramic crucible, in an electric furnace, at temperature about 1250 °C for 4 hr and primary glasses were yielded after cooling down. The physical and optical properties of the transparent and bubbles-free glass samples were measured. It was found that the density and the refractive index were increased as the increase of the concentration of Se and CdS. It was also found that the red colored glass could be obtained with the doping ratio of Se and CdS was 8:1. The modification and the morphology of glass structure were also studied.

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1. Introduction

Colored glasses can be prepared by different ways; one is in the bulk that is a common way to control the color of glass by adding colorants to the batch compositions. The hue and intensity of coloration are determined by the additive and concentration. This coloration may also be controlled by the glass structure and processing parameters. Gold ruby glass is usually prepared in the lead or acetate glass batch. The use of gold can be limited in its use by one factor alone, that of cost for the salts. There is also another point to consider when using gold that is in controlling the conditions and need to product the exact desired color in the finished article [1-8].

The addition small amounts of selenium powder (Se) and cadmium sulfide (CdS) into glass can produce bright transparent glasses with color ranging from intense yellow through to ruby red that called selenium ruby, depending upon the Se and CdS ratio. This red ruby has excellent light transmission in the red part of the spectrum with a sharp cut-off of the colors. Selenium ruby glasses are used to colored glasses for standard signal lamp for railway, marine, and other uses [9-12].

Considering the environmental issues as well as the human beings, lead, however, has been known for its toxicity and avoided to use in glass fabrication process. Some other heavy elements such as barium, bismuth, and zirconium have been used to replace lead for the new lead free high refractive index glass production. Up to now, barium compounds seem to satisfy for replacing lead oxide to produce lead free glasses [13].

The previous works found that the zircon sand, the basalt rock, and the quartz sands from various localities in Thailand can be used as a good raw material for the glass production. The refractive indices of the lead-free high refractive index glasses that fabricated from majority of the local sands and barium carbonate are very close to those of the lead crystal glasses [14-17]. In this work, Se and CdS were doped into the glass mixtures that prepared from the majority of the local sand and barium carbonate. The physical and optical properties were determined.

2. Experimental

The lead free glass samples were prepared in the laboratory scale. The seven glass samples with 150 g weight each were made with the primary glass mixtures with the refractive index of 1.542 that contained with local sand from Tak Province (the by-product from feldspar floatation plant), BaCO₃, K₂CO₃, Na₂CO₃, CaCO₃, Al₂O₃, and B₂O₃. Se and CdS were added into the primary glass as the colorant. The concentration of CdS was fixed at 1 wt% and the ratios of Se and CdS were varied as 1:1, 2:1, 4:1, 6:1, 8:1, and 10:1. Well-mixed and dried powders mixtures were melted in a ceramic crucible, in an electric furnace, at the maximum temperature of 1250°C for 4 hr dwelling time, poured into a cylindrical metal mould, and then cooled down to room temperature.

The color descriptions were carried out using the Color portable set; GIA Gem Instruments 324 GIA GemSet, in terms of the hue, tone, and saturation.

The density of the glass samples was measured in water by the Archimedeian buoyancy method at 25°C, using the analytical balance; Mettler Toledo AG104.

Prior to measure the refractive index, the surface of the glass samples was ground and then polished to a mirror finish with a 0.3 μm alumina paste. Refractive indices were determined using the refractometer; Rayner Duplex II with a refractometer fluid $n_D \leq 1.79$, operated at room temperature by using the sodium light. The absorption spectrum was recorded by UV-Vis-NIR spectrometer; Perkin Elmer Lambda 900, operated in a spectrum range 300-800 nm, with the wavelength accuracy was ± 0.8 nm in UV-Vis range. Phase identification was conducted on powder samples by X-ray diffraction (XRD) analysis and measurements were performed on the diffractometer; Jeol JDX-7E, operated in the 2θ angle between 10-58° with a scanning speed of 4°/min at 40 kV and 15 mA.

3. Results and discussion

Once the melting process was completed, the transparent and bubbles-free glass samples were obtained.

Fig. 1 provided representative visible spectra as a function of the varying Se to CdS weight ratio. As the ratio was increased as 1:1 to 8:1 in these compositions, the color changed from yellow to red, consistent with an increase in the wavelength of absorbance maximum. The absorption band at 527 nm was broadened somewhat at the higher concentration of selenium, and the peaks were shifted slightly to a longer wavelength.

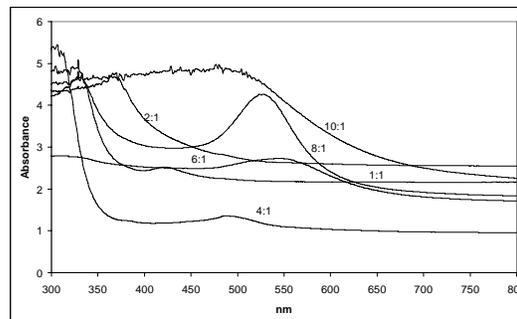


Fig. 1. The visible spectra of the prepared lead free glasses doped with various ratios of Se and CdS.

From the study, the doping ratio of Se and CdS less than 2:1 provided glasses that were yellow, less than 4:1 resulted the orange glasses, between 6:1 to 8:1 showed the red glasses, especially at 8:1 formed strong red color in glasses, and 10:1 produced the brown glasses, detailed in Table 1.

The density of the glass samples was found to be 3.0701 to 3.2317 g/cm^3 . The measured values of refractive index were 1.568 to 1.615, as shown in Table 2. It was found that the densities and the refractive indices were increased linearly as the increase of the additional amounts of selenium, as illustrated in Fig. 2(a) and 2(b), respectively.

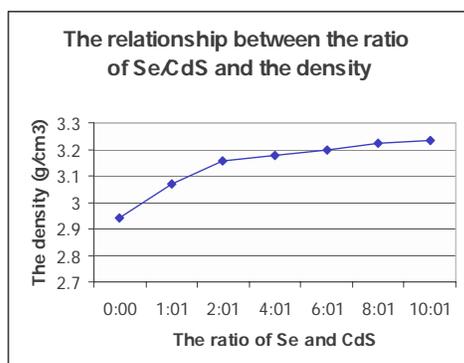
Table 1 The color descriptions and the absorption peaks of the prepared lead free glasses doped with various ratios of Se and CdS.

Glass sample	Ratio of concentration (wt%)		Color description code; tone, saturation, hue	Absorption peak nm
	Se	CdS		
1	-	-	Colorless	-
2	1	1	gY2/3; very light, very slightly brownish, greenish yellow	422
3	2	1	gY5/3; medium, very slightly brownish, greenish yellow	483
4	4	1	O2/3; very light, brownish, orange	490
5	6	1	R5/1; medium, brownish, red	543
6	8	1	R5/4; medium, moderately strong, red	527
7	10	1	yO7/4; dark, moderately strong, yellowish orange	-

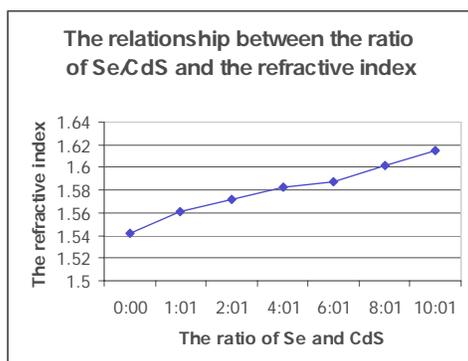
Table 2. The values of the density and the refractive index of the prepared lead free glasses doped with various ratios of Se and CdS.

Glass sample	Ratio of concentration		Density at 25°C g/cm^3	RI at 589 nm
	Se	CdS		
1	-	-	2.9432	1.542
2	1	1	3.0701	1.568
3	2	1	3.1546	1.572
4	4	1	3.1783	1.583
5	6	1	3.1983	1.587
6	8	1	3.2231	1.602
7	10	1	3.2317	1.615

The diffraction patterns of the lead-free high refractive index glasses doped with various ratios of Se and CdS showed in Fig. 3. The amorphous nature of various ratios was confirmed by XRD.



(a)



(b)

Fig. 2. The relationship between the density, the refractive index, and the ratio of Se and CdS doped in the prepared lead free glasses.

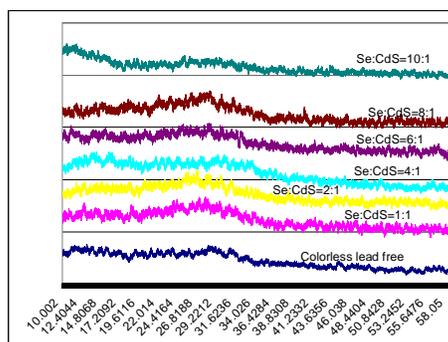


Fig. 3. The XRD patterns of the prepared lead free glasses doped with various ratios of Se and CdS.

4. Conclusion

A variety of the prepared glasses could be produced both in terms of clarity and color. The effects of concentrations of selenium and cadmium sulfide on the lead-free high refractive index glasses which were fabricated by adding with barium carbonate instead of lead oxide are the change not only in the density and the refractive index, but also in the color. The relationship between the density, the refractive index, and the

concentration of selenium and cadmium sulfide dissolved in the glass samples are linear. The colors are also changed from yellow to brown. The selenium ruby glass could be obtained with the doping ratio of Se and CdS is 8:1. The red selenium lead-free high refractive index glass is one of the environmental friendly materials.

Acknowledgements

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