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DENSITY AND MOLAR VOLUME OF SOME HIGH LEAD SILICATE GLASSES

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ABSTRACT

Density measurements and molar volume calculations of some high lead silicate glasses were studied with the view to throw some light on the structure of these glases. All glasses were melted in an electrically heated furnace at temperature ranged from 1100 to 1200 C for four hours. After complete melting, each molten glass was poured on an iron marver and was then annealed at the appropriate temperature. The experimental results obtained could be correlated to many factors such as the nature of the lead ion itself and also on the field strength, ionic radii and volume of the different incorporated cations

INTRODUCTION

Density is one of the most important properties of the glass, which can be used for finding out the structure of different types of glass and also for the quality control in the glass industry. Some investigators considered that[1-4] the density of the glass is additive and can, therefore, be calculated on the basis of the glass composition. This is, however, nor always true and a number of the involved formula was previously derived to relate the glass density to the glass composition[5-10]. It was also stated that[11] all the glass properties are functions of the density change. The subject of the glass density has been covered by many authors.

Jen et al[13] were able to suggest a model for describing the bridging to non-bridging oxygen ratio as a function of the glass composition; and the calculated values of the glass density, based on this model, were in excellent agreement with the experimental values. The molar volume, which is defined as the mean molecular weight of the composition

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divided by its density, is used for the glass structure. It is more likely to explain the glass structure in terms of the molar volume then the density as the former deals with the spatial distribution of the ions forming that structure. The change in the value of the molar volume with the change in the molar composition of an oxide is suggested to explain the preceding structural changes through a formation or modification process in the glass network[14].

The aim of the present work is to throw some light on the change of the density, molar volume and the structure of some lead silicate glasses when different monovalent, divalent, trivalent or tetravalent metal oxides are introduced in these glasses.

EXPERIMENTAL

Raw materials, melting and preparation of the glass samples:

The raw materials used were of chemically pure grade Silica was introduced in the form of finely pulverised and washed Dutch-silver sand. Lead oxide was introduced in the form of Pb_3O_4 and sieved to get rid of the coarse particles. Lithia, soda, potash, magnesia, lime, strontium oxide and barium oxide were introduced in the form of their respective carbonates, while zinc oxide, alumina, titania and zirconia were introduced as such. All the melts were made in Pt-2% Rh crucibles in an electrically heated furnace, in air atmosphesre. The temperature of melting ranged from 1100–1200°C and the duration of melting was four hours. After complete melting, the molten glass was annealed at the appropriate temperature.

Density measurements:

The density of each glass sample was determined by the Archimedes method in which the glass sample was weighed both in air and when immersed in xylene. The density of the glass is then calculated from the formula:

$$\rho = \frac{a}{a-b} \times 0.86$$

where, ρ is the density of the glass, a is the weight of the sample in air, b is the weight of the sample in xylene, and 0.86 is the density of xylene.

Molar volume calculations:

The following formula was used for calculating the molar volume of the glass studied

$$V_m = \Sigma \frac{MW \text{ x mole\%.}}{\rho} = \Sigma M_i X_i / \rho$$

Where, V_m is the molar volume, Mi is the molar mass of the constituent oxides, X_i means mole fraction of the constituents and ρ is the density of the glass sample.

RESULTS:

Density of some lead silicate glasses was measured by Archimedes method using xylene as the immersion liquid. the value of the molar volume for each glass sample was calculated. The following types of glasses were investigated.

1. Lead oxide-silica glasses

2. Lead silicate glasses containing one of the monovalent, divalent, trivalent or tetravalent metal oxides

The experimental results obtained are summarized as follows:

1- Lead oxide-silica glasses:

The composition of the glasses studied and the experimental results obtained are given in Table 1, from which it can be seen that the value of density increases from 5. 66 to 7.571 g/cm^3 while the value of the molar volume decreases from 2.474 to 27. 25 cm^{-3} with the gradual increase of the lead oxide content, Figs (1, 2).

2- Lead silicate glasses containing one of the monovalent, divalent, trivalent or tetravalent metal oxides:

Table 1. Chemical composition, density and molar volume of a number of lead silicate glasses.

Glass No.	Glass composition (wt. %)		Density (g/cm³)	Molar volume (cm³)
	PbO	S_iO_2		
1	70	30	5.366	32.474
2	75	25	5.787	31.521
3	80	20	6.281	30.340
4	85	15	8.866	28.943
5	90	10	7.571	27.325

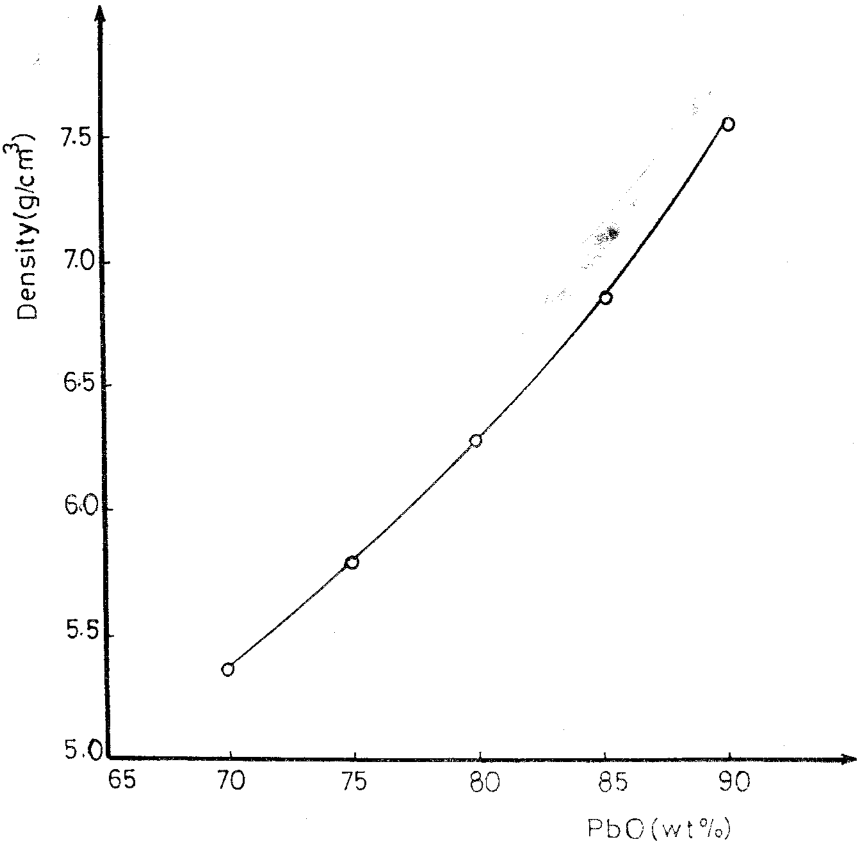

Fig. 1. Density of some lead silicate glasses versus the lead oxide content.

a) Lead silicate glasses containing monovalent metal oxides:

The experimental results obtained, from the glasses of the base composition PbO80%, SiO_2 20% (wt. %) in which parts

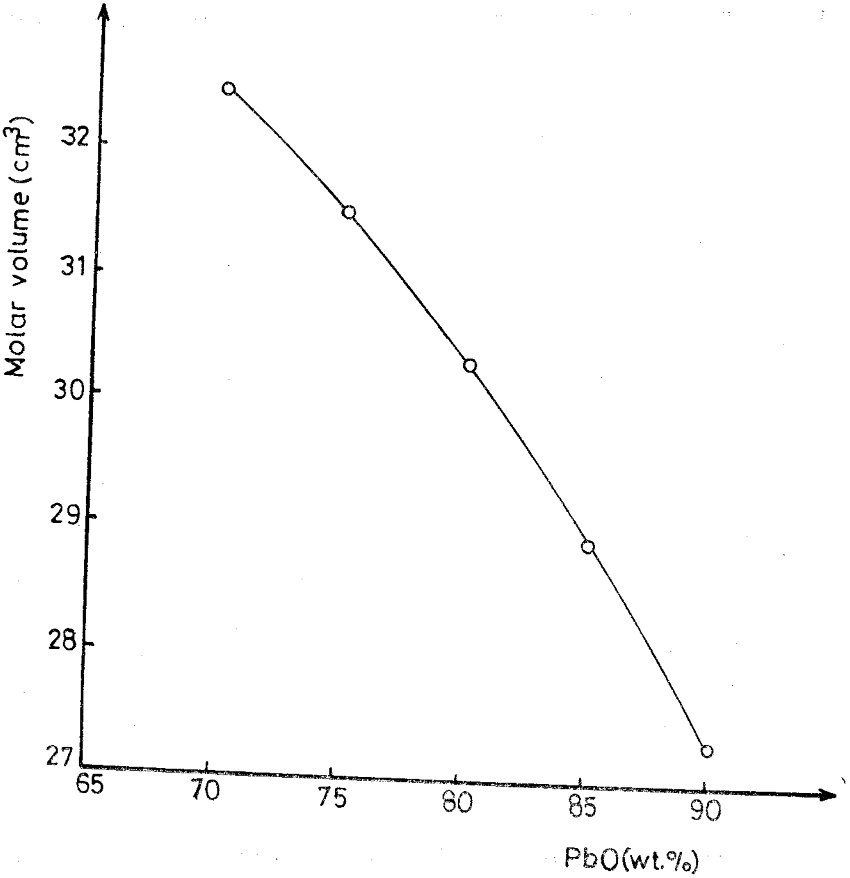

Fig. 2. Molar volume of some lead silicate glasses versus the lead oxide content.

of the lead oxide were replaced by one of the monovalent metal oxide lithia, soda or potash, Table 2 and Figs 3 4 show that the value of density decreases from 6.381 g / cm^3 in the base composition to 5.963, 5.962 and 5.836g / cm^3, while the value of the molar volume increases from 30.340 cm^3 to 31.156, 31.353, 31.669 cm^3 with the gradual increase of the lithia, soda and potash content, respectively.

b. Lead silicate glasses containing divalent metal oxides:

The results obtained, from the glasses of the above same base composition in which parts of lead oxide were replaced by one of the divalent metal oxides magnesia, zinc oxide, lime, strontium oxide or barium oxide showd that:

Table 2. Chepical composition, dedsity and molar volype of a number of lead silicate glasses of the base composition PbO 80 %, S_iO_2, 20 % (wt. %) with part of lead replaced by lithia, soda or potash.

Glass No.	Glass composition (wt. %)			Denstiy (g / cm³)	Molar (cm³)
	PbO	S_iO_2			
3	80	20		6.281	30.340
			$L_{i_2}O$		
6	79	20	≡ 1 % PbO	6.250	30.421
7	78	20	≡ 2 % PbO	6.219	30.501
8	70	20	≡ 5 %"	6.126	30.737
9	70	20	≡ %"	5.963	30.156
			Na_2O		
10	79	20	≡ 1 % PbO	6.244	30.439
11	78	"	≡ %"	6.207	30.537
12	70	"	≡ %"	5.902	31.353
			K_2O		
13	79	20	≡ 1 % PbO	6.237	30.469
14	78	"	≡ 2 %"	6.190	30.603
15	75	"	≡ 5 %"	6.060	30.992
16	70	"	≡ 10%"	5.836	31.669

All replacements were made cation for cation.

i. The value of density decreases form 6.281 g / cm³ in the base glass to 5.970 and 6.155 g / cm³, while the value of the molar volume increases form 30.340 to 30.829 cm³, with the gradual increase of the magnesia and zinc oxide content, respectively, Table 3 and Figs 5, 6.

ii. The value of density decreases from 6.281 g / cm³ in the base glass to 5.923, 5.967 and 6.027 g / cm³ while the value of the molar volume increase from 30.340 cm³ to 30.962, 30.645 and 30.622 cm³ with the gradual increase of the lime, strontium oxide and barium oxide content, respectively. Table 3 and Figs. 7, 8.

c. Lead silicate glasses containing trivalent metal oxide:

The results obtained from the glasses containing the trivalent metal oxide alumina replacing parts of silica are given in Table 4 and are shown in Figs. 9, 10, from which it can be seen that the value of density increases from 6.218 g / cm³ in the base glass to 6.871 g / cm³ with the gradual increase of the alumina content, while the value of the molar volume decreases from 30.340 cm³ to 28.55 cm³.

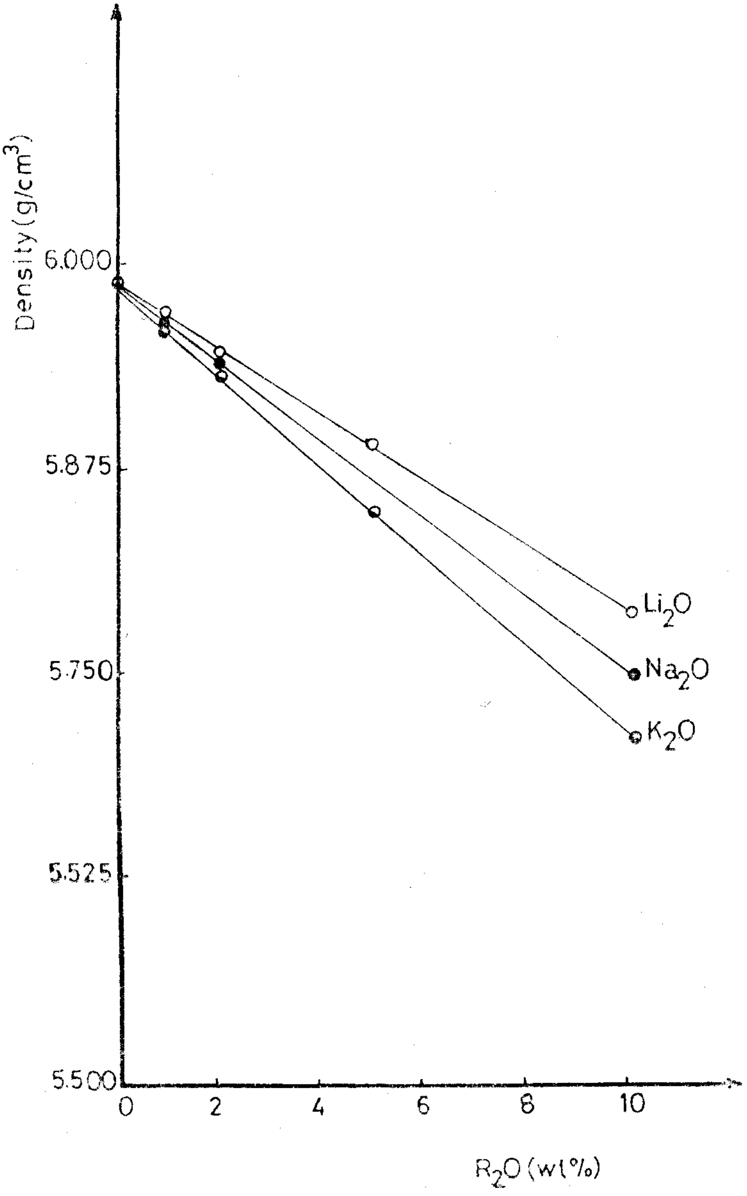

Fig. 3. Density of a lead silicate glass of the base composition PbO 80%, S_iO_2, 20 %, with parts of lead oxide replaced by lithia, soda or potash, versus the monovalent content.

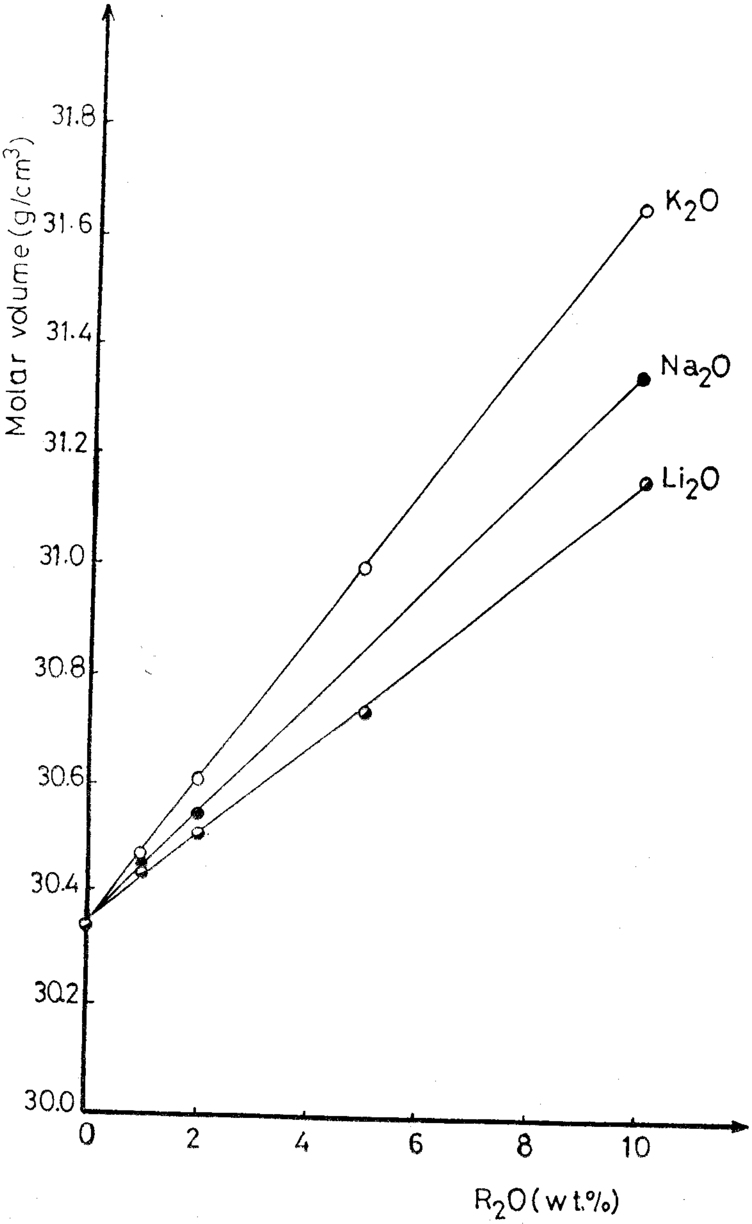

Fig. 4. Molar volume of a lead silicate glass of the base composition PbO 80 %, S_iO_2, 20 %, with parts of lead oxide replaced by lithia, soda or potash, versus the monovalcent content.

Table 3. Chemical composition, density and melar volume of a mumber of lead silicate glasses of the base composition PbO 80 %, S_iO_2 20 % (wt. %) with parts of lead oxide replaced by magnesia, zidc oxide, lime. strontium oxide or barium oxide.

Glass No.	Glass composition (wt. %)			Denstiy (g / cm^3)	Molar volume (cm^3)
	PbO	S_iO_2			
3	80	20		6.281	30.340
			MgO		
17	79	20	≡ 1 % PbO	6.251	30.389
18	78	”	≡ 2 %”	6.220	30.442
19	75	20	≡ 5 %”	6.128	30.589
20	70	”	≡ 10 %”	5.970	30.829
			ZnO		
21	79	20	≡ 1 % PbO	6.256	30.345
22	78	”	≡ 2 % ”	6.231	30.318
23	75	”	≡ 5 %”	6.155	30.353
			CaO	6.210	30.470
24	78	20	≡ 2 % PbO	6.210	30.470
25	75	”	≡ 5 %”	6.104	30.655
26	70	”	≡ 10 %”	5.923	30.962
			SrO		
27	78	20	≡ 2 % PbO	6.218	30.410
28	70	”	≡ 10 %”	6.967	30.645
			BaO		
29	79	20	≡ 1 % PbO	6.255	30.373
30	70	”	≡ 10 %”	6.027	30.622

All replacements were made catiod for cation.

d. Lead silicate glasses containing tetravalent metal oxides:

The results obtained from the glasses containing one of the tetravalent metal oxides titania or zirconia replacing parts of silica are given in Table 5 and are shown in Figs$^{11-12}$, from which it can be seen that:

i. The value of density increases from 6.281 g / cm^3 in the base glass to 6.516 g / cm^3 with the gradual increase of the titania content, while the value of the molar volume decreases from 30. 40 cm^3 to 29.120 cm^3.

ii. The value of density is 6.288 g / cm^3, while the value of the molar volume in the above same base glass containing zirconia is 30.305 cm^3.

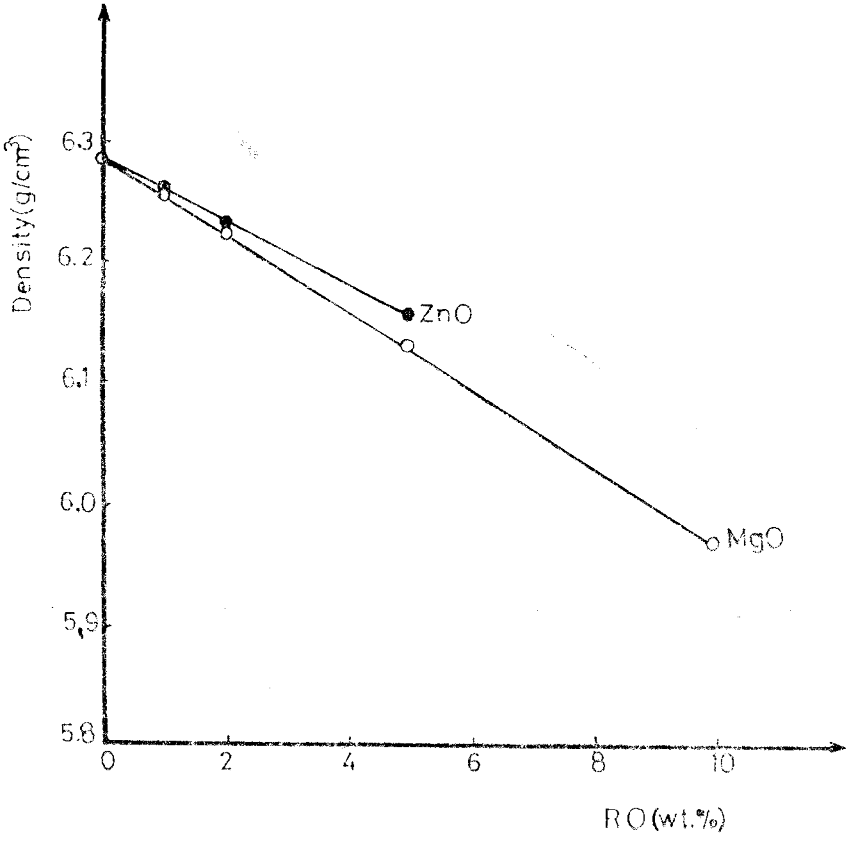

Fig. 5. Density of a lead silicate glass of the base composition PbO 80%, S_iO_2, 20 %, with parts of lead oxide replaced by magnesia or zinc oxide, versus the divalent content.

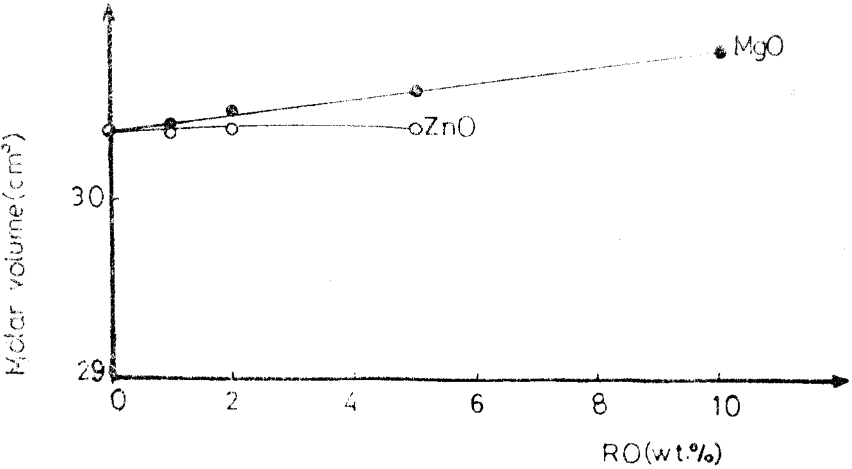

Fig. 6. Molar volume of a lead silicate glass of the base composition PbO 80%, $S_iO_2$20% with parts of lead oxide replaced by magnesia or zinc oxide, versus the divalent content.

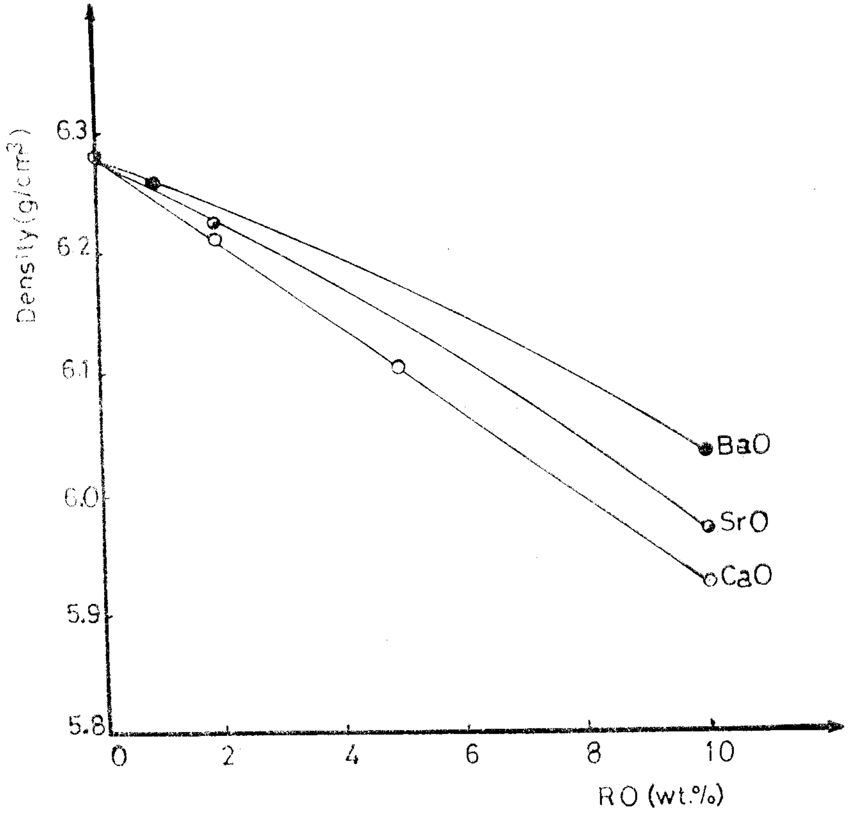

Fig. 7. Density of a lead silicate glass of the base composition PbO 80%, $S_iO_2$20%, with parts of lead oxide replaced by lime, strontium oxide or barium oxide, versus the divalent content.

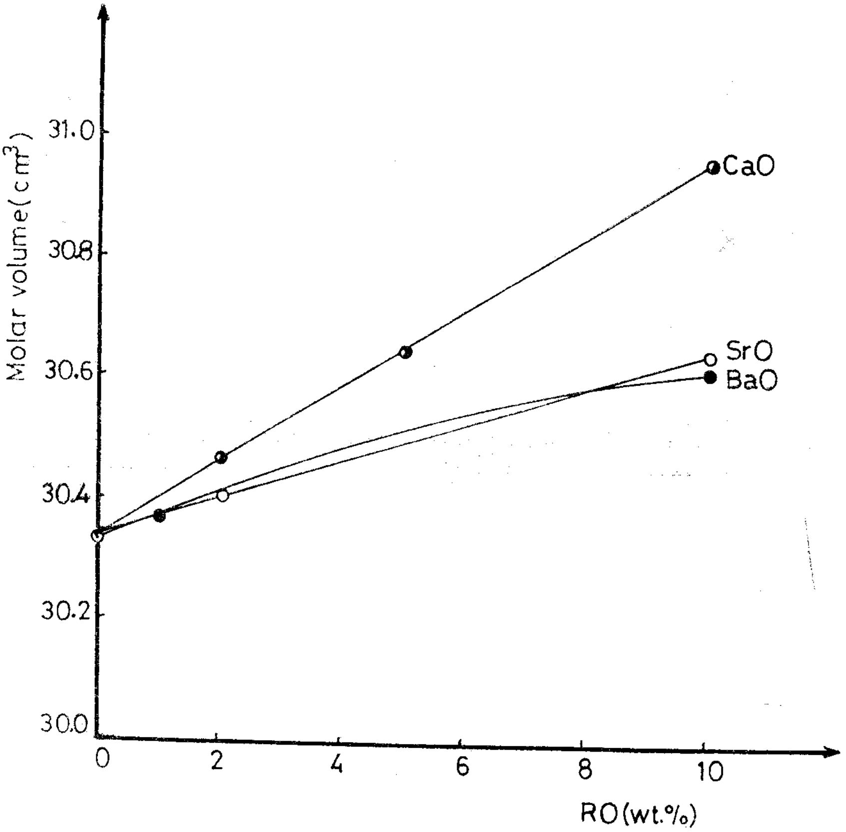

Fig. 8. Molar volume of a lead silicate glass of the base complosition PbO 80%, $S_iO_2$20%, with parts of lead oxide replaced by lime, strontium oxide or barium oxide, versus the divalent content.

Table 4. Chemical composition, density and molar volume of a number of lead silicate glasses of the base composition PbO 80%, $S_iO_2$20% (wt. %) with parts of silica replaced by alumina.

Glass No.	Glass composition (wt. %)			Density (g / cm^3)	Molar volume (cm^3)
	PbO	SiO_2	Al_2O_3		
3	80	20		6.281	30.340
31	”	19	≡ 1% SiO_1	6.334	30.174
32	”	18	≡ 2% ”	6.389	30.001
33	”	15	≡ 5% ”	6.560	29.475
34	”	10	≡ 10% ”	6.871	28.553

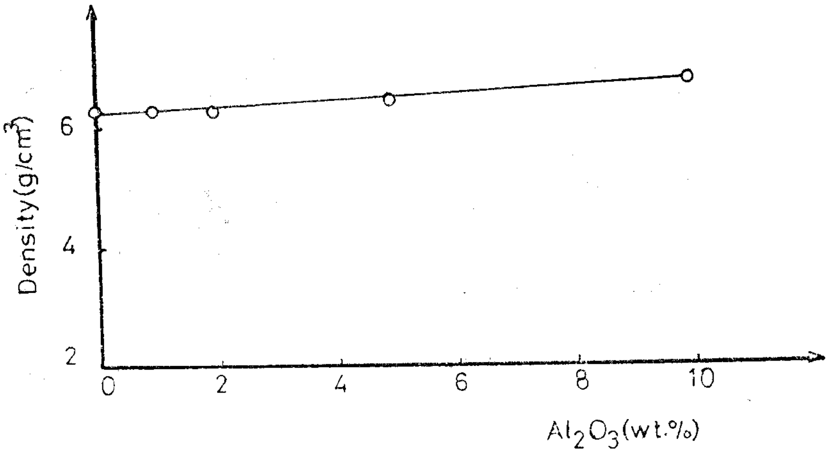

Fig. 9. Density of a lead silicate glass of the base composition PbO 80%, $S_iO_2$20%, with parts of silica replaced by alumina, versus the alumina content.

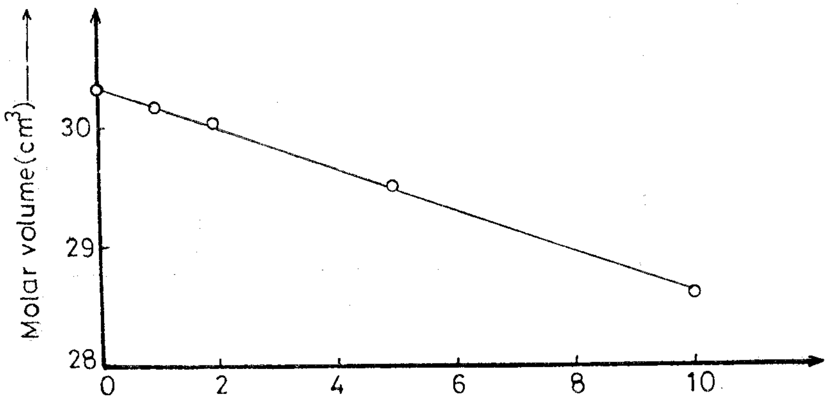

Fig. 10. Molar volume of a lead silicate glass of the base composition PbO 80%, $S_iO_2$20%, with parts of silica replaced by alumina, versus the alumina content.

Table 5. Compositions, density and molar volume of a lead silicate glass of the base composition PbO 80, $S_iO_2$20 (wt. %) with parts of silica replaced by titaniaor zirconia.

Glass No.	Glass composition (wt. %)			Density (g/cm³)	Molar volume (cm³)
	PbO	SiO_2	RO_2		
3	80	20		6.281	30.340
			T_iO_2		
35	80	19	≡ 1% SiO_2	6.327	30.094
36	"	18	≡ 2% "	6.373	29.850
37	"	15	≡ 5% "	6.516	29.120
			Z_rO_2		
38	80	19.9	≡ 0.1% SiO_2	6.288	30.305

All replacements were made cation for cation.

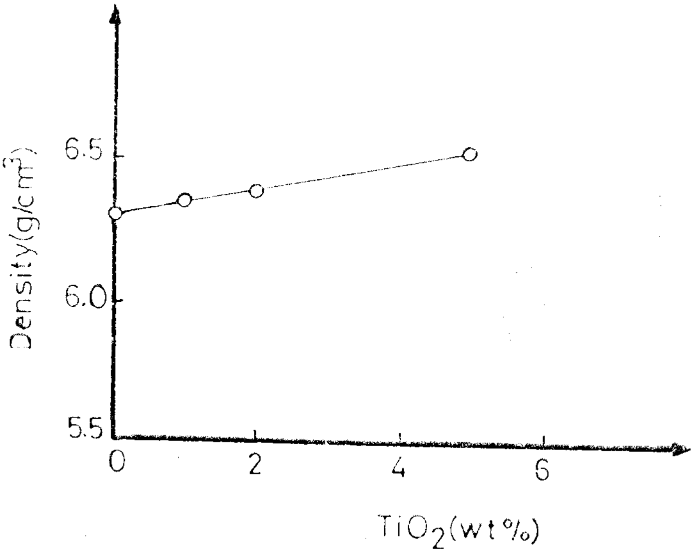

Fig. 11. Density of a lead silicate glass of the base composition PbO 80%, $S_iO_2$20%, with parts of silica replaced by titania versus the titania content.

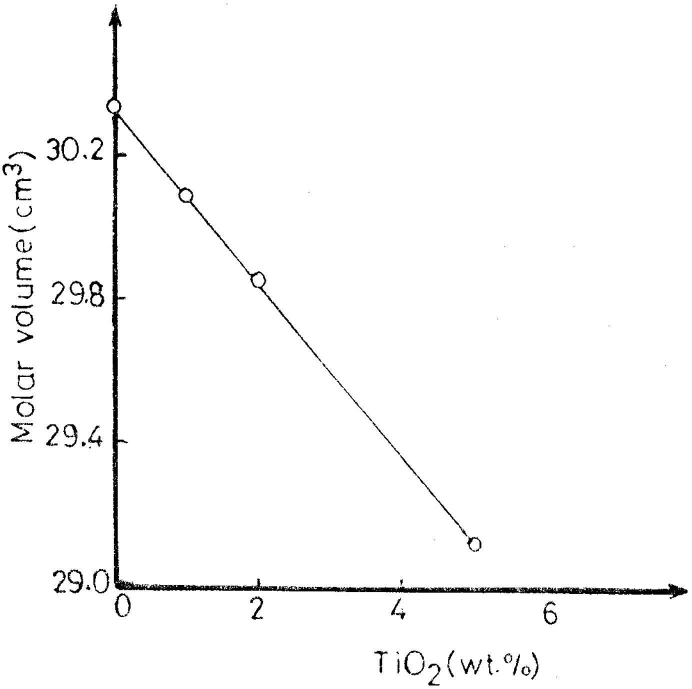

Fig. 12. Molar volume of a lead silicate glass of the base composition PbO 80%, $S_iO_2$20%, with parts of silica replaced by titania versus the titania content.

DISCUSSION

The structure of lead silicate glasses.

In these glasses, the high polarizability of the lead ions and the directional properties of the Pb-O bond were proposed. Also, the idea that a lead atom being bonded to two oxygen atoms only was previously postulated[15]. It was concluded from X-ray studies on some lead silicate glasses containing high proportions of lead oxide that[16] these glass have structures similar to that of the soda-silica glasses, two sodium atoms in the latter being replaced by a lead atom. It was stated that[17] in lead glasses containing low proportion of lead oxide, the lead ion would be larpely enclosed in the interstices of the glass structure, while in the glasses of the high lead oxide content a considerable proportion would be associated with the oxygen ions as structural building units. It was also showed that[18] a considerable proportion of the S_iO_4 tetrahedra are linked in the glass structure through the double bonded oxygens at all four corners. Recent investigations on the lead oxide-silica system showed that[11] all or most of the lead atoms act as network formers in the lead glasses, even of low concentration of lead oxide, while at high concentration of the lead oxide content the data obtained indicated that of the PbO_4 pyramides as the dominant lead-oxygen configuration.

Accordingly, the experimental results obtained can be interpreted as follows:

1– In the oxide-silica system containing low proportion of lead oxide, the lead ions would be largly enclosed in the interstices formed by S_iO_4 groups in the glass structure, while in the glasses of the high lead content a considerable proportion of the lead ions will act as double bridges between the adjacent SiO_4 tetrahedra beside the formation of the PbO_4 groups.

The lead ions are so easily polarizable and the structure becomes very open leading to easy movements of the atomic aggregates in the glass[19]. Therefore, the above considerations may account for the increase in the value of density, i.e decrease in the value of the molar volume with the gradual increase of the lead oxide content in the lead silicate glasses studied, Table 1 and Figs. 1 and 2.

2– In the glasses containing one of the monovalent metal oxides, lithia, soda or potash. the results obtained may be understood on the basis that, in these glasses, the alkali cations occupy holes in the glass structure which cause a change in the forces exerted on the oxygen ions of the S_iO_4 groups, not all the S^{i4+} ions will be directly linked to each other as in silica glasses but will become linked to each other through the PbO_4 groups or the bridges of the Pb^{2+} ions[20]. The flow of these glasses would be expected to be controlled by the silicon-oxygen bonds. The presence of an alkali ion in such glasses would weaken these bonds. Thus on replacing the more polarizable lead ion present in the interstices, by one of the alkali ion, the polarizability of the oxygen ion will decrease. Therefore, the results obtained, Table 2 and Figs. 3 and 4, may be due to the polarizability of the oxygen ions and also to the simultaneous occupation of the interstices by the different alkali cations and the tendency of the lead ions to be in the tetrahedral form. The relative effect of these alkali oxides was found to depend on their polarizing effect and also on the compactness of the alkali cations in the interstices.

3– In the glasses containing one of the divalent metal oxide magnesia, zinc oxide, lime, strontium oxide or barium oxide, the results obtained, Table 3 and Figs 5-8 may be explained on the basis of the fact athat, in these glass the divalent cations form bridges in the glass structure or are enclosed within the interstices of the glass. These cations have relatively high field strengths or ionic potentials on comparing with the effect of the lead ions.

Magnesia or zinc oxide can also enter the glass structure, at least partly, as network formers[21]. The effect of these divalent oxides in these glasses would be expected to depend upon the type, coordination number and quantity of the divalent cation introduced and also on the introduction of new structural units such as MgO_4 or ZnO_4 groups. The relative effect of these oxides can be attributed to their polarizing power.

4– In the glasses containing the trivalent metal oxide alumina, the results obtained, Table 4 and Figs 9 and 10 can be explained on the basis that[17] when alumina is introduced replacing silica in lead silicate glasses, every aluminium oxide molecule introduced will acquire an oxygen from the lead oxide content forming AlO_4 groups because, as far as it is known, this is the only stable state for the Al^{3+} ion in the glass structure beşide the S_iO_4 tetrahedra, having the lead ions in the interstices formed by S_iO_4 or AlO_4 groups.

5– In the glasses containing one of the tetravalent metal oxides titania or zirconia, the results obtained, Table 5 and Figs. 11 and 12 may be due to that when titania or zirconia is introduced replacing silica in the glasses studied, the T_iO_4 or ZrO_4 groups would be present and the oxygen ligands tend to be least polarizable in these glasses.

All the above conclusions are in complete agreement with the experimental results obtained.

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