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Optical and esr spectra of titanium (III) in Na_2O-B_2O_3 and Na_2O–P_2O_5 glasses

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The optical absorption and the esr spectra of titanium(III) in binary Na_2O–B_2O_3 and Na_2O–P_2O_5 glasses have been studied. Titanium(III) produces two optical absorption bands around 20 000 and 14 000 cm^{-1} which are assigned to the $^2B_{2g} \rightarrow {}^2B_{1g}$ and $^2B_{2g} \rightarrow {}^2A_{1g}$ transitions respectively of Ti^{3+} in a tetragonally distorted octahedral environment. The absorption bands in phosphate glasses are narrower and absorption coefficients higher than those in borate glasses. The esr spectrum of titanium(III) in all the glasses consists of a broad asymmetric line with $g \sim 1.94$ in borate glasses, and $g \sim 1.92$ in phosphate glasses; no hyperfine structure has been observed.

1. Introduction

A mixture of trivalent and tetravalent titanium in glass is well known to produce electronic conduction, the nature of conduction being dependent on the host matrix as well as on the relative proportion of the two oxidation states. Ti^{3+} being a $3d^1$ system invariably forms distorted polyhedra in glass. To explain the conduction mechanism in oxide glasses containing transition metal ions, the "small polaron" hypothesis has been invoked [1]. The size of the polaron is expected to be dependent on the distortion and site symmetry of Ti^{3+} and Ti^{4+} ions. The present paper reports optical and esr spectra of Ti^{3+} in some simple binary Na_2O–B_2O_3 and Na_2O–P_2O_5 glasses, from which the site symmetry of Ti^{3+} in these glasses has been deduced.

Under ordinary conditions of melting it is difficult to obtain trivalent titanium in silicate glasses, but in acid borosilicate and phosphate glasses titanium(III) is more readily obtained. Even in aqueous co-ordination chemistry relatively few complexes of titanium(III) have been studied, undoubtedly because of the experimental difficulties involved in their preparation. The best known complexes of titanium(III) are the hexahydrate [2] and the alum [3], in each of which the titanium(III) ion is octahedrally co-ordinated by six water molecules. The complexes of titanium(III) have a historical connection with ligand field theory in that Ilse and Hartmann [4] first interpreted the weak absorption band which occurs around 20 000 cm^{-1} as being caused by an electron transition between the levels formed by splitting the ^2D ground state term of titanium(III) by an octahedral ligand field.

The esr spectrum of titanium(III) has been studied in silicate glasses by Grif'yanov [5], Yafaev *et al.* [6], in borate glasses by Arafa *et al.* [7, 8], and in alkali titanate glasses by Kim *et al.* [9]. In most of the cases these workers have studied the esr of a high-energy induced titanium (III) centre. Since induced titanium(III) centres may be in a different environment [10] to that of titanium(III) occurring in glass made by the usual methods of melting, in this investigation the optical absorption and esr spectra of titanium (III) in sodium borate and sodium phosphate glasses melted under different reducing conditions have been studied.

2. Experimental

All the raw materials $NaH_2PO_4.2H_2O$, $NH_4H_2PO_4$, Na_2CO_3 and H_3BO_3 were of AnalaR quality. 0.5 wt % titanium as TiO_2 was added to the batch. 10 g batches of glass were melted in a silica crucible at 1000 ± 10° C in an electric furnace under a controlled atmosphere ($p_{O_2} = 10^{-6}$ to 10^{-15} atm depending upon the composition of the glass) for 1 h. The melt was cast as a rectangular slab and thoroughly annealed. The slabs were polished and optical absorption spectra measured on a Cary-14 spectrophotometer. Finally, the glass slab was coarsely powdered for esr measurements and chemical analysis.

The esr spectrum was obtained using a Hilger & Watts Microspin spectrometer which operated at about 9200 MHz. The magnetic field was calibrated using a proton resonance probe, and the g-value marker employed was DPPH. The coarsely powdered glass sample was introduced into the resonance cavity contained in a quartz tube. A typical spectrum is shown in Fig. 1.

All the glasses were chemically analysed. Titanium(III) was estimated by dissolving a known weight of the glass powder in ferric sulphate solution in ~ 1.5 N sulphuric acid and titrating the ferrous iron with standard ceric sulphate solution using ferroin as a redox indicator. Soda was estimated flame photometrically, P_2O_5 with lanthanum chloride [11], and B_2O_3 with standard acid-base titrations [12]. Silica was estimated by the molybdic acid method; 0.2 to 0.9 wt % SiO_2 was found to dissolve in these glasses.

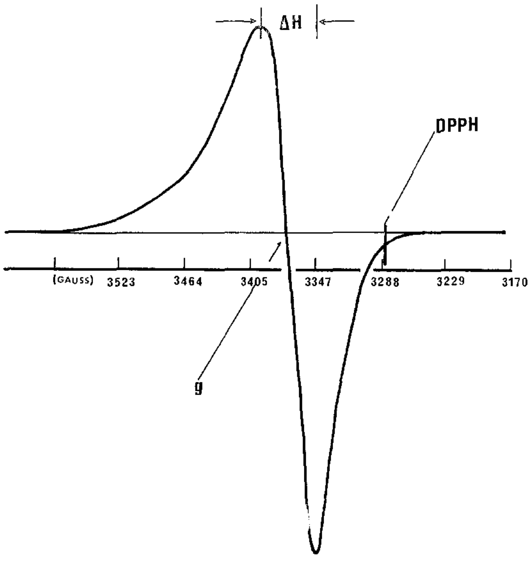

Figure 1 Typical esr spectrum of titanium(III) in $20Na_2O,80B_2O_3$ glass at room temperature (x-band frequency).

3. Results

Compositions of glasses studied in this investigation are given in Table I. Some typical absorption spectra of titanium(III) in borate and phosphate glasses are shown in Figs. 2 and 3. In the case of phosphate glasses two distinctly resolved band maxima were obtained, whereas in the case of borate glasses only an asymmetric envelope was obtained without any sign of band splitting. All these absorption envelopes were resolved into the minimum number of gaussian component bands (two in all cases were obtained); some typical examples are shown in Fig. 4. The details of the resolved bands are given in Table II. It is clear from Table II that in borate glasses splitting decreases whilst that in phosphate glasses increases with increasing soda content of the glass. The half-widths of the resolved bands in borate glasses are about double that in phosphate glasses. It may be noted that in a particular system of glass, although the position of the band maximum changes with alkali content, the half-width remains almost unchanged. For comparison a further two glasses of compositions: $10K_2O,90B_2O_3$ and $10Li_2O,90B_2O_3$ were made with titanium(III). Their optical

TABLE I Composition of glasses (after chemical analysis)

Glass number	Mol %					Wt %	
	K_2O	Na_2O	Li_2O	B_2O_3	P_2O_5	SiO_2	Titanium(III)
A_1		5.1		94.7		0.21	0.164
A_2		10.3		89.4		0.27	0.175
A_3		15.4		84.3		0.34	0.147
A_4		20.6		78.7		0.67	0.123
A_5		25.0		74.2		0.81	0.129
A_6		30.2		68.9		0.90	0.098
K	10.7			88.4		0.87	0.234
L			9.8	89.6		0.56	0.187
B_1		20			79.8	0.18	0.234
B_2		30			69.5	0.46	0.213
B_3		40			59.3	0.67	0.198
B_4		50			49.1	0.90	0.176

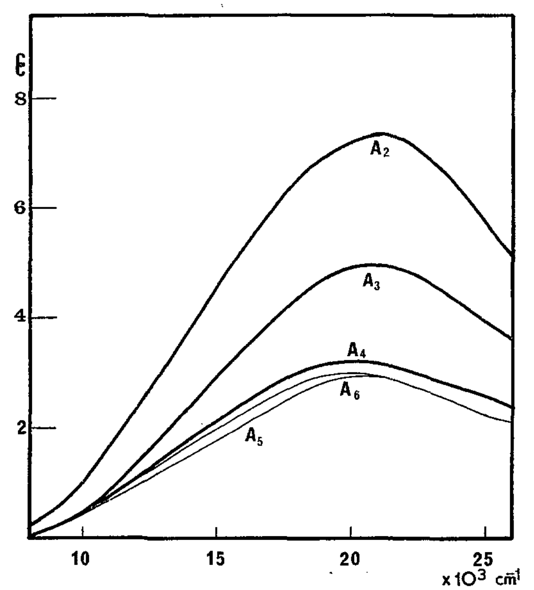

Figure 2 Optical absorption spectra of titanium(III) in Na_2O–B_2O_3 glasses.

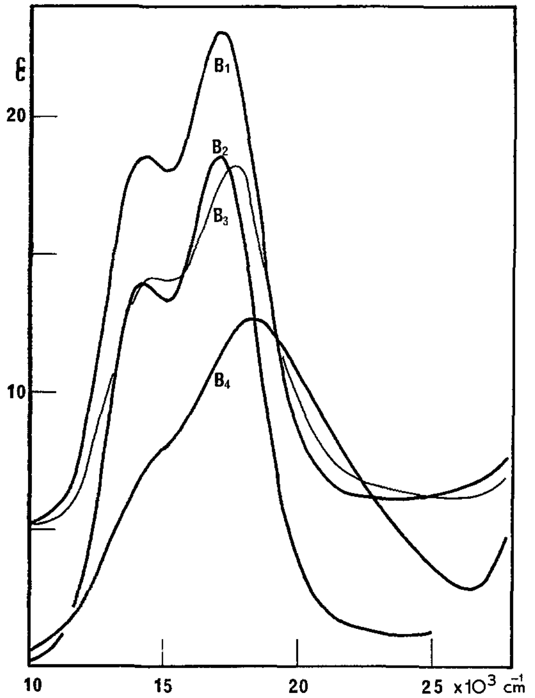

Figure 3 Optical absorption spectra of titanium(III) in Na_2O–P_2O_5 glasses.

absorption spectra are shown in Fig. 4; the intensity of the low-energy band and the overall absorption coefficient increase and the

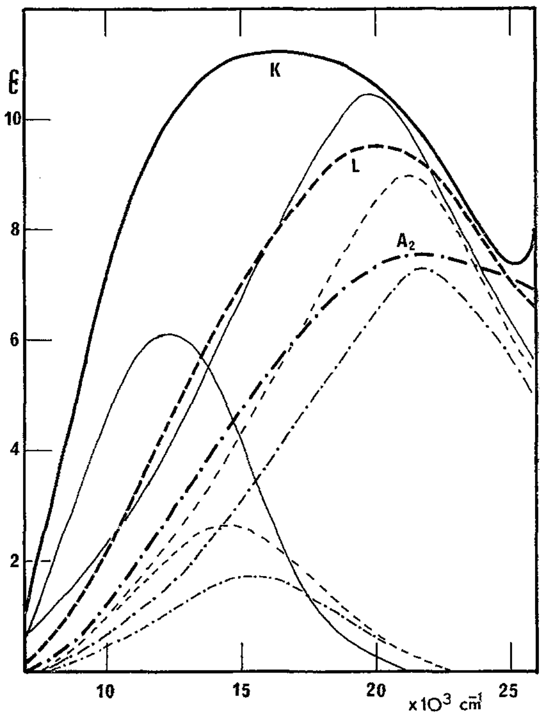

Figure 4 Typical resolution of titanium(III) absorption envelope.

splitting decreases with increasing size of the alkali ion.

The esr spectra have been measured at liquid nitrogen and at room temperature. At room temperature the esr spectra could be observed in all the borate glasses but only in phosphate glasses containing 40 and 50 mol % Na_2O. In $30Na_2O,70P_2O_5$ glass, esr could be obtained only at liquid nitrogen temperature, and in $20Na_2O$, $80P_2O_5$ glass esr spectra could not be obtained even at liquid nitrogen temperature. The width, ΔH (defined in Fig. 1) in all the glasses increases with decreasing temperature; in borate glasses ΔH increases while in phosphate glasses ΔH decreases with increasing Na_2O content of the glass. The details of estimated esr parameters are given in Table III.

4. Discussion

In all the reported absorption spectra of titanium(III) in octahedral environments, the ligand field band (around 20 000 cm^{-1}) shows distinct double structure, indicating that the field must contain at least a tetragonal com-

TABLE II Band maxima and half-widths of the resolved absorption bands

Glass number	Band maximum (cm^{-1})		Splitting (cm^{-1})
	${}^2B_{2g} \rightarrow {}^2B_{1g}$	${}^2B_{2g} \rightarrow {}^2A_{1g}$	
A_1	21 400 (7 400)*	14 400 (7 200)	7 000 (5 780)†
A_2	21 400 (7 420)	14 400 (7 200)	7 000 (5 780)
A_3	21 050 (7 400)	14 400 (7 200)	6 650 (5 670)
A_4	20 000 (7 380)	14 400 (7 210)	5 600 (5 570)
A_5	20 000 (7 400)	14 400 (7 200)	5 600 (5 280)
A_6	20 000 (7 400)	14 400 (7 200)	5 600 (4 945)
K	21 800 (7 400)	15 400 (7 200)	6 400
L	20 000 (7 400)	12 300 (7 200)	7 700
B_1	17 000 (3 080)	13 800 (2 310)	3 200
B_2	17 000 (3 080)	13 750 (2 310)	3 250
B_3	17 600 (3 120)	13 800 (2 330)	3 800 (3 490)
B_4	18 400 (3 450)	13 800 (2 890)	4 600 (3 930)

*Half-width in cm^{-1}.
†Calculated splitting from Equation 1.

ponent. The latter has the effect of splitting both the ground ${}^2T_{2g}$ and the upper ${}^2E_g$ term (Fig. 5) so that two transitions are expected: ${}^2B_{2g} \rightarrow {}^2A_{1g}$ and ${}^2B_{2g} \rightarrow {}^2B_{1g}$ in D_{4h} symmetry. The splitting of the ${}^2E$ state has been reported to be of the order of 1500 to 3000 cm^{-1} and is believed to be the result of Jahn-Teller distortion [13, 14].

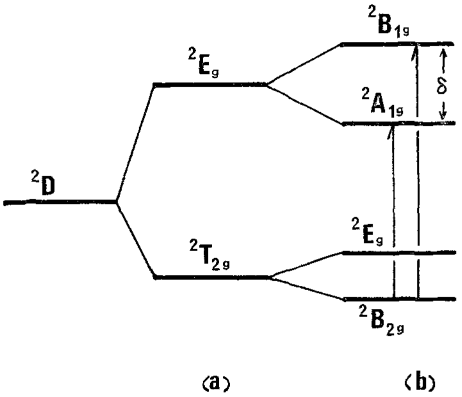

Figure 5 Splitting of the ground term of titanium(III) (${}^2D$) with (a) an octahedral field (b) a tetragonal field, D_{4h}.

In all glasses of the present investigation, two absorption bands have been obtained around 14 000 and 20 000 cm^{-1}. The absorption bands in phosphate glasses are narrower and absorption coefficients higher than those in borate glasses. This is a common feature shown by almost all the transition metal ions and can be accounted for by assuming that in glass instead of a single type of site the transition metal ions occupy a number of sites of nearly equal energy and symmetry; the spread of this distribution in phosphate glasses is narrower than that in borate glasses.

The esr spectra (as shown in Fig. 1) of all the glasses consist of one broad asymmetric line which may be assigned to the Ti^{3+} ion in a tetragonally distorted octahedral field [7-9]. The g-value for a Ti^{3+} ion is known to vary remarkably from compound to compound [15-19]. Natural titanium contains about 7% of ${}^{47}Ti$ with $I = 5/2$ and 5% of ${}^{49}Ti$ with $I = 7/2$. Thus hyperfine structure may arise [20, 21]. However, no hyperfine structure was observed in the present study. The reasons for this may be that

TABLE III g-value and line-width (G) of titanium(III) in different glasses

Glass number	$\Delta H_{77\,K}$	$\Delta H_{300\,K}$	$\Delta H_{77\,K} - \Delta H_{300\,K}$	$g_{300\,K}$
A_1	40.1	37.1 ± 1.2	3.0	1.949
A_2	49.7	41.8 ± 1.6	7.9	1.949
A_3	57.5	46.0 ± 1.6	11.6	1.948
A_4	61.9	48.5 ± 1.7	13.4	1.947
A_5	67.6	53.2 ± 1.4	14.4	1.944
A_6	71.1	53.2 ± 3.2	17.9	1.940
B_1	no signal	no signal	—	—
B_2	165.4 ± 7.4	no signal	—	—
B_3	—	90.3 ± 4.9	—	1.914
B_4	115.2 ± 6.9	61.9 ± 3.7	—	1.924

(a) the natural abundance of both isotopes ^{47}Ti and ^{49}Ti is very small; (b) the anisotropy of g and A tensors, if any, would broaden the hyperfine components; and (c) a distribution of g-values (which can not be ruled out particularly in glass) could also cause the hyperfine components to be spread over a certain range.

The observed g-values can be used to obtain the separation (and thereby the distortion) between the Ti^{3+} energy levels (Fig. 5) if certain crude assumptions are made. The presence of a perfect cubic field cannot explain the experimentally observed anisotropy of the g-value of Ti^{3+}. Such anisotropy can only be accounted for if a ligand field with symmetry lower than that of a cubic field acts upon the metal ion. For example, a trigonal or tetragonal field will cause a further splitting of the lower triplet and upper doublet states. These additional splittings cause the g-value of the Ti^{3+} to depart markedly from the free electron g-value, 2.0023. Using the theoretical expression for g-values

$$g_{ij} = (g_e \delta_{ij} - 2\lambda \Lambda_{ij})$$

calculated by Pryce [22] and the energy level scheme shown in Fig. 5, the g-values for the Ti^{3+} centre in the tetragonally distorted octahedral symmetry can be obtained as follows:

$$g = g_{\perp} = g_{xx} = g_{yy} = g_e - 2\lambda/\delta \qquad (1)$$

where g_e is the g-value of the free electron, δ is the energy splittings shown in Fig. 5, and $\lambda = 154$ cm^{-1} is the spin-orbit coupling constant for the Ti^{3+} ion [23].

Using Equation 1 the splitting energies have been calculated with the estimated g-values, and these are also given in Table III where a reasonably good agreement between the experimental and calculated splitting energies can be seen.

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