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PHYSICAL PROPERTIES OF SPECTACLE GLASS AS A FUNCTION OF THE CATION SIZE

Ahmad Din, M. Zafar Hussain, M. Rashid Sheikh and K.A. Shahid

PCSIR Laboratories, Lahore 16

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Abstract. Seven soda–potassia–lime–silica glasses were melted with small changes in alkali and alkaline earth content; in three glasses small amounts of MgO, SrO and BaO were introduced. The densities and refractive indices were determined, the specific refractivity dispersion and polarisation constants were calculated and related to the size of the cations.

The quality of spectacle glass is not only determined by its freedom from imperfections but also judged by its refractive index. Therefore, in a typical glass composition; different network modifier replacing silica to the extent of 5% and the corresponding change that occurs in the physical properties of the glass is to be followed. This was done with a view to develop better varieties of the Crown type of glasses by incorporating two or more network modifiers which can increase the refractive index without impairing the other properties like chemical durability and dispersion.

Experimental

Batch Ingredients. The quartz used had SiO_2 content of 99.98% whereas the other batch material like soda ash, $CaCO_3$, Sb_2O_3 and ZnO were of analytical grade. B_2O_3 was introduced in the form of boric acid.

Preparation of Glasses. The glasses were melted in Pt/10 Rb crucibles at 1380°C. The melts were made free of bubbles and seeds and were poured on cast iron plates. After proper annealing the samples were stored in a dessicator for further measurements. The glass compositions found by chemical analyses and those calculated from batch composition agreed within reasonable limits of experimental error (Table 1).

Measurement of the Density and Refractive Index. The glass grains used for measuring the density possessed a grain size of —25+60 mesh B.S.I. Density was determined by weighing in air and in water. Refractive index was measure by the immersion method[2] (Table 2).

Determination of the Polarization of the Cations. The values of the polarization were calculated through the Lorentz–Lorentz equation,[3] which shows a relationship between the density, refractive index and polarization (Table 2).

Calculation of the Abbe's Value. The Abbe's values of the glasses were calculated by the method mentioned in literature[4] and the values are shown in Table 2.

Results and Discussion

Spectacle glass is basically a soda–lime glass of conventional composition of 69–72% SiO_2, 14–16% Na_2O (K_2O) and 10–13% CaO. Alkali metal oxides in glasses give better working and refining properties. The alkaline earth metal oxides have similar function. However, they impart chemical stability to glass. The presence of more than one of these oxides improves the qualities of the glass.

A base glass composition containing 69.4% SiO_2, 0.25% B_2O_3, 5.95% Na_2O, 14.75% K_2O, 12.07% CaO and 0.90% Sb_2O_3 (wt. basis), was selected for the present studies. This base composition was varied by replacement of 5% SiO_2 by various oxides, viz. Na_2O, K_2O, MgO, CaO, SrO and BaO. The compositions on molecular basis have also been given in Table 1, to facilitate the comparison.

The density values of the glasses given in Table 2 show that density increases with the replacement of silica by various alkali and alkaline earth oxides. The increase is related to the molar weight of the oxides introduced except for glass No. 3 in which K_2O has replaced silica. Although the molecular weight of K_2O is greater than that of Na_2O, the density of the K_2O–substituted glass is lower than that of Na_2O. The apparently anomalous effect of K_2O is readily accounted for by remembering that potassium is a large ion which will cause the silica to occupy a greater total volume in order to accommodate it compared with sodium. This increase in volume can more than compensate for the mass of the large ion and, as has been shown, can lead to a decrease in density compared with Na_2O.

The refractive indices for the glasses also show a

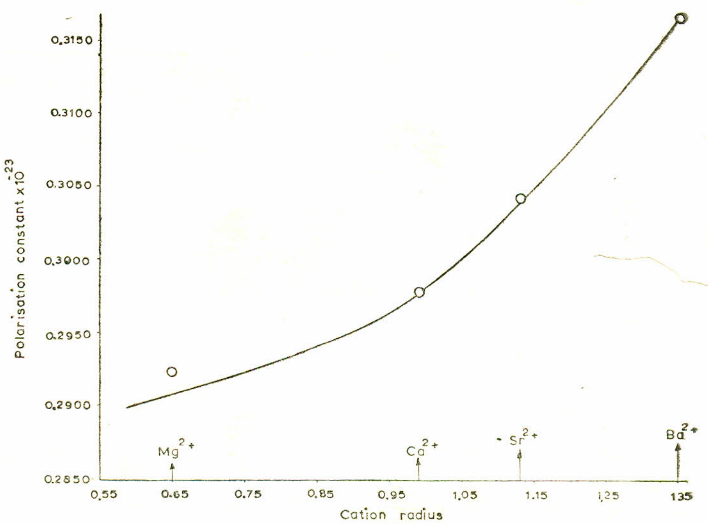

Fig. 1. Dependence of polarisation constant on cation-size.

TABLE 1. CHEMICAL COMPOSITION OF THE SPECTACLE GLASSES.

Specification	SiO_2(%)		B_2O_3(%)		Sb_2O_3(%)		Na_2O(%)		K_2O(%)		MgO(%)		CaO(%)		SrO(%)		BaO(%)	
	mole	wt	mole	wt	mole	wt	mole	wt	mole	wt	mole	wt	mole	wt	mole	wt	mole	wt
1	72.2	69.08	0.23	0.25	0.19	0.90	6.10	5.95	7.89	11.75	—	—	13.60	12.07	—	—	—	—
2	67.09	64.08	0.23	0.25	0.19	0.90	11.10	10.95	7.85	11.75	—	—	13.53	12.07	—	—	—	—
3	68.27	64.08	0.23	0.25	0.20	0.90	6.10	5.95	11.39	16.75	—	—	13.78	12.07	—	—	—	—
4	65.30	64.08	0.22	0.25	0.18	0.90	7.60	5.95	7.60	11.75	7.60	5.00	13.20	12.07	—	—	—	—
5	66.73	64.08	0.23	0.25	0.19	0.90	6.00	5.95	7.81	11.75	—	—	19.05	17.07	—	—	—	—
6	68.50	64.08	0.23	0.25	0.20	0.90	6.11	5.95	8.02	11.75	—	—	13.82	12.07	3.08	5.00	—	—
7	69.18	64.08	0.23	0.25	0.20	0.90	6.22	5.95	8.10	11.75	—	—	13.96	12.07	—	—	2.12	5.00

TABLE 2. OPTICAL PROPERTIES OF THE SPECTACLE GLASSES.

Glass no.	Density (d=g/ml)	Refractive index(n^D)	Specific refractivity	Polarisation constant $\alpha=\frac{0.75\ RM}{II\ N}$	Abbe's value $\nu=\frac{n^D-1}{n^F-n^C}$
1	2.5225	1.5320	0.1224	0.3065×10^{-23}	52.8
2	2.5608	1.5335	0.1206	0.2989×10^{-23}	47.97
3	2.5406	1.5340	0.1221	0.3148×10^{-23}	46.40
4	2.5841	1.5340	0.1209	0.2928×10^{-23}	46.5
5	2.5905	1.5332	0.1202	0.2977×10^{-23}	45.2
6	2.6109	1.5360	0.1196	0.3042×10^{-23}	46.4
7	2.6278	1.540	0.1194	0.3167×10^{-23}	48.6

progressive increase as SiO_2 is substituted by oxides of alkaline and alkaline earth metals, in order of increasing molar weights (Table 2). The same conclusion has been reached by previous workers.[5] Further, the plot of the refractive indices against ionic radii of the substituting ions shows that refractive indices are a function of the ionic radii of the cations with equal charge. The only exception is the magnesium ions. Although the cation radius for Mg^{++} is less than that of the calcium ions, yet the former result is a glass of higher refractive index. This abnormal behaviour is due to the probable presence of Mg^{++} ions in coordination No. 4 and thereby forming a lose structure which leads to higher refractive index value than expected.[6]

Specific refractivity values have been calculated from the observed values of density (d) and refractive index (n) by using the relation:

$$R=\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$$

The values have been given in Table 2. As can be seen from the Table, the specific refractivity decreases as the refractive index increases. The specific refractivity values in general are directly proportional to the field strength of the cations added to the base glass no. 1.

The values of polarisation given in Table 2, show an increase with the increase in ionic size of cation, except for glass composition no.4 containing MgO. The lower polarisation value for glass no.4, as compared to that of base glass composition, may be due to smaller size and greater change of Mg^{2+} (i.e. greater field strength). Thus some of the Mg^{2+} ions may become a part of the silica network, giving a soothering effect on the destroyed silica network. The major contribution towards polarisation values in silicate glasses, is made by the anions (mostly oxygen). The effect of presence of the cations is, however, not insignificant. The values calculated from Lorentz–Lorentz equation have been plotted against the cation size in Fig. 1, which shows that polarization is proportional to cation size. It is clear from these studies that Fajon's rule,[7] viz. the cations of similar configuration destroy their outermost shells according to their size, holds good even for complex silicate glasses.

The first additions of modifiers lower the Abbe's values and in turn, the dispersion values show an increase (Table 2). The increase in Abbe's values means a corresponding decrease in dispersion.[1] The barium containing glass has the lowest dispersions (Table 2) and the most needed high refractive index. The increase in refractive index can also be had through PbO but the dispersion increases as well. Therefore, glasses of high refractive index and low dispersion can be obtained by small additions of BaO to the conventional Crown type optical glasses.

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