

STRUCTURE OF HIGH LEAD SILICATE GLASSES CONTAINING DIFFERENT DIVALENT, TRIVALENT OR TETRAVALENT CATIONS AS DETERMINED BY VIBRATIONAL SPECTROSCOPY

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(Received Aug. 26, 1994; Accepted Jan. 10, 1995)

ABSTRACT

The effect of the different cations Mg^{2+} , Cd^{2+} , Zn^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Al^{3+} , Ti^{4+} and Zr^{4+} on the frequencies and intensities of the characteristic infrared absorption bands of some selected high lead silicate glasses, was investigated.

The raw materials used were all of chemically pure grade and finely pulverised. The temperature of melting ranged from 1100 to 1200 C, depending on the glass composition. All the absorption measurements were recorded in the range of 4000-200 cm^{-1} using URIO fully automatic double beam infrared spectrophotometer. Alkali halide disc technique was used.

The effect of these different cations on the deformation of SiO_4 tetrahedra was studied, and it has been found that their behaviour depend on the type, coordination number and quantity of the cations introduced; and also on the introduction of new structural units.

INTRODUCTION

Recently, there has been a growing interest in the glass ceramic materials and their applications in the modern technology.

Inorganic oxide glasses are of commercial importance and lead silicate glasses have been of particular scientific and technological interest for many years. They have been extensively studied by several techniques such as X-ray, ultraviolet, Raman and infrared spectroscopy. Infrared absorption spectra can provide many informations on the structure of different oxide glasses¹. The vibrational spectra can be used to identify the glasses or the specific groups which are present in it^{2,3}.

Piriou¹ concluded that the structure of lead silicate glasses appears different from that of the alkali silicate glass; while Baire⁵ suggested that the structure of lead silicate glasses was identical with that obtained by Warren et al⁶ for soda-silica glasses, except that, two sodium atoms were replaced by a lead atom. Abou El-Azm et al⁷ stated that the effect of the divalent metal ions on the deformation of SiO_4 tetrahedra in glass is smaller than that of the monovalent ion; also the effect of alumina on the glass structure was found to depend partly on the formation of AlO_4 groups. It was concluded that⁸ the main absorption bands due to SiO_4 groups were displaced towards longer wavelength with the increase of the lead oxide content.

It was also stated that^{9,10} there is a correspondance in the shift direction of the band maxima with varying lead oxide content in lead glasses. Furukawa et al¹¹ measured the infrared absorption spectra for some lead silicate glasses and the results obtained were interpreted in terms of the glass structure. In the present paper, infrared absorption spectra of some selected high lead silicate glasses containing one of the divalent, trivalent or tetravalent metal oxides was studied using the potassium-bromide method; the absorption peaks show some different features as compared with the author's previous work on infrared spectra for different types of glasses.

EXPERIMENTAL

All the glasses were prepared in wt. % using chemically pure grade materials. The replacements were made on cation for cation basis. Magnesia, lime, strontium and barium oxides were introduced in the form of their respective carbonates, while zinc oxide, alumina, titania and zirconia were introduced as such. Lead oxide was introduced in the form of PbO and sieved to get rid of the coarse particles. Silica was introduced in the form of finely pulverized Dutch-silver sand washed with 1:1 hydrochloric acid followed by 5% hydrofluoric acid solutions. Melts were made in Pt. 2% Rh crucibles in an electric furnace. The temperature of melting ranged from 1100 to 1200°C, depending on the glass composition. The duration of melting was four hours. After complete melting, the molten glass was annealed at the appropriate temperature. The infrared absorption spectra, for all the glasses studied, were recorded in the range of 4000-200 cm^{-1} using the alkali halide disc- technique at 27°C.

RESULT

Infrared absorption spectra for some lead silicate glasses containing one of the divalent, trivalent or tetravalent metal oxides were measured in the region $4000\text{--}200\text{ cm}^{-1}$ using the alkali halide disc-technique. The chemical compositions of the glasses studied are given in Table 1

Table 1. Chemical compositions of the lead silicate glasses containing divalent, trivalent and tetravalent metal oxides.

Glass No.	Glass composition (wt. %)				
	PbO	SiO ₂	RO	R ₂ O ₃	RO ₂
1	80	20			
2	79	20	MgO		
3	78	"	≡ 1 % PbO		
4	75	"	≡ 2 % "		
5	70	"	≡ 5 % "		
6	79	20	≡ 10 % "		
7	78	"	CdO		
8	75	"	≡ 1 % PbO		
9	70	"	≡ 2 % "		
10	79	20	≡ 5 % "		
11	78	"	≡ 10 % "		
12	75	"	ZnO		
13	70	"	≡ 1 % PbO		
14	78	20	≡ 2 % "		
15	75	"	≡ 5 % "		
16	70	"	≡ 100 % "		
17	78	20	CaO		
18	70	"	≡ 2 % PbO		
19	79	20	≡ 5 % "		
20	70	"	≡ 10 % "		
21	80	19	SrO		
22	"	18	≡ 2 % PbO		
23	"	15	≡ 10 % "		
24	"	10	BaO		
25	80	19	≡ 1 % PbO		
26	"	18	≡ 10 % "		
27	"	15		Al ₂ O ₃	
28	80	19.9		≡ 1 % SiO ₂	
				≡ 2 % "	
				≡ 5 % "	
				≡ 10 % "	
					TiO ₂
					≡ 1 % SiO ₂
					≡ 2 % "
					≡ 5 % "
					ZrO ₂
					≡ 0.1 % SiO ₂

All replacements were made cation for cation.

In order to study the effect of replacing parts of the lead oxide content by one of the divalent metal oxides or replacing parts of the silica content by one of the trivalent or tetravalent metal oxides, it should be recalled that the four main absorption bands given by a lead silicate base glass were as follows:

Composition of a base glass (wt. %)	Positions of the absorption bands
PbO 80 %, SiO ₂ 20 %	3455, 1500, 937 and 370 cm ⁻¹

Effect of the divalent metal oxides:

The experimental results obtained from the glass of the base composition PbO 80 %, SiO₂20%, in which one, two, five or ten parts of the lead oxide content were replaced by one of the divalent metal oxides magnesia, cadmium oxide, zinc oxide, lime, strontium oxide or barium oxide, Table 2 and Figs. 1-6 showed that:

- 1- The positions of the absorption bands at 1500 and 937 cm⁻¹ in the glass of the base composition PbO 80 %, SiO₂20 % (wt. %) changed to 1236-1132 and 914-817 cm⁻¹ respectively according to the content, while the positions of the absorption bands at 455 and 470 cm⁻¹ were not affected.
- 2- The intensity of all the absorption bands slightly increased with the gradual increase of the divalent metal oxide content.

Effect of the trivalent and tetravalent metal oxides:

Effect of alumina:

The experimental results obtained, from the glasses in which one, two, five or ten parts of silica were replaced by alumina, Table 3 and Fig. 7 showed that.

- 1- The positions of the absorption bands at 1500 and 937 cm⁻¹ changed to 1200-1128 and 914-820 cm⁻¹ respectively according to the amount of alumina content, but the position of the absorption bands at 455 and 470 cm⁻¹ were not affected.
- 2- A new absorption band at 741-671 cm⁻¹ was observed.
- 3- The absorbancies increased with the gradual increase in the alumina content.

Table 2. Composition, values, and positions of the infrared absorption bands for a number of lead silicate glasses of the base composition PbO 80, SiO₂20 (wt. %) in which parts of lead oxide were replaced by magnesia, cadmium oxide, zinc oxide, lime or strontium oxide.

Glass No.	Glass Composition (wt.%)		Absorption Bands			
	PbO	SiO ₂	Band (A)	Band (B)	Band (C)	Band (D)
	R ₂ O					
1	80	20	0.276 at 3455 cm ⁻¹	0.226 at 1500 cm ⁻¹	0.178 at 937 cm ⁻¹	0.183 at 470 cm ⁻¹
2	79	20	0.481 at 3455 cm ⁻¹	0.225 at 1236 cm ⁻¹	0.262 at 914 cm ⁻¹	0.247 at 470 cm ⁻¹
3	78	"	0.603 " "	0.403 at 1186 "	0.510 at 851 "	0.463 " "
4	75	"	0.715 " "	0.648 at 1164 "	0.714 at 827 "	0.643 " "
5	70	"	0.834 " "	0.813 at 1136 "	0.839 at 812 "	0.869 " "
6	79	"	0.321 at 3455 cm ⁻¹	0.193 at 1221 cm ⁻¹	0.281 at 922 cm ⁻¹	0.327 at 470 cm ⁻¹
7	78	"	0.340 " "	0.233 at 1178 "	0.340 at 882 "	0.335 " "
8	75	"	0.445 " "	0.261 at 1150 "	0.435 at 856 "	0.439 " "
9	70	"	0.671 " "	0.340 at 1100 "	0.831 at 827 "	0.776 " "
10	79	"	0.402 at 3455 cm ⁻¹	0.191 at 1228 "	0.280 at 890 "	0.321 at 470 cm ⁻¹
11	78	"	0.432 " "	0.281 at 1195 "	0.361 at 867 "	0.357 " "
12	75	"	0.551 " "	0.322 at 1175 "	0.472 at 843 "	0.480 " "
13	70	"	0.584 " "	0.473 at 1134 "	0.558 at 804 "	0.561 " "
14	78	20	0.495 at 3455 cm ⁻¹	0.267 at 1214 cm ⁻¹	0.373 at 914 cm ⁻¹	0.387 at 470 cm ⁻¹
15	75	"	0.543 " "	0.361 at 1171 "	0.464 at 882 "	0.483 " "
16	70	"	0.682 " "	0.588 at 1134 "	0.653 at 843 "	0.675 " "
17	78	20	0.409 at 3455 cm ⁻¹	0.281 at 1214 cm ⁻¹	0.384 at 922 cm ⁻¹	0.391 at 470 cm ⁻¹
18	70	"	0.709 " "	0.473 at 1178 "	0.564 at 874 "	0.618 " "
19	79	20	0.481 at 3455 cm ⁻¹	0.372 at 1186 cm ⁻¹	0.490 at 874 cm ⁻¹	0.434 at 470 cm ⁻¹
20	70	"	0.676 " "	0.526 at 1132 "	0.613 at 817 "	0.637 " "

All replacements were made cation for cation.

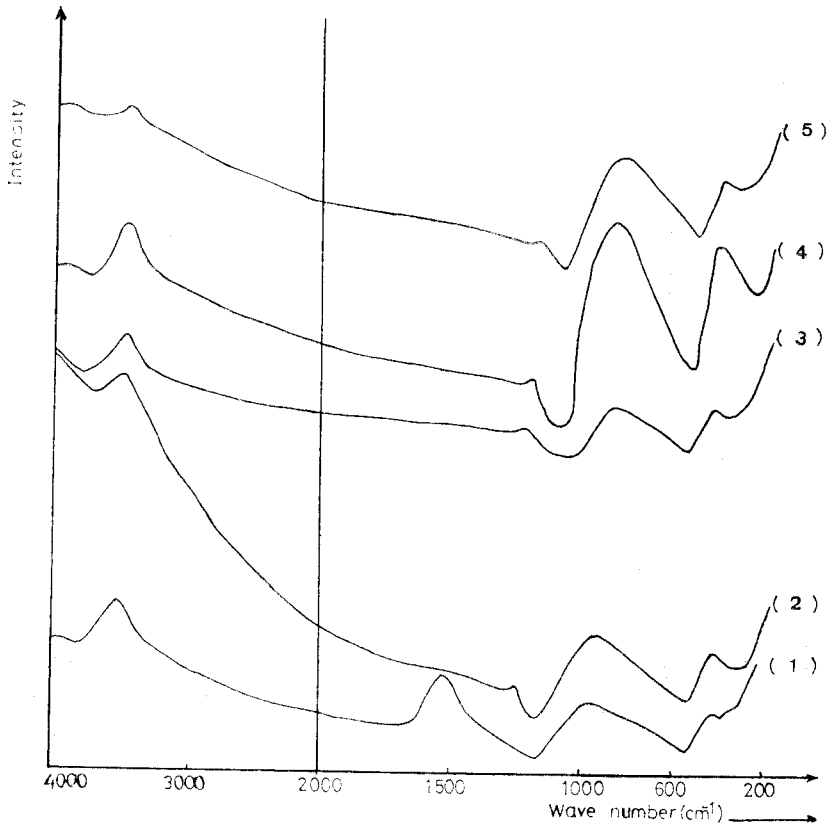


Fig 1. Infra-red absorption spectra for lead silicate glasses of the composition PbO 80 %, SiO₂ 20 % containing magnesia replacing lead oxide:

- 1- PbO 80 %, SiO₂ 20 %.
- 2- PbO 79 %, SiO₂ 20 %, MgO ≡ 1 % PbO.
- 3- PbO 78 %, SiO₂ 20 %, MgO ≡ 2 % PbO.
- 4- PbO 75 %, SiO₂ 20 %, MgO ≡ 5 % PbO.
- 5- PbO 70 %, SiO₂ 20 %, MgO ≡ 10 % PbO.

(The curves are displaced vertically relative to each other to avoid confusion.)

EFFECT OF TITANIA:

The results obtained from the glasses in which one, two or five parts of silica were replaced by titania, Table 4 and Fig 8 revealed that:

- 1- The characteristic absorption bands were observed at 3455, 1214-1171 874-827 and 470 cm⁻¹ according to the amount of the titania content.

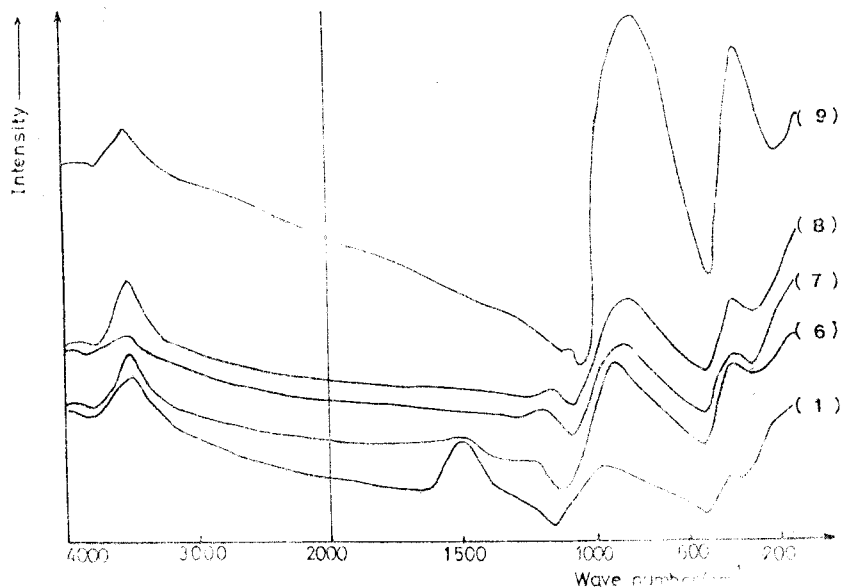


Fig 2. Infra-red absorption spectra for lead silicate glasses of the composition PbO 80 %, SiO₂ 20 % containing cadmium oxide replacing lead oxide:

- 1- PbO 80 %, SiO₂ 20 %.
- 6- PbO 79 %, SiO₂ 20 %, CdO ≡ 1 % PbO.
- 7- PbO 78 %, SiO₂ 20 %, CdO ≡ 2 % PbO.
- 8- PbO 75 %, SiO₂ 20 %, CdO ≡ 5 % PbO.
- 9- PbO 70 %, SiO₂ 20 %, CdO ≡ 10 % PbO.

(The curves are displaced vertically relative to each other to avoid confusion.)

2- A new absorption bands at 769-741 cm⁻¹ was observed.

3- The intensity of absorption increased with the gradual increase of the titania replacing silica.

EFFECT OF ZIRCONIA:

When one tenth part of zirconia was introduced replacing silica, into the same base glass, the positions of the characteristic absorption bands were at 455, 1186, 774 and 470 cm⁻¹, Table 4 and Fig. 9

DISCUSSION

Inorganic oxide glasses have been extensively studied by several techniques such as X-ray, ultraviolet and infrared spectroscopy¹²⁻¹⁵. Infrared absorption spectra can provide many informations on the st-

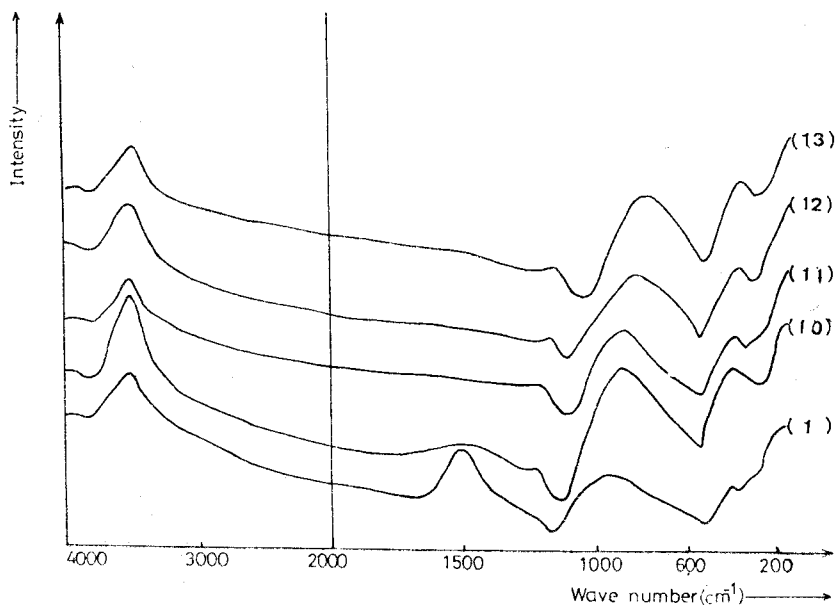


Fig. 3. Infra-red absorption spectra for lead silicate glasses of the composition PbO 80 %, SiO₂ 20 % containing zinc oxide replacing lead oxide:

- 1- PbO 80 %, SiO₂20 %.
- 10- PbO 79 %, SiO₂20 %, ZnO ≡ 1 % PbO.
- 11- PbO 78 %, SiO₂20 %, ZnO ≡ 2 % PbO.
- 12- PbO 75 %, SiO₂20 %, ZnO = 5 % PbO.
- 13- PbO 70 %, SiO₂20 %, ZnO ≡ 10 % PbO.

(The curves are displaced vertically relative to each other to avoid confusion.)

structure of different oxide glasses. The vibrational spectra can be used to identify the glasses of the specific groups which are present in it^{2,3}.

To explain the effect of different divalent, trivalent and tetravalent metal oxides on the frequencies and intensities of characteristic infrared absorption bands of the lead silicate glasses studied. It must be put into consideration the following, assignments, which had been suggested by several authors¹⁶:

- 1- 3460-3000 cm⁻¹ corresponds to O-H stretching vibrations;
- 2- 1625-1620 cm⁻¹ is due to SiO₆ vibrations;
- 3- 1100 cm⁻¹ is attributed to Si-O-Si stretching vibrations;
- 4- 1050 cm⁻¹ is due to Si-O-Si groups (non-bridging);

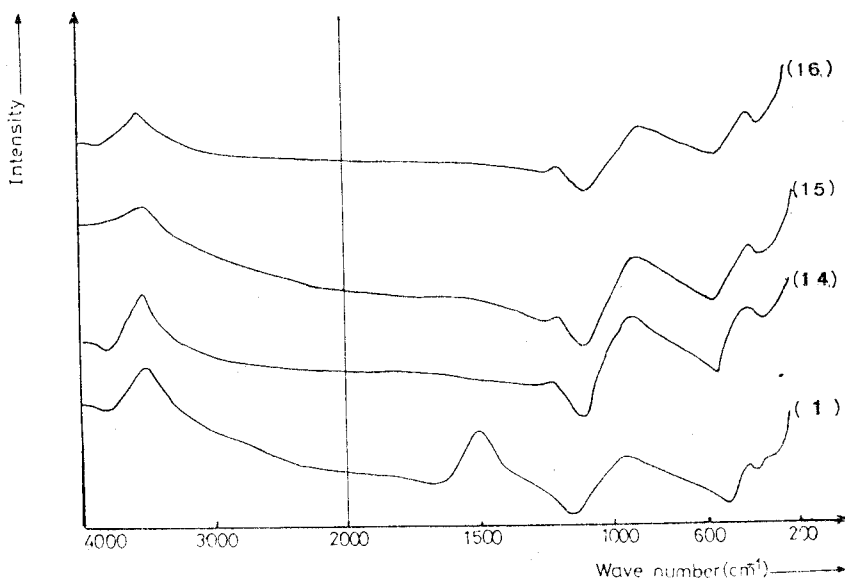


Fig. 4. Infra-red absorption spectra for lead silicate glasses of the composition PbO 80 %, SiO₂ 20 % containing lime replacing lead oxide:

- 1- PbO 80 %, SiO₂ 20 %.
- 14- PbO 78 %, SiO₂ 20 %, CaO ≡ 2 % PbO.
- 15- PbO 75 %, SiO₂ 20 %, CaO ≡ 5 % PbO.
- 16- PbO 70 %, SiO₂ 20 %, CaO ≡ 10 % PbO.

(The curves are displaced vertically relative to each other to avoid confusion.)

5- 920-900 cm⁻¹ corresponds to SiO₄ tetrahedra;

6- 765-675 cm⁻¹ is attributed to Si-O-Si stretching vibrations;

7- 590-570 cm⁻¹ is due to Si-O non-bridging vibrations; and

8- 485-450 cm⁻¹ may be due to Si-O-Si bending vibrations or to the formation of PbO₄ groups.

Under condition of experiments, no significant absorptions were found lower than the absorption band at 85-450 cm⁻¹

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

Effect of the divalent metal oxides:

The experimental results obtained, Table 2 and Figs. 1-6 can be discussed as follows:

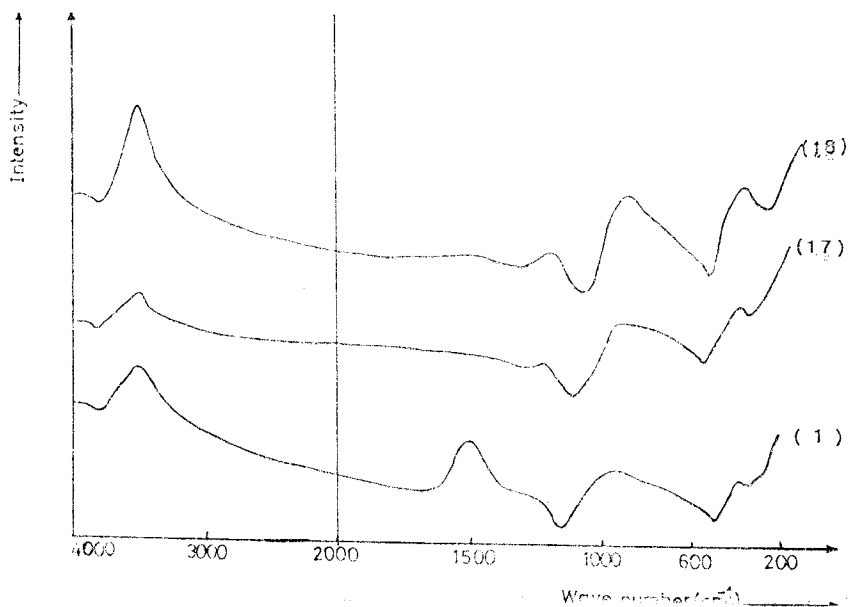


Fig. 5. Infra-red absorption spectra for lead silicate glasses of the compositio PbO 80 %, SiO₂20 % containing strontium oxide replacing lead oxide:

- 1- PbO 80 %, SiO₂20 %.
- 17- PbO 78 %, SiO₂20 %, SrO ≡ 2 % PbO.
- 18- PbO 70 %, SiO₂20 %, SrO ≡ 10 % PbO.

(The curves are displaced vertically relative to each other to avoid confusion.)

The absorption bands at 3455, 126-1132, 914-817 and 470 cm⁻¹ may be attributed to O-H stretching vibrations, Si-O stretching vibrations, SiO₄ tetrahedra and Si-O-Si bending vibrations or formation of PbO₄ groups, respectively⁷.

The conclusions drawn as above can be explained on the basis of the fact that¹⁷. in the lead silicate glasses containing one of the divalent metal oxides, magnesia, cadmium oxide, zinc oxide, lime, strontium oxide or barium oxide, the divalent cations like Mg²⁺, Cd²⁺, Zn²⁺, Ca²⁺, Sr²⁺ or Ba²⁺ 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 which contrapollorize the oxygen ligands as compared with the effect of the lead ions. Magnesia, cadmium oxide or zinc oxide can also enter the glass structure, at least partly, as network formers (MgO₄, CdO₄ or ZnO₄)¹⁸.

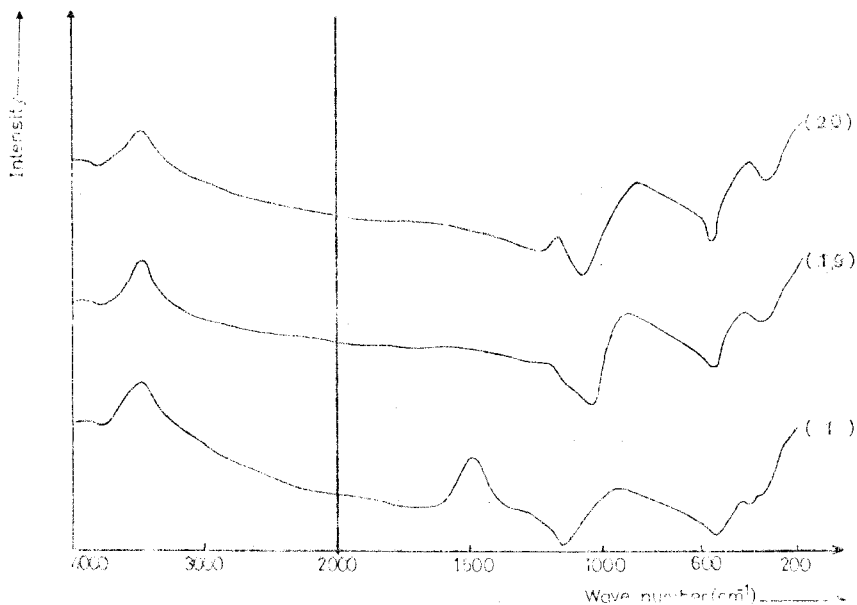


Fig. 6. Infra-red absorption spectra for lead silicate glasses of the composition PbO 80 %, SiO₂ 20 % containing barium oxide replacing lead oxide:

1- PbO 80 %, SiO₂ 20 %.

19- PbO 79 %, SiO₂ 20 %, BaO ≡ 1 % PbO.

20- PbO 70 %, SiO₂ 20 %, BaO ≡ 10 % PbO.

(The curves are displaced vertically relative to each other to avoid confusion.)

The effect of these divalent metal oxides would be expected to depend upon¹⁹: (i). The type, coordination number and quantity of the divalent cation introduced and (ii). The introduction of new structural units such as MgO₄ or ZnO₄ groups. The relative effect of these oxides can be attributed to their polarizing power.

Effect of the trivalent and tetravalent metal oxides:

Effect of alumina.

The results obtained, Table 3 and Fig 7 can be explained as follows.

The absorption bands at 455, 1200–1128 914–820 470 and 741–671 cm⁻¹ may be attributed to O-H stretching vibrations, Si-O stretching vibrations, SiO₄ tetrahedra and Si-O-Si bending vibrations or formation of PbO₄ tetrahedra and Si-O-Si bending vibrations or formation of PbO₄ groups, respectively¹⁶. The new absorption band at 741–671 cm⁻¹ may

Table 3. Compositions, values and positions of the infrared absorption bands for a number of lead silicate glasses of the base composition $\text{PbO } 80\%$, $\text{SiO}_2 20$ (wt. %) in which parts of silica were replaced by alumina.

Glass No.	Glass Composition (wt.%)		Absorption Bands					
	PbO	SiO ₂	Al ₂ O ₃	Band (A)	Band(B)	Band(c)	Band(D)	Band(E)
1	80	20		0.27 at 3455 cm ⁻¹	0.226 at 1500 cm ⁻¹	0.178 at 937 cm ⁻¹	0.183 at 470 cm ⁻¹	
21	80	19	≡ 1% SiO ₂	0.335 at 3455 cm ⁻¹	0.243 at 1200 cm ⁻¹	0.251 at 914 cm ⁻¹	0.264 at 470 cm ⁻¹	0.243 at 741 cm ⁻¹
22	"	18	≡ 2%	0.470 "	0.276 at 1170 cm ⁻¹	0.325 at 882 cm ⁻¹	0.271 at 470 cm ⁻¹	0.268 at 718 cm ⁻¹
23	"	15	≡ 5%	0.637 "	0.430 at 1150 cm ⁻¹	0.432 at 851 cm ⁻¹	0.419 at 470 cm ⁻¹	0.49 at 694 cm ⁻¹
24	"	10	≡ 10%	0.741 "	0.585 at 1128 cm ⁻¹	0.651 at 829 cm ⁻¹	0.671 at 470 cm ⁻¹	0.632 at 671 cm ⁻¹

All replace ments were made cation for cation.

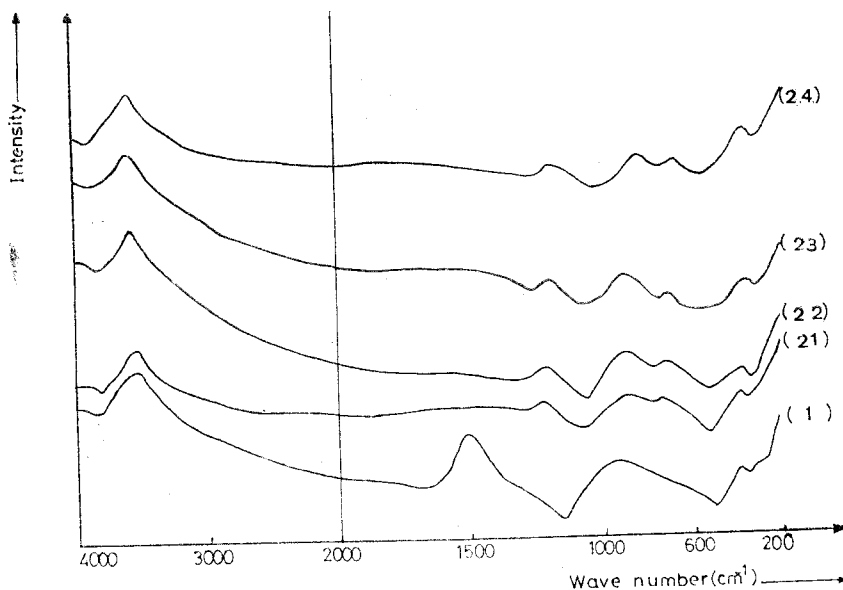


Fig. 7. Infra-red absorption spectra for lead silicate glasses of the composition PbO 80 %, SiO₂20 % containing alumina replacing silica:

1- PbO 80 %, SiO₂20 %.

21- PbO 80 %, SiO₂19 %, Al₂O₃ ≡ 1 % SiO₂.

22- PbO 80 %, SiO₂18 %, Al₂O₃ ≡ 2 % SiO₂.

23- PbO 80 %, SiO₂15 %, Al₂O₃ ≡ 5 % SiO₂.

24- PbO 80 %, SiO₂10 %, Al₂O₃ ≡ 10 = SiO₁.

(The curves are displaced vertically relative to each other to avoid confusion.)

be due to Si-O-Si stretching vibrations¹⁶ The above attributions can be explained on the basis of the fact that⁸, when alumina is introduced replacing silica in the glasses studied, every aluminium oxide molecule introduced will acquire an oxygen from the lead oxide forming AlO₄ groups because, as far as it is known, this is the only stable state for the Al⁺³ ion in the glass structure, beside the SiO₄ tetrahedra, having the lead ions in the interstices formed by SiO₄ or AlO₄ group.

Effect of titania or Zirconia:

The results obtained in this case can be explained as follows:

1- In the glasses containing titania replacing parts of silica, the displacement of the absorption bands, which are due to SiO₄ groups, with the gradual increase of titania content may be due

Table 4. Composition, values and positions of the infrared absorption bands for a number of lead silicate glasses of the base composition PbO 80 SiO_2 20 (wt. %) in which parts of silica were replaced by titania or zirconia.

Glass No.	Glass Composition (wt. %)			Absorption Bands				
	PbO	SiO_2	RO_2	Band(A)	Band(B)	Band(C)	Band(D)	Band(E)
1	80	20		0.276 at 3455 cm^{-1}	0.226 at 1500 cm^{-1}	0.178 at 937 cm^{-1}	0.183 at 470 cm^{-1}	
25	80	19	$\equiv 1\%SiO_2$	0.441 at 3455 cm^{-1}	0.217 at 1214 cm^{-1}	0.217 at 874 cm^{-1}	0.183 at 370 cm^{-1}	0.193 at 796 cm^{-1}
26	"	18	$\equiv 2\%$	0.646 " "	0.364 at 1193 cm^{-1}	0.456 at 859 cm^{-1}	0.465 at 859 cm^{-1}	0.375 at 772 cm^{-1}
27	"	15	$\equiv 5\%$	0.745 " "	0.638 at 1171 cm^{-1}	0.700 at 827 cm^{-1}	0.721 at 470 cm^{-1}	0.668 at 741 cm^{-1}
28	80	19.9	$\equiv 0.1\%SiO_2$ ZrO_2	0.520 at 3455 cm^{-1}	0.365 at 1186 cm^{-1}	0.426 at 774 cm^{-1}	0.458 at 470 cm^{-1}	

All replacements were made cation for cation.

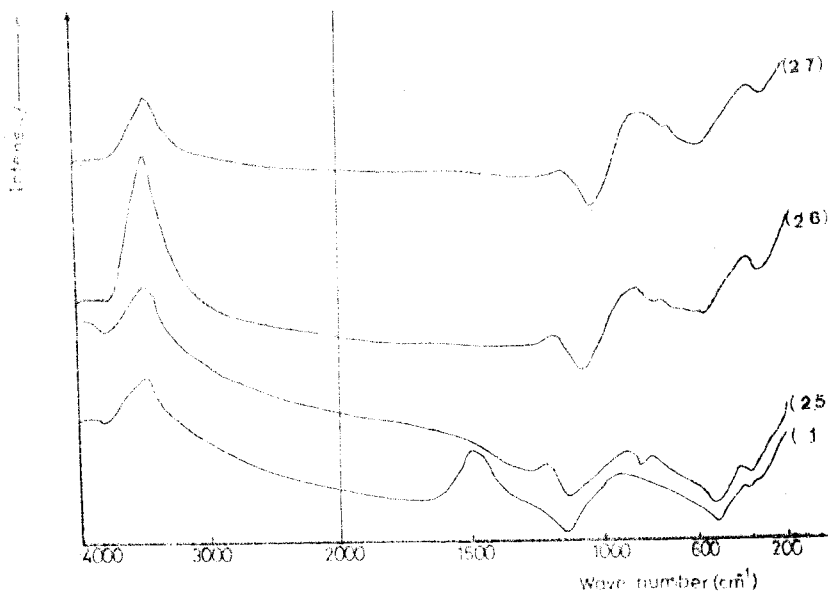


Fig. 8. Infra-red absorption spectra for lead silicate glasses of the composition PbO 80 %, SiO₂ 20 % containing titania replacing silica:

- 1- PbO 80 %, SiO₂ 20 %.
- 25- PbO 80 %, SiO₂ 19 %, TiO₂ ≡ 1 % SiO₂.
- 26- PbO 80 %, SiO₂ 18 %, TiO₂ ≡ 2 % SiO₂.
- 37- PbO 80 %, SiO₂ 15 %, TiO₂ ≡ 5 % SiO₂.

(The curves are displaced vertically relative to each other to avoid confusion.)

to the effect of TiO₄ groups on the frequency of SiO₄ groups, while the displacement of the absorption bands may be due to the vibrations of the TiO₄ groups¹⁰ Table 4 and Fig. 8.

- 2- In the glass containing zirconia replacing 0.1 part of silica, the results obtained can be explained on the same basis as in the case of the glasses containing titania, Table 4 and Fig 9.

The above conclusions can be understood by putting into consideration that when titania or zirconia is introduced replacing silica in lead silicate glasses, TiO₄ or ZrO₄ groups would be present and the oxygen ligands tend to be less polarizable.

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

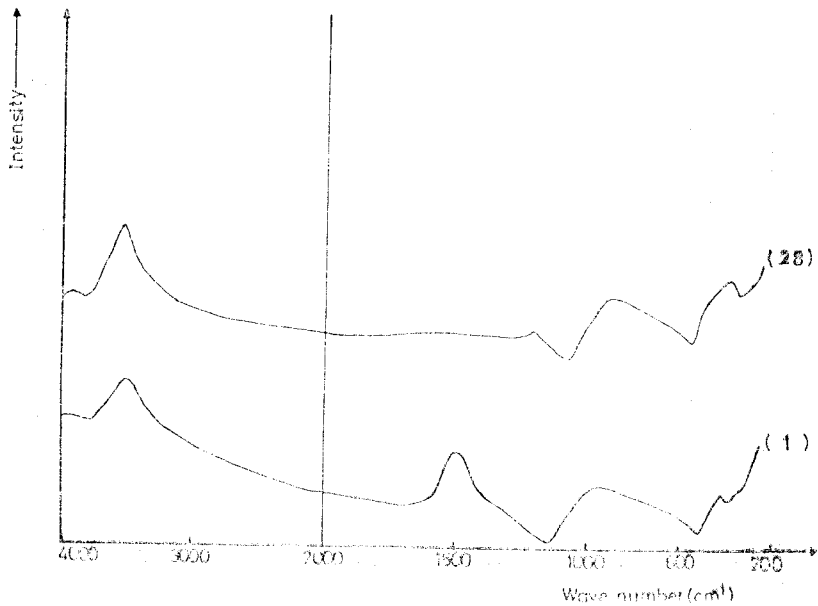


Fig. 9. Infra-red absorption spectra for lead silicate glasses of the composition PbO 80 %, SiO₂ 20 % containing zirconia replacing silica:

1- PbO 80 %, SiO₂ 20 %.

28- PbO 80 %, SiO₂ 19.9 %, ZrO₁ ≡ 0.1 % SiO₂.

(The curves are displaced vertically relative to each other to avoid confusion.)

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