Chiang Mai J. Sci. 2017; 44(3): 1083-1090
http://epg.science.cmu.ac.th/ejournal/
Contributed Paper

UV-vis Spectroscopic and Dielectric Properties of Bismuth Borosilicate Glasses Doped with Potassium Chromate

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Received: 12 February 2015
Accepted: 8 June 2015

ABSTRACT

Bismuth borosilicate glasses doped with various amounts of potassium chromate (Cr doping) were prepared by a normal melt quenching technique. The glass texture was clear and bubble free and the glass colors changed from light green to opaque green with increased Cr doping. The glass density was found to vary with Cr doping, and the maximum density of about 3.34 g/cm^3 was obtained in the specimen doped with 0.5 mass% Cr. The UV-Vis spectra of Cr doped glass showed a strong UV absorption with a sharp increase of transmission spectra beyond the so-called cutoff wavelength, and it was found to shift to a longer wavelength from about 397 nm to 506 nm as the Cr doping content increased from 0.02 to 3%. Thecutoff wavelengths of Cr doped glasses and the Cr doping content were found to reflect a logarithmic relationship. Furthermore, the increase of Cr doping was found to affect not only the opacity of the glass but also the shift of the characteristic wavelengths from about 537 nm to 576 nm. Results from dielectric measurement showed that both dielectric constant and loss tangent were rather low, with the values deviating in the range of about 12-23 and 0.1-0.5 at 1 kHz respectively.

Keywords: bismuth borosilicate glass, chromium doping, dielectric, UV-VIS spectra, cutoff wavelength

1. INTRODUCTION

Glasses containing silica, such as fused-silica glass, soda-lime glass, sodium borosilicate glass, lead crystal glass and so on, are the most common types of silicate glasses. In the recent years, many kinds of silica-free glasses have been prepared and studied, e.g. borate glasses [1-6], tellurate glasses [7-12], germanate glasses [13-14] and phosphate glasses [15-17]. From physical properties point of view, most glasses are amorphous materials and possess specific properties which are hard, brittle, transparent and poor electrical conduction at room temperature. The optical, electrical, dielectric and spectroscopic properties of the prepared glasses are the most topics to be studied and discussed. Electrical conductivity of glasses is mostly studied at high temperatures e.g. at 500K in mixed alkali doped cobalt borate glass [18], 526K in lithium sulfoborosilicate glass [19], 550K in bismuth silicate and bismuth germinate glasses [20]. The silver dependent AC conductivity of silver bismuth borate tellurite glasses was observed in the temperature range of 298-645K [21].

Dielectric and optical transmission spectroscopic properties of strontium tetraborate glass containing bismuth titanate with cyclic variation of dielectric properties and the UV cutoff wave length shift due to the increase of the Bi-Ti content have been reported [1]. The shift of the UV cutoff wavelength due to the increase of Na or Mg in alkali and aluminosilicate glasses has also been found [22]. Both cutoff wavelengths in the UV and IR ranges in lithium-barium-lead-bismuth glasses and the shift due to variation of Bi content have been observed [23]. The cutoff wavelength in the visible region at around 500 nm and the temperature dependent dielectric constant and loss tangent of Li-Bi-Ge-W glasses have been reported [24]. A low dielectric constant of about 10 at low frequency (100Hz-100KHz) in Nd doped lead silicate glass has been observed and been found to decrease at high frequency (2.45 GHz) [25]. From the electromagnetic theory, the relationship of the dielectric constant, relative permeability and the refractive index of materials can be written as [26]:

$$n = \sqrt{\varepsilon_r \mu_r} \tag{1}$$

where, n is the refractive index,

ε_r is the dielectric constant and

μ_r is the relative permeability.

For non-magnetic materials, μ_r is one, therefore,

$$n = \sqrt{\varepsilon_r} \tag{2}$$

Emission spectroscopic properties of Cr^{3+} doped phosphate glass and Cr^{+3} doped in silicate glass were reported [15, 27]. At low temperature Cr^{3+} provides green color and the color changes to yellow due to an oxidizing of Cr^{3+} to Cr^{6+} [27]. Bismuth silicate glass doped with some rare earth elements was studied and recommended for fiber laser applications [28]. In this research work, bismuth borosilicate glasses doped with chromium were prepared. Dielectric and UV-VIS spectroscopic properties of the prepared glasses are investigated and discussed.

2. MATERIALS AND METHODS

Bismuth borosilicate glasses doped with potassium chromate (Cr doping) were prepared using reagent-grade chemicals with a fixed mol% composition of $62SiO_2$ - $10Na_2CO_3$ - $2KNO_3$ - $12K_2CO_3$ - $7B_2O_3$ - $7Bi_2O_3$ and doped with 0.02 to 10 mass% K_2CrO_4. The sodium composition used in these experiments was higher than that in normal borosilicate glass but lower than that in soda-lime glass. The high sodium and potassium levels were added in order to lower the melting temperature. The mixtures were heated at 1250°C for 4 hours using an electric furnace and left in the furnace for annealing and cooling to room temperature. The small glass specimens were crushed down to a millimeter size for density measurement using the Archimedes principle. The glass specimens for further measurement were shaped into thin plate glasses by re-melting and then pressing into a thin plate with a thickness of about 1 mm and annealing at 500°C for 10 minutes.

The thin plate glass specimens for optical and dielectric measurements were ground and polished on both surfaces to a mirror finish. Optical transmission spectra were recorded at room temperature using the Varian Cary 50 UV-Vis spectrophotometer working in the spectrum range of 300-800 nm. Both sides of the glass specimens for dielectric measurement were coated with a high-purity silver paste (SPI 5002) and measured by using the Agilent 4284A precision LCZ meter in the frequency range of 100 Hz-1 MHz at room temperature.

3. RESULTS AND DISCUSSION

The prepared glass texture was homogeneous, clear and free of bubbles. The color tone of the Cr doped glasses varies from pale green to dark green depending on the Cr doping content as the real image shown in Figure 1. The green color arises from the oxidation state of Cr^{+3} and is similar to that found in [27].

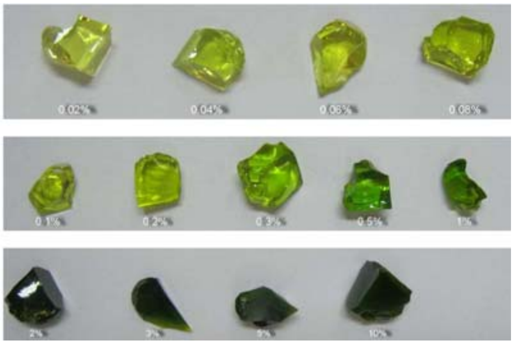

Figure 1. Real images showing color tone of bismuth borosilicate glasses doped with various amounts of Cr.

Figure 2 shows the density of glasses, which is found to increase with an increase of the Cr doping content from 0.02 to about 0.5 %. This is because the Cr atom is heavier than others in the glass structure (except Bi). The highest density of 3.34 g/cm^3 is obtained in the specimen containing 0.5% Cr, and decreasing of the glass density at higher Cr doping beyond 0.5% is expected to occur due to the glass structure expansion.

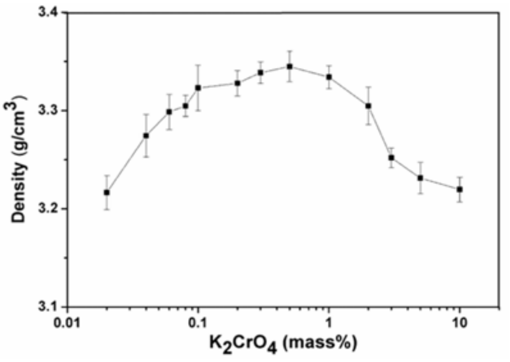

Figure 2. Variation of glass density with various amount of Cr doping content.

The UV-Vis transmission spectra in the wavelength range of 300-800 nm are shown in Figure 3. The transmission spectra are similar to those observed in colored organic-inorganic coating on glass but with different colors and cutoff wavelengths [29]. The spectra of all Cr doped glasses show strong UV absorption, which occurs as the curves of zero transmission and the sharp increase of transmission spectra beyond the so-called cutoff wavelengths are observed. As the Cr doping content increases, the cutoff wavelength shifts to the longer wavelength or to the violet light. This means that the glasses with high Cr doping absorb not only the UV light but also the violet or blue lights depending on the percentage of Cr doping. Due to the high number of glass specimens prepared in these experiments, the dashed line parallel to the base line at 10% transmission was drawn in order to indicate the spectrum lines at the intercepts with the number from (1) to (13) corresponding to the spectrum of each specimen with the specific Cr doping content. The order details of the cutoff wavelengths of each specific Cr doped glass are indicated in Figure 3, and they are in order with the increase of the Cr doping content. The cutoff wavelengths in this work are determined from the tangential line of the linear steep slope of the transmission spectra to the base line at zero transmission. This work found that the increase of Cr doping results in the increase of the cutoff wavelength, the characteristic wavelength, but the decrease of the maximum transmittance (Tmax) as shown by the curves in Figure 4. The curve of the cutoff wavelength and the Cr doping content in Figure 4(a) indicates a logarithmic relationship. The cutoff wavelengths increase from about 397 nm to 506 nm as the Cr doping increases from 0.02 to 3 %, and the cutoff wavelengths are in a similar range to those found in strontium tetraborate glasses [1] and in Li-Ba-Pb-Bi glasses [23]. The minimum Cr doping of 0.02% in bismuth borosilicate glass of this work provides a very light transparent green color, but it still shows a strong UV absorption with a cutoff wavelength of about 397 nm. In the curve illustrating the cutoff wavelength and the Cr doping content, a logarithmic relationship between the cutoff wavelength and the percentage of Cr doping with an R^2 value of 0.965 is observed and can be written as

$$\lambda_C = 360+24\ \ln(200x) \qquad (3)$$

where λ_C is the cutoff wavelength, and x is the mass percentage of Cr doping.

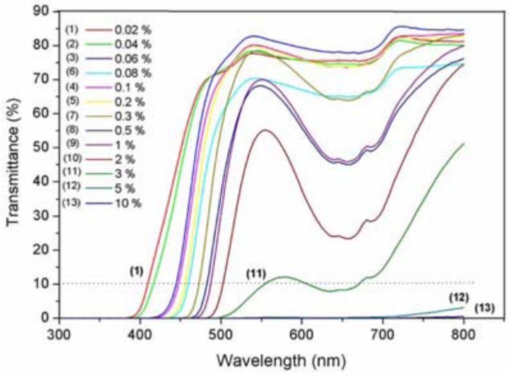

Figure 3. UV-Vis spectra of bismuth borosilicate glasses doped with various amounts of Cr from 0.02 to 10 % in the wavelength range of 300-800nm.

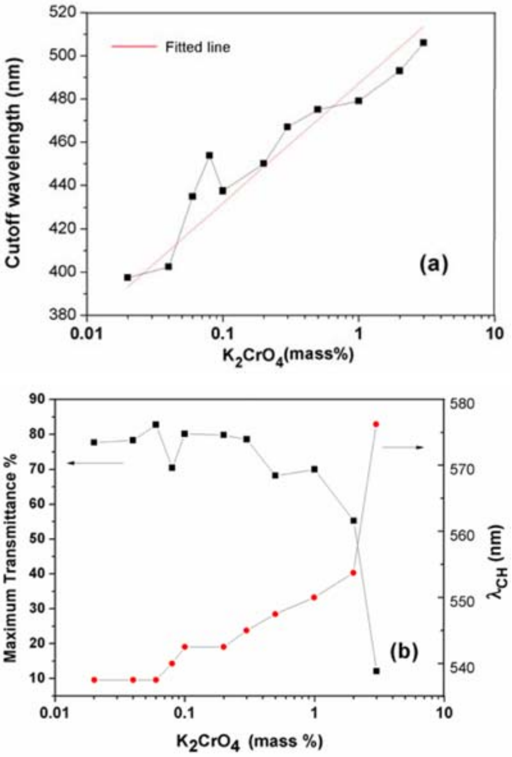

Figure 4. Effects of variation of the Cr doping content on (a) cutoff wavelength (b) maximum transmittance and characteristic wavelengths.

All glasses with various Cr doping show maximum peaks of transmission determining the green color of glass with the central wavelength of about 550 nm and denoted as the characteristic wavelength (λ_{CH}). Primary effects from increasing of the Cr doping content result in an increase of the Cr^{3+} and then the glass opacity which can be seen as the decrease of the overall transmittance of each specimen. Results from increasing of the Cr doping content give rise to the more evident decrease of transmittance in the wavelength range of 600-700 nm which subsequently results in the different shade of green color. The low transmittance in this range occurs due to the absorption band caused by Cr^{3+} which, in fact, there are three individual absorption bands in this wavelength range [30]. The results agree well with that found in soda-lime-silica glass doped with 0.23 mol % Cr_2O_3 [30]. Secondary effects from the decrease of transmittance are the shift of the cutoff wavelength from about 397 nm to 506 nm and the shift of the characteristic wavelength from about 537 nm to 576 nm. When the Cr doping content increased, the decrease of the overall transmittance including Tmax at the characteristic wavelength of each glass specimen is observed. The percentage of Tmax and the characteristic wavelengths plotted versus various amounts of Cr doping are shown in Figure 4(b) and found to be an inverse relationship. At the Cr doping content higher than 3%, the opacity increases and light properties become hardly to investigate.

Figure 5 shows the simulated UV-Vis transmittance spectra versus wavelength at the low end close to the cutoff wavelength by using the Gaussian function calculated with various Tmax values and a constant λ_{CH}. From the simulated spectra, it is seen that the decrease of transmittance in conjunction with broadening effect of spectra gives rise to the shift of the cutoff wavelengths as indicated by λ_{C1}, λ_{C2} etc. Glass colors, maximum transmittance, cutoff and characteristic wavelengths of glasses with various amounts of Cr doping are summarized in Table 1.

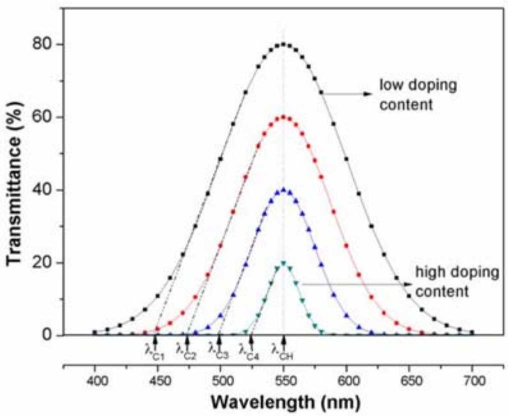

Figure 5. Simulation of the transmittance lowering effect of characteristic wavelengths on the cutoff wavelength shift.

Table 1. Glass colors, maximum transmittance, cutoff and characteristic wavelengths of glasses with various amounts of Cr doping.

Cr (mass%)	Colors	Maximum Transmittance (%)	Cutoff wavelength (nm)	Characteristic wavelength (nm)
0.02	Light green 1	77.7	397.5	537.5
0.04	Light green 2	78.3	402.5	537.5
0.06	Light green 3	82.7	435	537.5
0.08	Light green 4	70.4	453.7	540
0.1	Light green 4	80.1	437.5	542.5
0.2	Light green 4	79.8	450	542.5
0.3	Green 5	78.6	467	545
0.5	Green 6	68.2	475	547.5
1	Green 7	69.9	479	550
2	Dark green 8	55.2	493	553.7
3	Dark green 9	12.1	506	576.2
5	Dark green 10 (almost opaque)	-	-	-
10	Dark green 10 (almost opaque)	-	-	-

The dielectric constant (ε_r) of glasses doped with various amounts of Cr in the frequency range of 100 Hz to 1 MHz is shown in Figure 6. An value of about 12-23 at 1 KHz is obtained, and higher deviation is observed at a lower frequency. The value in this work is slightly higher than that of the soda-lime glass with the value of about 7 at a frequency lower than 1 MHz [31]. At high frequency, the fluctuation of the values decreases; however, the values are not in order with the increase of the Cr doping content, which is rather different from the order of the cutoff wavelength with Cr doping as discussed above. The behavior of curves of versus frequency of each specimen with specific Cr doping is indicated using the number from (1) to (13) at the intercepts with the vertical dashed line at 5 KHz, as shown in Figure 6. The curves of the plotted against Cr doping contents are shown in Figure 7. From the measured dielectric constant and the relationship to the refractive index in Eq. (1), the corresponding refractive indices at 1 KHz in the range of 3.46 to 4.79 are obtained. These values are rather high when compared with that obtained from optical measurement with the value of about 1.61 at 589 nm. The lost tangent (tan δ) of the same glass specimens plotted against frequencies is shown in Figure 8, with high values and high deviations at low frequency. At 1 kHz, is found to deviate in the range of 0.1-0.5 and decrease with the increasing of frequency. The behavior of curves of versus frequency of each specimen with specific Cr doping is also indicated using the number from (1) to (13) at the intercepts with the vertical dash line at 500 Hz as shown in Figure 8.

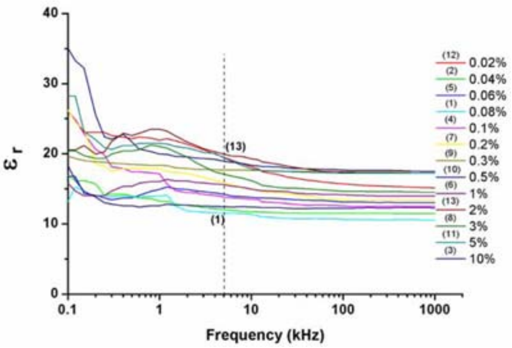

Figure 6. Dielectric constant versus frequency of Bi borosilicate glasses doped with various amounts of Cr.

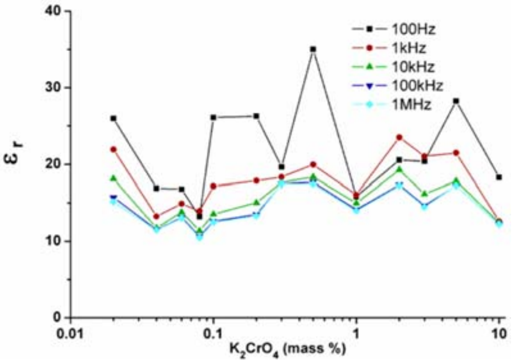

Figure 7. Dielectric constant of glass at different frequencies plotted against Cr doping content.

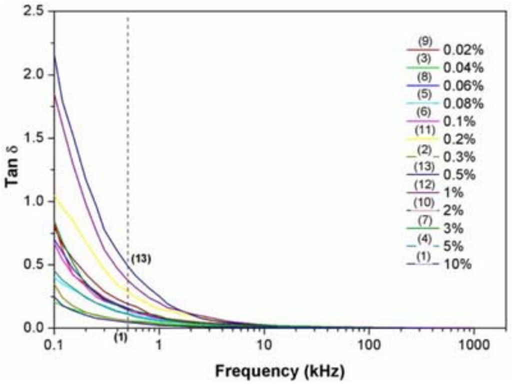

Figure 8. Loss tangent versus frequency of Bi borosilicate glasses doped with various amounts of Cr.

4. CONCLUSIONS

Bismuth borosilicate glass samples with a relatively high Cr doping of up to 10 mass% were successfully fabricated with a clear and bubble-free texture. All Cr doped glass specimens are green with the central wavelength of about 550 nm and the color tone changes from light green to dark green with an increase of the Cr doping content. The maximum transmittance from UV-Vis spectra which dominates the green color indicates not only an increase of the opacity of Cr doped glasses but also the characteristic wavelength shift from about 537 to 576 nm. Chromium doping in all glasses results in strong UV absorption, and the increase of Cr doping content from 0.02 to 3% shifts the onset of the cutoff wavelength to the longer wavelengths, from about 397 to 506 nm. The decrease of transmittance in conjunction with spectrum broadening is found to result in the shift of the cutoff wavelengths. The cutoff wavelengths and Cr doping are found to be in a logarithmic relationship with an R^2 value of 0.965. High deviations of both dielectric constant and loss tangent are observed at low frequency, and the values deviated in the range of about 12-23 and 0.1-0.5 at 1 kHz respectively. From the measured dielectric constant at 1 kHz, the corresponding refractive indices of about 3.46 to 4.79 are obtained.

ACKNOWLEDGEMENTS

This research work was partially supported by the Graduate School, Chiang Mai University and also partially supported by Thailand's Office of the Higher Education Commission under the National Research University Project. The authors would like to thank Mr. Joel N. Akins for his kind assistance in the preparation of the manuscript.

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