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Effect of Alkaline and Earth Oxides on the Chemical Durability of Borosilicate Opal Glasses Opacified with P_2O_5.

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ABSTRACT

This investigation is disclosed a type of borosilicate opal glasses that provide new compositions of borosilicate glasses, opacified with P_2O_5, which have high chemical durability and low thermal expansion coefficient, with the general composition SiO_2 73.0, B_2O_3 11.70, Al_2O_3 3.30, P_2O_5 1.30, Na_2O (9.6-(X+Y)), CaO (X=0.1-050) and BaO (Y=4.5-2.9)wt%. Effects of Na_2O, CaO and BaO, which are available in glass, were examined in acidic, water and steam leaching, and alkaline corrosion. The results showed ideal properties which were dependent to the limited ratio of Na_2O/ BaO + CaO. This research has been scaled-up in the laboratory successfully and has been registered as patent No. 49441 in 28 June 2008 in Iranian Innovations Organization.

INTRODUCTION

Kunkel (1630-1705) was the first invented borosilicate opacified opal glasses via adding small amounts of bore ash containing calcium phosphate to the glass batch. In addition, arsenates, particularly lead arsenate and other phosphates, have been evaluated to produce "opaque" and "milk" glasses. Usually, about 1-5% mass was sufficient, but occasionally much more has been added. The basic studies about the glasses opacified by phosphates were carried out in 1899-1925 [1,2,3]. Then, the dependence of opacification on heat treatment, effects of additives, and studying mechanism of opacification were studied thoroughly [4,5,6,7]. Vogel in 1964 carried out investigations on the perfectly transparent composition of a specific kind of glass close to the borosilicate glasses by adding CaO and P_2O_5.[1,3]

In commercial borosilicate glasses, chemical durability is the result of phase separation, microstructure, RO oxides, characterization, and industrial production techniques.[8-12] Opal glass, resistant to thermal shock, begins to happen as the improved borosilicate glasses. The mean coefficient of linear thermal expansion of borosilicate opal glasses is the lowest among industrial multi-component glasses along with easy handling and satisfactory chemical durability.[6, 7, 10, 11]

Opacifying with phosphate has numerous advantages for opals resistant to thermal shock. P_2O_5 does not volatilize from the molten, as fluoride ions which corrode refractories; then, the stability and the time of industrial furnace and refractory would be increased. The usage of this formulation has many advantages for the furnace and melting process. Heat resisting opal borosilicate glasses is used for bake ware and other applications, wherein heat resistance and white opal appearance are desired.

In commercial borosilicate glasses for kitchenware, there are some parts of artistic items in which all the pieces have the same thermal coefficient expansion, particularly those having a new luxury in multiple glasses. Furthermore, they would be suitable for coating as stable glass layer and metallic internal body of reservoir for chemical reaction with corrosive reagents in high temperatures.

In this research, a novel type of borosilicate opal glass is provided, with improved chemical and thermal durability characteristics. It has white appearance as a unique color. In the current study, as a systematic effort, effect of Na_2O to BaO and CaO wt% ratio was considered on chemical durability and thermal coefficient expansion of borosilicate opal glasses which are opacified with phosphate.

EXPERIMENTAL SECTION

High purity chemicals Quartz (Carl Roth Gmbh & Co., Ltd., 99%, Germany) and AR grade H_3BO_3, $Al(OH)_3$, Na_2CO_3, $NaPO_3$,$CaCO_3$ and $BaCO_3$ were used as the starting raw materials. At first, to obtain the best glass molten, the general chemical composition, molar ratio, and weight percent of B_2O_3 to SiO_2 (0.13-0.17), molar ratio of B_2O_3 to Al_2O_3 (3.7-5.2), molar ratio of Na_2O to BaO and CaO (3.5-10.4), and P_2O_5 (0.8-1.54 wt %) were selected. After acquiring the best general composition including ideal physical and chemical characteristics, some new specimens with the fixed chemical composition of SiO_2, B_2O_3, Al_2O_3 and P_2O_5 were prepared in which the amount of Na_2O to BaO and CaO were varied as BaO (2.9-4.5wt%), CaO (0.1-1.5wt%), and Na_2O (0.3-0.6wt%). Finally, the composition of SiO_2 (73.0), B_2O_3 (11.70), Al_2O_3 (3.30), P_2O_5 (1.30), NaCl (1.1), Na_2O [9.6-(x+y)], CaO (x= 0.1-1.5) and BaO (Y= 4.5-2.9) wt%, and Sb_2O_3 (<0.06) wt% were selected. The batch composition based on oxides is presented in Table 1.

Table 1: Chemical composition of glass specimens.

sample/oxide	SiO_2	B_2O_3	Al_2O_3	P_2O_5	Na_2O	BaO	CaO
01	73.0	11.70	3.30	1.3	5.0	4.5	0.1
02	73.0	11.70	3.30	1.3	5.0	3.9	0.7
03	73.0	11.70	3.30	1.3	5.3	4.2	0.1
04	73.0	11.70	3.30	1.3	5.3	3.4	0.9
05	73.0	11.70	3.30	1.3	5.6	3.9	0.1
06	73.0	11.70	3.30	1.3	5.6	2.9	1.1

The batch for borosilicate opal glass mostly was contained the components that were added in very small amounts, e.g., sodium meta phosphate, calcium carbonate, and barium carbonate, which must be weighed very carefully. In order to ensure uniform distribution of these batches in laboratory scale, the total dry raw material was mixed in 250 g quantities, divided into some parts, gradually added to Pt crucible, and was melted in an electrical furnace by using a thermal program at 1250-1600 °C for 3 h. Then, the molten glass in the crucible was poured into a plate of Zn/Cu alloy moulds, transferred to an annealing furnace and annealed at 630 ˚C.

Crystalline and non-crystalline glass phases were identified by X-ray diffraction method (XRD). Thermal expansions and glass transition temperature were measured by dilatometry method. The density of samples was measured by Archimedes method [13]. The ISO procedure, designated as 695, 698,719 and 720, was used to determine the chemical durability of glasses in alkaline solutions, acidic solutions, water, and steam [14,15,16,17]. In alkaline and acidic resistance test, the resistances were calculated by the loss in mass per unit area of the glass (mg/dm^2) after 3 h immersion in a boiling alkaline aqueous solution. The same procedure was achieved for acidic resistance by immersion in a boiling aqueous solution for 6 h. In the hydrolytic resistance in water and steam, amount of alkali released into the water at 98 and 121 ˚C was measured after immersion through titration with hydrochloric acid solutions.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the first glass samples (1-7) and the specimens (01-06) are presented in Figure 1. One large and broad peak around $2\theta=23°$ was observed in all of the patterns with similar amount and concentration. This feature is typical for opal glasses with amorphous nature, in which nucleation is incomplete. Phase separation is the reason for crystalline nucleation in these glasses and relates to CaO and BaO content with different polarizing effect ($Ca^{2+}>Ba^{2+}$).

Effect of phosphate addition on nucleation has been observed in all of the samples. However, sample No.7 had amorphous phase with crystalline peak with low intensity. Since the amount of P_2O_5 influenced on the crystal nucleation, and the ratio of glassy to crystalline phase in this sample was more than the other samples, addition of phosphate and BaO in minimum amount has been effective in the formation of the nuclei in glassy parent phase.

In all the XRD patterns, the initiated region for crystallization was common. Sample 1, in comparison with other samples, showed lower initiating region for crystallization; thus, a quartet peak in this area was observed. However, other samples revealed the same region for crystalline peak 2θ values for similar observed broad and sharp peaks. The XRD pattern of No.06 specimen was unusual, thus the crystalline phase was diminished than the glassy phase, but the configuration of the pattern was similar to the other specimens. It seems that decreasing BaO content led to divers effects on the amorphous phase and ratio of Na_2O, BaO, and CaO affected opacification. XRD patterns of sample 2 and 5 were adapted, without any differences, because the ratio of Na_2O to CaO and BaO in No.2 (0.03) was more than No.5. Moreover, P_2O_5 content in No.2 (0.34) was lower than in No.5; thus, differences in nucleation agent functioned similarly in glassy and crystalline phases.

In sample No. 7, the ratio of amorphous to crystalline phase was higher than in other samples, due to the minimum amounts of P_2O_5 and BaO. Meanwhile, the weakest crystallization was observed in No. 3 including high content of Al_2O_3. In the presence of minimum amount of BaO, crystalline phase was decreased, although crystal nucleation was occurred. This trend was probably due to the minimum amount of BaO and maximum amount of CaO. Because of higher content of phosphate, initiated region for crystallization in glassy phase was nearly the same in the samples 1 and 6. These samples had little similarity to sample 5, because Al_2O_3 was effective in crystal formation and immiscibility; however, the rate of crystallization was dependent on the BaO and CaO contents.[18] In the case of sample 3, in comparison with other parents, significant peaks were wide and weak. This observation would probably due to the high content of Al_2O_3. In comparison with patterns in specimens, a small shift in peak was observed, probably due to the presence of high content of CaO and low content of BaO. These amounts cause decreasing initial crystallization and less intense peaks. On the other hand, crystal growth in No.02 was more satisfactory and the significant peak was broader than in the other samples. In a short study of the influence of heating on glass, it was revealed that improving of the crystalline phase was independent to the heating range.

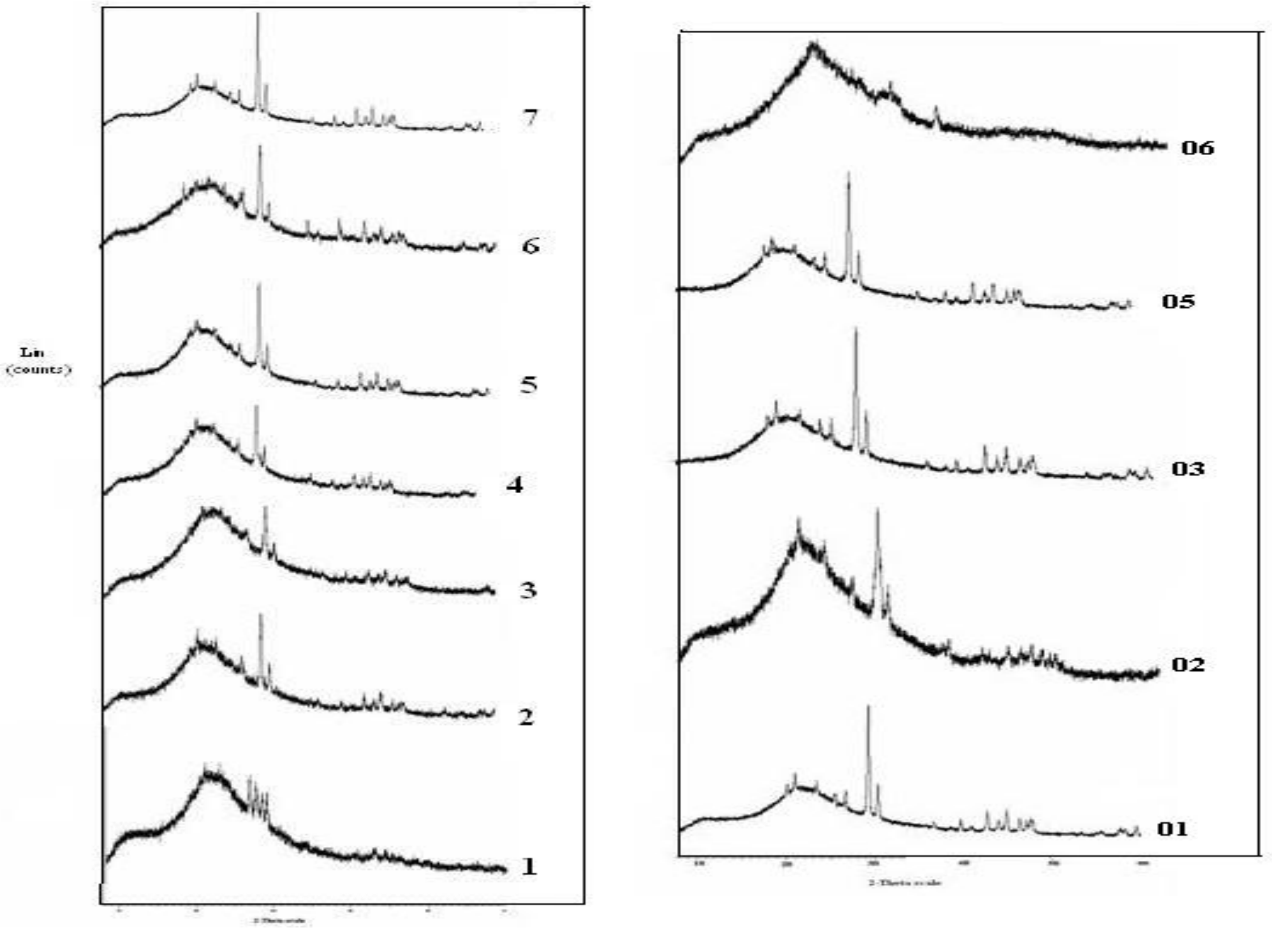

Figure 1: (a) X-Ray diffraction patterns of the first samples (1-7) and (b) specimens (01-06).

Thermal expansion was affected by thermal history, so similar thermal conditions were used for all of the samples.[14] Tables 2-5 show some thermal expansion characteristics of samples and specimens. Among glass samples in Table 2, No.3 with $K_\alpha=3.2071\times10^{-6}$ K^{-1} and $K_\alpha=3.5938\times10^{-6}$ K^{-1} had minimum and maximum values, respectively, for thermal coefficient expansion. Moreover, T_g (glass transition temperature), T_s (softening point temperature), and T_s-T_g values for No.3 were the least. However, glass specimens showed different patterns and K_α values were increased with decreasing T_g (Table 3).

The ratios of Na_2O to BaO and CaO for sample No.3 were similar to No.1 and 2; however, the contents of Al_2O_3, B_2O_3 and P_2O_5 were mainly different. K_α values in samples 3 and 7 were low; it seems that addition of Al_2O_3 and B_2O_3 significantly affected improving thermal coefficient expansion. Due to the fixed Al_2O_3, B_2O_3 and P_2O_5 contents in glass specimens, little differences in K_α values were observed. One of the most important thermal parameters which are found in this study would be the direct relation of K_α with Tg-Ts. The samples and specimens involving the lowest difference between T_g and T_s, showed the lowest thermal coefficient expansion, due to the minimum phase separation. The ratio content of α^-/α with 10 °C above and below T_g were collected for samples and specimens borosilicate opal glasses in Tables 4 and 5. The ratio content of α^-/α was increased with decreasing K_α in specimens (01-06) and in samples. The coefficient thermal expansion was increased with widening of temperature range, 25-200, 25-300,25-400, 25-500, 25-570 °C, etc; this increase was again approximately linear.

This phenomenon was therefore characteristic for 3.3 glasses and borosilicate opal glasses that were prepared in this investigation.

Table 2. Mean coefficients of linear thermal expansion, T_g, T_s, T_d and $|T_g-T_s|$ of samples in the temperature range of 20-300 °C.

	$K_\alpha.10^{-6}/K$	T_g °C	T_s °C	T_d °C	$|T_g-T_s|$ °C
1	3.6183	555.9	648.9	520	93
2	3.4076	560.0	649.2	500	89
3	3.2071	557.5	645.7	510	88.2
4	3.5938	584.0	674.9	540	90.9
5	3.4661	577.6	671.7	560	94.1
6	3.5047	558.6	669.4	515	110.8
7	3.3936	551.4	654.9	510	103.5

Table 3: Mean coefficients of linear thermal expansion, T_g, T_s, T_d and $|T_g-T_s|$ of specimens in the temperature range 20-300 °C.

	$K_\alpha.10^{-6}/K$	T_g °C	T_s °C	T_d °C	$|T_g-T_s|$ °C
01	3.7040	572.3	668.9	530	96.6
02	3.3988	584.0	674.9	540	90.9
03	3.8656	572.0	667.0	540	95.0
04	3.8700	582.3	664.2	510	81.9
05	4.0968	568.2	687.4	510	116.2
06	3.8243	572.3	652.0	510	79.7

Table 4: The ratio of α^-/α with 10 °C above and below T_g for the samples.

Sample 4, thermal expansion	$K_\alpha.10^{-6}/K$	T_g °C	α^-	α	α^-/α
1	3.6183	555.9	13.8957	5.3396	2.6024
2	3.4076	560.0	12.9322	4.6899	2.7574
3	3.2071	557.5	12.9615	5.2622	2.4631
4	3.5938	584.0	16.2390	4.1246	3.9371
5	3.4661	577.6	12.7407	1.7030	7.4813
6	3.5047	558.6	14.6699	5.3075	2.7640
7	3.3936	551.4	14.4681	4.83	2.9954

Table 5: The ratio of α^-/α with 10 °C above and below T_g for the samples.

Sample thermal expansion	$K_\alpha.10^{-6}/K$	T_g °C	α^-	α	α^-/α
01	3.7040	572.3	14.3488	5.1233	2.8007
02	3.3988	584.0	17.1951	5.5452	3.1009
03	3.8656	572.0	14.7956	5.1555	2.8698
04	3.8700	582.3	17.6367	5.8919	2.99
05	4.0968	568.2	19.2701	6.2381	3.0890
06	3.8243	572.3	17.2556	5.6312	3.0643

The chemical stability and durability of borosilicate opal glasses were affected by the chemical composition of the crystalline phase. Alkali metal ions were much more stable in the crystalline phase and rapidly were removed from the glass phase during the action of water on glasses [15,16,19,20]. This process was intensified by increasing temperature, the results showed leaching at 98 °C and sterilization in 121 °C [17,19,21,22]. Water and steam behaved according to the diffusion phenomenon.[19] Hydrolytic resistance observed at 98 and 121 °C, as depicted in figures 2 and 3 for the glass samples (1-7) and the specimens (01-06). Glass samples No. 6 and 4 revealed maximum HGB obtained and mass of sodium oxide per gram of glass grains were 89 and 160 (Na_2O) µg/g of glass, respectively. The glass specimens of No. 01 and 03 had minimum and maximum values and their HGB were obtained with 90 and 124 µg of Na_2O per each gram of glass, respectively.

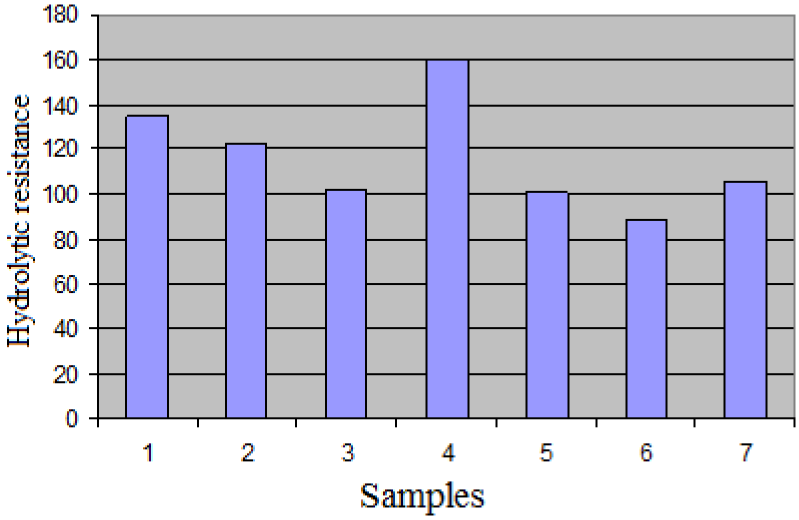

Figure 2: Hydrolytic resistance of glass samples.

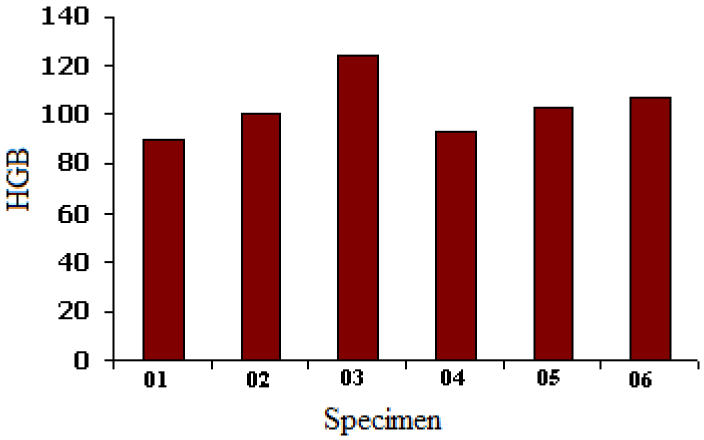

Figure 3: HGB for glass specimens at 98 °C.

The glass samples of No.6 and 5 have minimum and maximum values for water resistance, respectively, and accomplished HGB with 1001 and 1032 μg of Na_2O per each gram of glass grains, respectively (Figures4 and 5). The glass specimens No.05 and 01 as minimum and maximum values, showed HGA with 900 and 990 μg of Na_2O per each gram of glass, respectively.

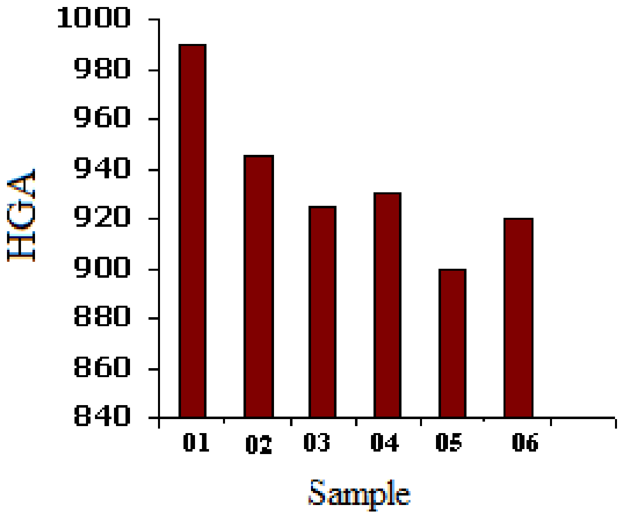

Figure 4: Variation of hydrolytic resistances of the samples in 121 °C.

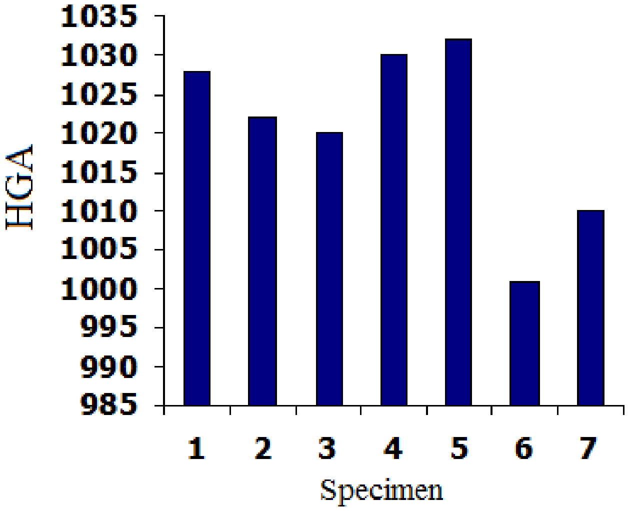

Figure 5: Variations of hydrolytic resistances of the specimens in 121 °C.

For better describing of alkaline oxide in specimens, three categories per value of Na_2O/ BaO+CaO wt% were considered. Results showed that the HGB value was increased as a function of alkaline ratio (Figure 6) with a smooth slope; and HGA value was decreased as a function of alkaline ratio in (Figure 7).

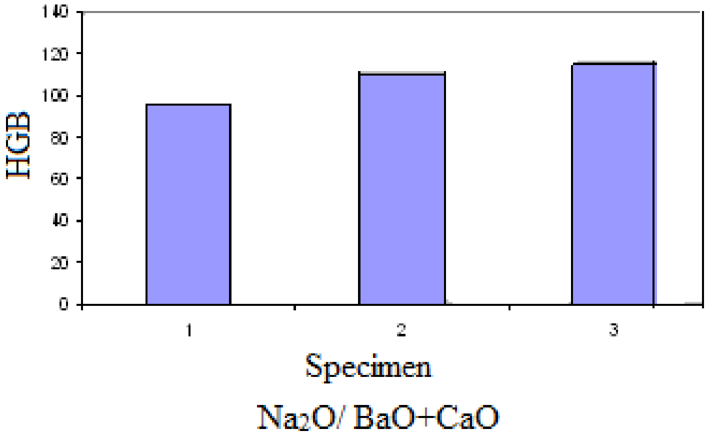

Figure 6: HGB values against Na_2O/ BaO+CaO for the specimens.

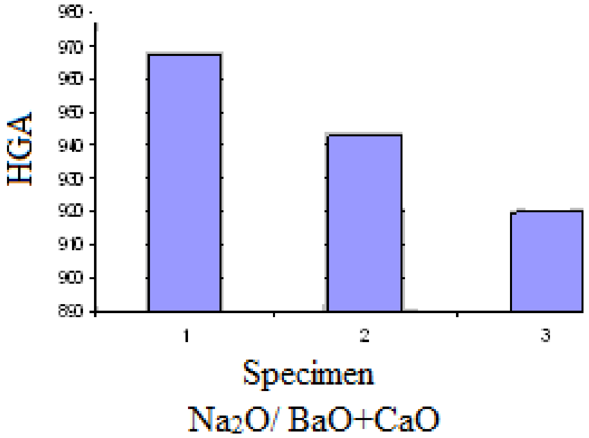

Figure 7: HGA values against Na_2O/ BaO+CaO for the specimens.

Variation of alkaline resistance in glass samples and specimens are shown in Figures 8 and 9. The glass samples of No.4 and 7 showed minimum and maximum values, respectively. The A (or LBK) was obtained through removal of glass thin plate 11.0 and 30.0 mg/dm^2, respectively, and the other values for the selected samples were 21.1, 21.2, 22.0, 26.4 and 25.1, mg/dm^2. These are included in A class1or in LBK class1, because of alkaline solutions had slight attack and weight loss are lower than 75 mg/dm^2. In the glass specimens of No.05 and 06, as minimum and maximum values, A was obtained with 0.9 and 25.0 mg/dm^2, respectively, and are included in class A-1. In addition, specimens No.01, 03, 05, 06 and 07 with 11.4, 12.0, 11.7, 11.6 and 11.1 mg/dm^2 with a little difference of loss in mass per total surface area, respectively, were categorized in class A-1. In comparison with borosilicate glasses, these results showed high durability in alkaline solution for borosilicate opal glasses, so they would have more applications in industry. Similarly, results of acidic resistance for glass samples and specimens are exhibited in Figures 10 and 11 as grade S (mg/dm^2). The glass specimens of No.06 and 04 showed minimum and maximum values, and the S was obtained with 0.5 and 2.1, respectively; therefore, they should be included in S class 1 and 3. In addition, specimens No.01, 02, 03 with 1.0, 0.9, 1.0 mg/dm^2, respectively, were in class 2.

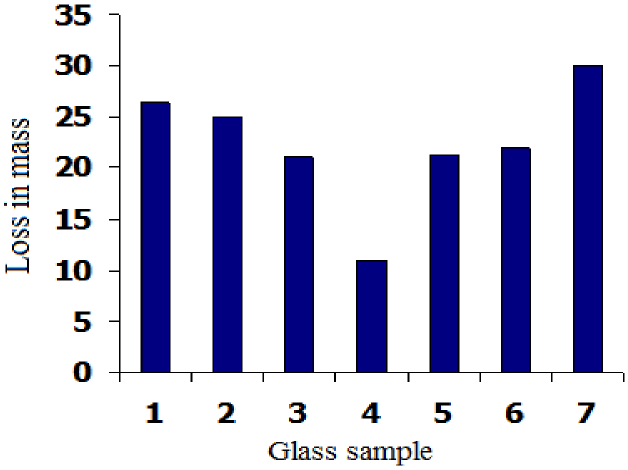

Figure 8: Alkaline resistance in the glass samples. Loss in mass per total surface area after 3h is depicted in Y axis.

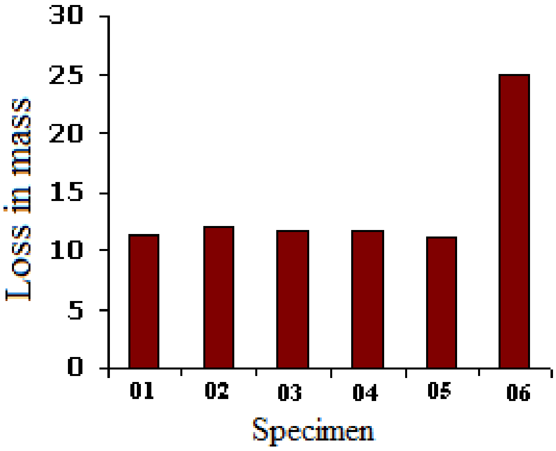

Figure 9: Alkaline resistance in the specimens. Loss in mass per total surface area after 3h is depicted in Y axis.

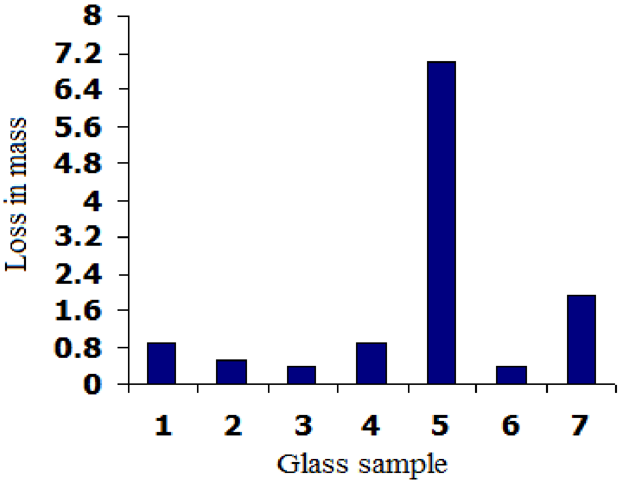

Figure 10: Acidic resistance of the glass samples. Loss in mass per total surface area is depicted in Y axis.

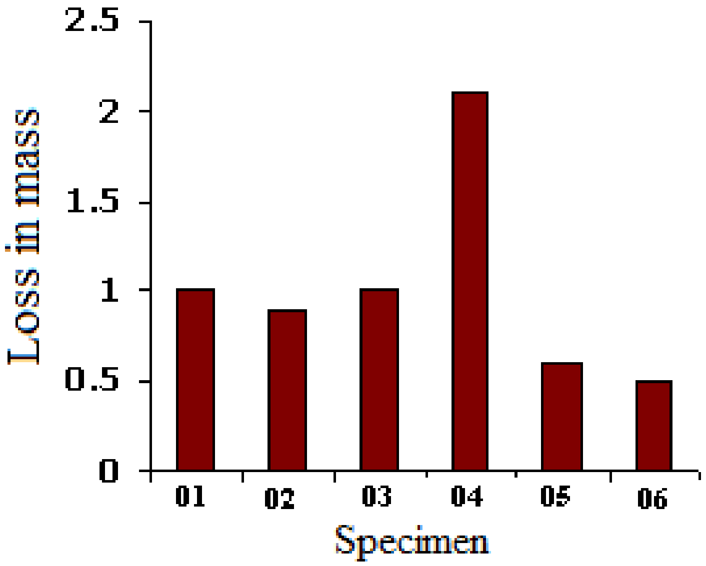

Figure 11: Acidic resistance of the specimens. Loss in mass per total surface area is depicted in Y axis.

The role of alkaline oxide in specimens in three categories for specimen's glasses is considered. Results showed the A values increased and the S values decreased as a function of alkaline ratio. The relation between resistance alkaline, acidic resistance, and $Na_2O/BaO+CaO$ ratio are shown in figures 12 and 13.

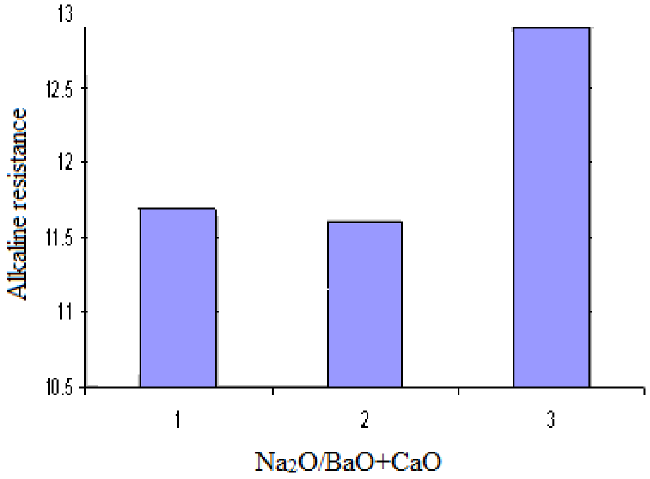

Figure 12: Alkaline resistant test as a function of $Na_2O/BaO+CaO$.

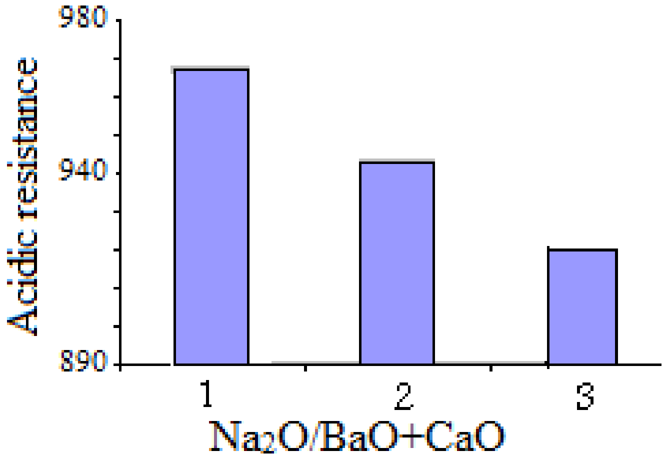

Figure 13: Acidic resistance of the specimens against $Na_2O/BaO+CaO$.

Values of densities for the first glass samples were nearly the same (approximately 0.09 more than 3.3 glasses), and for glass specimens, this quantity averaged between 2.33-2.36, which is extended with the ratio of $Na_2O/BaO+CaO$. In all XRD patterns, crystallite or other crystalline phases of SiO_2 was very unfavorable to be existed; thus, identification of a meaningful relation between Tg-Ts and phase separation was impossible. Moreover, differences between T_g and T_s in these results did not affect the chemical durability.

CONCLUSION

In order to produce borosilicate opal glasses with ideal chemical resistance, it is necessary that the ratio of R_2O and RO be limited and do not contain high concentrations of alkaline oxides in particular. However, all conditions should be controlled and other oxide ratios should be constant. Therefore, the glass does not affected by the heat treatment or any changes in the processing conditions. Observation of phase separation in the opal borosilicate glass confirms existence of crystals, which can react with water, alkaline, and/or acidic solutions; so that, the product would be unstable in this condition and chemical durability would be lowered down. However, in this investigation, under the identified conditions, chemical composition of crystalline phases was lowered down; thus, high chemical durability and high stability in leaching and corrosive solutions were obtained.

It seems that addition of Al_2O_3 and B_2O_3 has significantly affected improving of thermal coefficient expansion. Direct relation between K_α and $|T_g-T_s|$ proved that the samples and specimens were contained the lowest difference between T_g and T_s and the lowest thermal coefficient expansion obtained, due to the least phase separation.

The value of P_2O_5 influenced the crystal nucleation; in addition, phosphate and BaO in minimum value were effective in the formation of nuclei in glassy parent phase. Undoubtedly, the initiating role of P_2O_5 was necessary for crystallization and low values of P_2O_5 decreased the density of opacity, similar to the opaque glasses. BaO in 0.8 wt% was the minimum content which was needed for initial crystallization. BaO showed divers effects on amorphous phase and it was effective on opacification. All of these results showed that there are clear relation between the ratio of Na_2O, BaO and CaO.

Al_2O_3 was effective in crystal formation and immiscibility, but the rate of crystallization was dependent on the BaO and CaO contents. When 5 wt% of alumina was added, initiating of crystallization and size of the crystals were changed.

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