Optical Properties of Opal Glass on the Various Contents of Chemical Composition

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Abstract Opal glass samples having different chemical compositions were synthesized and transparent glass was obtained after melting. The effects of TiO_2 , BaF_2 , and CeO_2 content on the color of the opal glass were studied by observing images of the opal samples and analyzing the results via ultraviolet visible spectroscopy and color spectrometry. The aesthetic properties of the opal glass were determined by studying the transmittance of visible light in the 400 nm to 700 nm range. The basic chemical composition of opal glass was SiO_2 52.9 wt%, Al_2O_3 12.35 wt%, Na_2CO_3 15.08 wt%, K_2CO_3 10.35 wt%, $\text{Ca}_3(\text{PO})_4$ 4.41 wt%, MgCO_3 1.844 wt%, LiCO_3 2.184 wt%, and TiO_2 0.882 wt%. The glass samples were prepared by varying the weight percentage of TiO_2 , BaF_2 , and CeO_2 . The transmittance of visible light was decreased from 95 % to 75 % in the glass samples in which TiO_2 content was increased from 0 to 3.882 wt%. In the blue spectrum region, as the content of TiO_2 increased, the reflectance value was observed to become higher. This implies that TiO_2 content induces more crystal formation and has an important effect on the optical properties of the glass. The opalescence of opal samples that contained CeO_2 or BaF_2 is stronger than that in the samples containing TiO_2 . Opal glass samples comprising TiO_2 had tetragonal lattice structures; samples including CeO_2 as an additive had cubic lattice structures (FCC, CeO_2).

Key words opal glass, TiO_2 , BaF_2 , CeO_2 , optical properties.

1. Introduction

Recently, the development and synthesis of Opal glass has attracted a great deal of attention because of its optical properties.¹⁻³⁾ Opal glasses are desirable for consumer product applications, such as tableware and are widely used in dental application and jewel fields. The artificial Opal mainly contains silicate nano sized spheres ordered in a hexagonal or cubic close-packed lattice. The interference and diffraction of light passing through the microstructure of the Opal produces the internal colors.⁴⁾ The propagation of electromagnetic waves of certain energy is thus forbidden due to the strong diffraction of light by the sphere planes (partial or total suppression of the photon density of states).^{5,6)} This property leads to their application in a wide range of products, such as novel chemical and biological sensors or low threshold laser design, etc.⁶⁾ It has already been shown that optical properties of opal glass are influenced by their structural parameters, chemical

composition, the defect density and the refractive index contrast inside the photonic crystal.^{1,7,8)}

Some investigators have shown the effect of composition and heat treatment on the microstructure, and the optical properties of opal glasses.^{2,9,10)} It has also been shown that the addition of RO oxides ($R = \text{Ti}, \text{Ca}, \text{Na}, \text{Al}, \text{Ba}, \dots$) to silicate glasses, though is essential for enhanced opacity, may generally be detrimental for chemical durability.¹¹⁾

In this paper, a systematic effort is made to show and compare the effect of Titanium Dioxide (TiO_2), Barium Fluoride (BaF_2), and Cerium Dioxide (CeO_2) additions on optical properties of Opal glass. Titanium oxide or Cerium oxide has been commonly recognized as the most important candidates of opal glasses due to its high chemical stability, with wide applications in photovoltaic cell, photocatalysis, and catalytic supports.⁴⁾ The important role of TiO_2 , BaF_2 and CeO_2 are well known for the nucleation and crystalline growth,^{12,13)} which induce more crystal

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formation and is the main reason causes opalescence property of glass. Due to opalescence is caused by the reflection of short wavelength light, which is affected by crystal formation in the glass structure. Therefore, this experiment applied chemical additives such as TiO_2 , BaF_2 and CeO_2 to investigate the optical properties of Opal glass.

2. Experimental Procedure

In the present investigation, the main purpose is synthesis of opal glass and studying the effect of chemical compositions such as TiO_2 , BaF_2 and CeO_2 on optical properties of opal glass. The basic chemical composition of opal glass was SiO_2 52.9 wt%, Al_2O_3 12.35 wt%, Na_2CO_3 15.08 wt%, K_2CO_3 10.35 wt%, $\text{Ca}_3(\text{PO})_4$ 4.41 wt%, MgCO_3 1.844 wt%, Li_2CO_3 2.184 wt% and TiO_2 0.882 wt%. The chemicals in the SiO_2 - Al_2O_3 - Na_2CO_3 - K_2CO_3 - $\text{Ca}_3(\text{PO})_4$ - MgCO_3 - TiO_2 - BaF_2 - CeO_2 system were prepared, varying the weight percentage of TiO_2 , BaF_2 and CeO_2 , one at a time, while other additive components kept constant or changed slightly.

The experiment was carried out in three groups to study the effect of each of the three chemicals :

- + Group 1: Effect of Titanium Oxide(TiO_2)
- + Group 2: Effect of Barium Fluoride(BaF_2)
- + Group 3: Effect of Cerium Oxide(CeO_2)

The compositions of samples were listed in following Table 1, Table 2 and Table 3. The opal glass was prepared by the conventional solid state method. The process to prepare opal glass is schematically illustrated in Fig. 1. Each sample had the final mass of 10 gram. The experiment was carried out with 15 samples for 3 groups(5 samples per group). One important thing to pay attention is the weight percentage of TiO_2 , BaF_2 and CeO_2 .

The stoichiometric composition of opal glass was first mixed in ethanol for 1 hour using the pestle and the mortar. Then the mixture was dried at 100°C in a drying oven(SW-90D Sangwoo scientific company). Next the mixtures were put into a Platinum crucible (50 cc) and carefully placed into the chamber of an electrical furnace(CBF-S001).

The mixed powder was then melted at 1500°C for around 60 minutes in the electrical furnace(Set up speed of melting : $5^\circ\text{C}/\text{minute}$). After the melting process, samples were taken out using the gloves and protective glasses. Water quenching was conducted after the melt. The opal

Table 1. Chemical composition of experiment samples of group 1 (weight percent and mole percent).

Chemical composition	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	% wt	% mole	% wt	% mole	% wt	% mole	% wt	% mole	% wt	% mole
SiO_2	53.4	68.57	52.9	68.41	51.9	67.81	51.9	67.98	51.4	67.5
Al_2O_3	12.73	9.63	12.35	9.328	12.35	9.407	12.00	9.263	11.85	9.147
Na_2CO_3	15.18	11.02	15.08	11.04	15.08	11.13	14.53	10.79	14.58	11.19
K_2CO_3	10.25	5.722	10.35	5.83	10.35	5.879	10.25	5.837	10.00	5.713
$\text{Ca}_3(\text{PO}_4)_2$	4.41	1.095	4.41	1.105	4.41	1.114	4.41	1.119	4.26	1.083
MgCO_3	1.844	1.691	1.844	1.706	1.844	1.721	1.844	1.721	1.844	1.731
Li_2CO_3	2.186	2.272	2.184	2.291	2.184	2.314	2.184	2.326	2.184	2.326
TiO_2	0	0	0.882	0.29	1.882	0.625	2.882	0.959	3.882	1.297
Sum %	100		100		100		100		100	

Table 2. Chemical composition of experiment samples of group 2 (weight percent and mole percent).

Chemical composition	Sample 6		Sample 7		Sample 8		Sample 9		Sample 10	
	% wt	% mole	% wt	% mole	% wt	% mole	% wt	% mole	% wt	% mole
SiO_2	61.0	69.93	60.5	69.63	60.0	69.32	59.5	68.99	59.5	69.095
Al_2O_3	14.5	9.774	14.5	9.808	14.5	9.843	14.5	9.88	14.0	9.552
B_2O_3	6.0	6.073	6.0	6.094	6.0	6.116	6.0	6.142	6.0	6.151
Na_2O	9.0	9.98	9.0	10.01	9.0	10.05	9.0	10.09	9.0	10.109
K_2O	4.0	2.928	4.0	2.939	4.0	2.949	4.0	2.962	4.0	2.966
$\text{Ca}_3(\text{PO}_4)_2$	5.0	1.11	5.0	1.114	5.0	1.118	5.0	1.123	5.0	1.124
CeO_2	0.5	0.2	0.5	0.2	0.5	0.201	0.5	0.202	0.5	0.203
BaF_2	0	0	0.5	0.197	1.0	0.396	1.5	0.596	2.0	0.797
Sum %	100		100		100		100		100	

Table 3. Chemical composition of experiment samples of group 3 (weight percent and mole percent).

Chemical composition	Sample 11		Sample 12		Sample 13		Sample 14		Sample 15	
	% wt	% mole	% wt	% mole	% wt	% mole	% wt	% mole	% wt	% mole
SiO ₂	60.5	69.63	60.25	69.47	60.0	69.32	59.75	69.14	59.75	69.242
Al ₂ O ₃	14.5	9.809	14.5	9.826	14.5	9.843	14.5	9.868	14.25	9.663
B ₂ O ₃	6.0	6.095	6.0	6.105	6.0	6.116	6.0	6.131	6.0	6.133
Na ₂ O	9.0	10.01	9.0	10.03	9.0	10.05	9.0	10.07	9.0	10.08
K ₂ O	4.0	2.939	4.0	2.944	4.0	2.949	4.0	2.957	4.0	2.958
Ca ₃ (PO ₄) ₂	5.0	1.114	5.0	1.116	5.0	1.118	5.0	1.121	5.0	1.121
BaF ₂	1.0	0.395	1.0	0.395	1.0	0.396	1.0	0.397	1.0	0.397
CeO ₂	0	0	0.25	0.10	0.5	0.201	0.75	0.303	1.0	0.404
Sum %	100		100		100		100		100

Fig. 1. Schematic representation of processing steps for the synthesis of opal glass.

samples were dried in the drying oven at 60 °C and then taken out of the crucible. The opal powders was made

from the quenched glass by using pestle and mortar.

The opal powders thus made were characterized. The crystal structure by measurement of X-ray diffraction (XRD, CuK α_1 radiation($\lambda = 0.15406$ nm), D1w, Shimadzu, Japan) over the 2θ range of 20° to 80° at a scan rate of 2°/min. Besides, particle size and morphology were observed by transmission microscopy TEM(Sirion, FEI, Netherland). The optical properties and transparency of opal glass was measured by using the Ultraviolet visible spectroscopy and Color spectrometer.

3. Results and Discussion

The chemical composition of opal glass as shown in Table 1, Table 2 and Table 3 were prepared to form group 1, 2 and 3 respectively. Fig. 1 shows schematic representation of processing steps for the synthesis of opal glass and the photo images of opal glass samples after quenching are shown in Fig. 2. Effect of TiO₂, BaF₂, CeO₂ on color of opal glass was observed through the optical images of the samples. The color of opal glass changes with corresponding change in the content of TiO₂, BaF₂ and CeO₂. This was confirmed by the observations carried out by the naked eyes. In particular, the samples which contain the highest TiO₂, BaF₂ and CeO₂ content have shown color changes more apparently than other samples that include lower additive content. In addition, the changes of color are more prominently observed and analyzed by ultraviolet visible spectroscopy, color spectrometer and transmission microscopy(TEM).

3.1 XRD measurement

X-ray diffraction pattern was studied to investigate the effect of additive on opal glass and to determine the crystal structure. XRD patterns collected from opal samples in group 1, group 2 and group 3 is shown in Fig. 3, 4 and 5, respectively. In XRD results, opal powders basically appears to be in non-crystalline form. This clearly shows

Fig. 2. The images of opal glass sample after quenching.

that opal powders are amorphous regardless of the kind of additives and its content.

In the vicinity of $2\theta \approx 12-13^\circ$ in Fig. 3, the XRD

pattern of opal samples belonging to group 1 shows wide width and asymmetric peak. Amorphous structure was observed in all the groups, however, different peaks were

Fig. 3. XRD patterns of opal powder samples obtained at various TiO_2 content (group 1); (a) 0% mole, (b) 0.29% mole, (c) 0.6251% mole, (d) 0.959% mole and (e) 1.297% mole TiO_2 .

Fig. 4. XRD patterns of opal powder samples obtained at various BaF_2 content (group 2); (a) 0% mole, (b) 0.197% mole, (c) 0.396% mole, (d) 0.596% mole and (e) 0.797% mole BaF_2 .

Fig. 5. XRD patterns of opal powder samples obtained at various CeO_2 content (group 3); (a) 0% mole, (b) 0.1005% mole, (c) 0.201% mole, (d) 0.303% mole and (e) 0.4042% mole CeO_2 .

observed by varying contents of TiO_2 , BaF_2 and CeO_2 .

3.2. UV transmittance measurement

The samples were optically characterized. Transmittance measurements are the best way to evaluate the quality of photonic crystals. Transmittance is the fraction of incident light (or other electromagnetic radiation) at a specified wavelength that passes through a sample. UV transmittance spectra for opal powder (15 samples) are shown in Fig. 6, Fig. 7 and Fig. 8.

UV transmittance spectra was recorded in Fig. 6 at different chemical composition of 5 samples in group 1 which was intended to investigate the effect of Titanium oxide (TiO_2). The effect of TiO_2 on opal microstructure was clearly compared in sample 5 and sample 1, with 1.297 mole% of TiO_2 composition and without TiO_2 , respec-

Fig. 6. UV transmittance spectra of 5 opal samples obtained at various TiO_2 content (group 1); (a) 0% mole, (b) 0.29% mole, (c) 0.6251% mole, (d) 0.959% mole and (e) 1.297% mole TiO_2 .

tively in Fig. 6. It is clearly seen that the sample 5 which contain 1.297 mole% of TiO_2 shows the transmittance maximum (96 %) in range of visible light wavelength (400-700 nm). However, in the wavelength range of 200 nm to 400 nm, transmittance of samples in group 1 tend to show the convex spectrums from 95 % to 10 %.

Functional opals prepared by TiO_2 additive where the play of color reflected strongly in the far ultraviolet and blue region of 200~400 nm but reflections of the red and green region were very poor. In blue spectrum region, as the content of TiO_2 increases, the reflectance value was observed to be higher in the wavelength region. This result and the Opal images in Fig. 2 proved the role of TiO_2 additive on opalescence property of the glass. Opalescence phenomenon usually occurs in the blue spectrum and is caused by the reflection of short wavelength light. However, the structural pattern of Opal is the reason of

Fig. 7. UV transmittance spectra of 5 opal samples obtained at various BaF_2 content (group 2); (a) 0% mole, (b) 0.197% mole, (c) 0.396% mole, (d) 0.596% mole and (e) 0.797% mole BaF_2 .

Fig. 8. UV transmittance spectra of 5 opal samples obtained at various CeO_2 content (group 3); (a) 0% mole, (b) 0.1005% mole, (c) 0.201% mole, (d) 0.303% mole and (e) 0.4042% mole CeO_2 .

opalescence phenomenon thus the reflection of short wavelength.

One more apparent thing is the difference between the spectrum in group 1 and other group. There is a constant and high transmittance at around 300 nm in group 2 and group 3, the end of the UV range and the beginning of visible range, which confirms observations carried out by the naked eyes. Fig. 7 shows UV transmittance spectra recorded at different chemical composition of five samples in group 2. A bimodal shape reflectance was observed in the region of 200–450 nm. The peaks with highest reflectance were observed in wavelength of 260 and 350 nm regardless of contents of the additive. The synthesized opal in Fig. 7 showed the transmittance of 70 to 95 % in region of 200–450 nm. However, the reflectance of approximately 40 % and 35 % in range of 260 nm and 350 nm were shown in sample 10 which contained the highest BaF₂ mole percent(0.797 %).

UV transmittance spectra of the samples in group 3 are exhibited in Fig. 8. The noticeable difference between transmittance spectra of Opal sample in 3 groups is the number of peaks was shown in the diagram. Due to the number of peaks were shown as the influence of chemical composition on light propagation in the photonic crystal. In the wavelength range of 200–450 nm, the transmittance spectra of group 1(effect of TiO₂) have only one peak, while those of group 2(effect of BaF₂) and group 3(effect of CeO₂) have 2 shift peaks except the sample 11. This fact is thought to be due to the effect of CeO₂ content. The samples in both group 2 and group 3 that comprise CeO₂ have two spectral peaks and the sample 11 which contains CeO₂ has only one peak spectra. Further observations indicate that, with the increasing content of CeO₂, the reflectance of Opal sample increased and reflected range became wider.

As a consequence, a number of peaks were illustrated as the effect of CeO₂ composition on the light propagation in the photonic crystal. Moreover, the reduction of transmittance led to opalescence feature.

3.3 Color spectrometer measurement

Other method to characterize the morphologies of the Opal samples is the use of color spectrometer. The phenomenon of opalescence or the change of color can be

determined quantitatively with the color spectrophotometer. For this purpose, the L , a , b values were measured in transmission and in reflection on a black base in the photometer. In the L , a , b color system, a positive b value represents the yellow part of the light; on the other hand, a negative b value represents its blue part. The higher the absolute amount, the more intense the color. The color spectral diagram and standard scale units were investigated to observe the change of the color of the samples or to determine the exact color of Opal glass. Graphical representation of the L , a , b color sphere system is shown in Fig. 9.

In the present work, the experiment measured L , a , b values for samples as shown in Table 4. The increase of mole ratio of TiO₂ corresponded to fluctuation of a value and b value while L value changed slightly. Transmittance of sample 5(1.297 mole% of TiO₂ content) was shown as 10 %(Fig. 5) and minimum a value(−0.077), maximum b value(−0.214). Color change of the Opal sample 5 was most clearly expressed in group 1. In addition, the decrease of the transmittance corresponded to the increase of opalescence. Based on the Table 4 and Fig. 7, L values of the samples in group 2 were similar. However, transmittance of sample 10(0.797 mole% of BaF₂ content) was 63 %~68 %, negative a value(−0.104), positive b value(0.21). It implies color change was most apparent in opal sample 10 of group 2. In another case, transmittance of sample 15(0.404 mole% of CeO₂ content) was 65 % and 71 %, negative a value(−0.117) and maximum b value(−0.062). As a result, color change of the opal sample 15 was most apparent in group 3. These results indicate the important role of chemical additives(TiO₂, BaF₂ and CeO₂) in the

Fig. 9. Graphical representation of the Lab color sphere.

Table 4. L , a , b values of opal samples obtained at various TiO₂, BaF₂, CeO₂ content.

Group 1: Effect of TiO ₂	Group 2: Effect of BaF ₂	Group 3: Effect of CeO ₂
Sample 1: $L = 98.298$ $a = -0.013$ $b = -0.383$	Sample 6: $L = 98.314$ $a = -0.022$ $b = -0.385$	Sample 11: $L = 98.226$ $a = 0$ $b = -0.314$
Sample 2: $L = 98.239$ $a = 0.034$ $b = -0.482$	Sample 7: $L = 98.298$ $a = -0.049$ $b = -0.289$	Sample 12: $L = 98.276$ $a = -0.057$ $b = -0.239$
Sample 3: $L = 98.238$ $a = 0.034$ $b = -0.482$	Sample 8: $L = 98.317$ $a = -0.003$ $b = -0.384$	Sample 13: $L = 98.280$ $a = 0.001$ $b = -0.348$
Sample 4: $L = 98.247$ $a = -0.009$ $b = -0.316$	Sample 9: $L = 98.296$ $a = -0.001$ $b = -0.409$	Sample 14: $L = 98.288$ $a = 0.013$ $b = -0.377$
Sample 5: $L = 98.247$ $a = -0.077$ $b = -0.214$	Sample 10: $L = 98.043$ $a = -0.104$ $b = 0.210$	Sample 15: $L = 98.211$ $a = -0.117$ $b = -0.062$

play of color of the glass.

3.4 Schematic illustration of the opal structure

The sample 5 (3.882 % TiO_2) and sample 15 (1 % CeO_2) were characterized by TEM and HRTEM in order to investigate effect of TiO_2 and CeO_2 on crystallization.

BaF_2 was not crystallized after quenching at 1500 °C because the melting point of BaF_2 is 1368 °C. The TEM images of sample 5 and sample 15 are shown in Fig. 10. TiO_2 crystal used as functional additive was observed within amorphous opal glass as shown in Fig. 10A. The size of TiO_2 crystal was 10~20 nm.

Fig. 10. TEM images of the opal powders Opal sample 5 (A, a) and opal sample 15 (B, b).

Fig. 11. HRTEM images of the opal structure and schematic illustration of the opal structure; (a) Tetragonal structure (TiO_2 - rutile) and illustration Tetragonal structure (TiO_2 - rutile) and (b) Face centered cubic structure (CeO_2) and illustration Face centered cubic structure (CeO_2).

The schematic illustration of crystal structures and HRTEM image of TiO_2 within opal powder (sample 5) are shown in Fig. 11a, it can be seen that there are many ordered crystals. These crystals are thought to be of TiO_2 (0.2459 nm). According to schematic illustration, the distance between planes of crystal lattice d value (AH side) calculated using the lattice constant of the tetragonal structure of rutile from plane of (101). As schematic illustration shows, d value is equal to length of AH of triangle ABD. The length of AH was calculated according to congruent triangles (HBA and ABD):

$$\frac{AH}{DA} = \frac{AB}{BD} \rightarrow d = AH = \frac{DA \cdot AB}{BD} = \frac{ac}{\sqrt{c^2 + a^2}} = 2.4640(\text{\AA}) = 0.2460 \text{ nm}.$$

The calculated d value is very similar to that estimated by analysis of the HRTEM image ($d = 0.2459 \text{ nm}$). It means Opal glasses belonging to group 1 have tetragonal lattice structure of TiO_2 (rutile).

Basically, the content of the samples in all the three groups are similar and their remarkable difference is TiO_2 , CeO_2 and BaF_2 content. Therefore, ordered forms of inter-plane distance in crystal structure arrange differently. A schematic illustration representing the cubic structure of CeO_2 and HRTEM image of Opal powder in group 3 are shown in Fig. 11b. The spacing between planes of crystal lattice d value ($d = 5.412/2 = 2.706 \text{ \AA} = 0.2706 \text{ nm}$) calculated using the lattice constant of the face centered cubic structure (FCC) from direction of [010] and plane of (200) is very similar to that estimated by analysis of the TEM image ($d = 0.272 \text{ nm}$). As a result, opal glasses of group 3 have lattice structure of cubic structure.

4. Conclusion

Opal glass having different chemical compositions were synthesized and transparent of glass were obtained after melting. Effect of TiO_2 , BaF_2 and CeO_2 content on color of opal glass was studied by observing images of the Opal samples.

Effect of TiO_2 , BaF_2 and CeO_2 on color of opal samples was also studied by comparing L, a, b scale index. The samples which contain the highest TiO_2 , BaF_2 and CeO_2 (L value min, a min, b max) have the most noticeable color. With the increasing mole of TiO_2 , a decrease in the value of a and rise in the value of b was observed while L value changed slightly. However, effect of CeO_2 is most clear because of the appearance of second spectral peaks.

Opalescence of opal samples in group 2 and group 3 are stronger than that in group 1 because of the shift

peaks. In the wavelength range of 200–450 nm, the transmittance spectra of group 1 (effect of TiO_2) have only one peak, while those of group 2 (effect of BaF_2) and group 3 (effect of CeO_2) have 2 shift peaks except the sample 11. This is because of the CeO_2 content. The samples in both group 2 and group 3 that comprise CeO_2 are having two peaks spectra and the sample 3 which does not include CeO_2 have only one peak spectra. A number of peaks were illustrated as the effect of chemical composition on light propagation in the photonic crystal. This expresses the optical property of Opal glass.

The ordered forms of inter-plane distance in crystal structure arrange differently (d -spacing between planes sized nanometer: 0.246–0.2706 nm). The distance between planes of crystal lattice d value calculated using the lattice constant of the tetragonal structure (rutile, TiO_2) is very similar to that estimated by analysis of the HRTEM image. It implies Opal glasses which belong to group 1 having lattice structure as tetragonal structure and group 3 having lattice structure as cubic structure (FCC, CeO_2).

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