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EPR and optical absorption of Cr^{3+} in binary $Na_2O–B_2O_3$ glasses

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The optical absorption and EPR spectra of Cr^{3+} in binary sodium borate glasses have been studied as functions of chromium concentration and Na_2O/B_2O_3 ratio in the glass; the ligand field and EPR parameters have been calculated and were found to be independent of Cr^{3+} concentration in any particular glass. In low-alkali borate glasses (Na_2O = ~ 11 or ~ 14 mol %) a single symmetrical EPR line was observed with $g_\parallel = g_\perp = 1.984 \pm 0.001$ corresponding to perfect octahedral symmetry of the Cr^{3+} ion in these glasses. With increasing Na_2O content of the glass, the EPR line becomes more asymmetric (characteristic two-peaked pattern); this has been explained as being due to axial elongation of the six co-ordinated Cr^{3+}-complex in these glasses.

1. Introduction

Ruby, natural or synthetic, is α-Al_2O_3 (corundum) containing occasional Cr^{3+} ions in place of Al^{3+} ions. The environment of the Cr^{3+} in ruby is a slightly distorted (D_{3d}) octahedron of oxide ions and energy-level diagram of Cr^{3+} in an octahedral field is shown in Fig. 1. The frequencies of the spin-allowed bands of Cr^{3+} in ruby indicate that the Cr^{3+} ion is under considerable compression, since the value of the ligand field strength, Δ_{oct}, calculated from the optical transition energies is significantly higher than that in the $[Cr(H_2O)_6]^{3+}$ complex or in other oxide crystals and silicate or phosphate glasses. Spin-forbidden transitions from the $^4A_2$ ground state to the doublet states arising from the ^2G state of the free ion are also observed in ruby. The transitions to the ^2E and $^2T_1$ states give rise to extremely sharp lines, as the slopes of the energy lines for these two states are identical to that of the ground state (except in extremely weak fields).

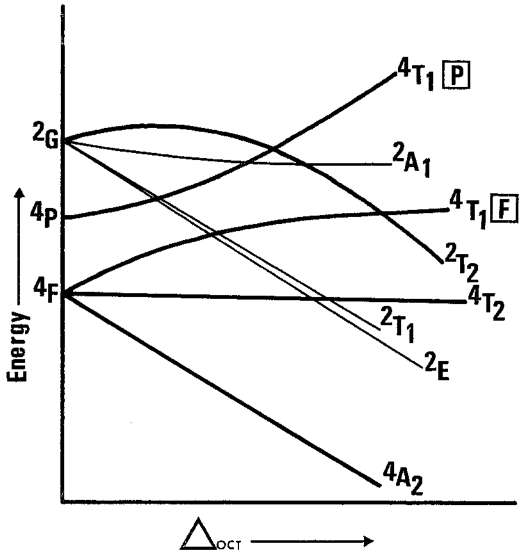

Figure 1 Energy level diagram of Cr^{3+} in an octahedral field.

If a large single crystal of ruby is irradiated with electromagnetic radiation of the precise frequency to cause excitation to the $^4T_2(F)$ state, the exact magnitudes of certain energy differences and relaxation times in the ruby are such that the system rapidly makes a radiationless transition (i.e. by loss of energy to the crystal lattice in the form of vibrations) to the ^2E and $^2T_1$ states, instead of decaying directly back to the ground state. The system then returns from the doublet states to the ground state by spontaneous emission of very sharp fluorescence lines, commonly known as the R-lines of the ruby laser.

Because the making and fabrication of glass is much easier than single crystals, much interest has arisen in recent years in exploring the possibility of using Cr^{3+}-doped oxide glasses as laser material. This has lead to extensive spectroscopic (both absorption and emission) studies of Cr^{3+} in different silicate and phosphate glasses. In all the oxide glasses studied so far, Cr^{3+} has been found to occur in an octahedral environment. To understand the finer details of electronic energy levels, a large amount of work has been undertaken and reported on the EPR of Cr^{3+} in different crystalline materials [1-6]; however, the corresponding work in glass is only very meagre.

Zakharov *et al.* [7] have studied the EPR spectrum of Cr^{3+} in complex phosphate glasses at 9.3 GHz and found that $g_\perp = 1.78 \pm 0.05$ and $g_\parallel = 5.0 \pm 0.2$. Landry *et al.* [8] studied the EPR spectrum of Cr^{3+} in a zinc-aluminium phosphate glass containing different amounts of dissolved Cr_2O_3 (0.098 to 8.69 wt% Cr_2O_3); they observed isolated Cr^{3+} ions with $g_{eff} = 5.0$ both at 9.49 and 2.05 GHz. However, for heavily doped samples the authors observed a prominent line in the vicinity of $g_{eff} = 2.0$ which they attributed to exchange-coupled pairs of Cr^{3+} ions. In this paper our observations on the EPR and optical absorption studies of Cr^{3+}-doped binary sodium borate glasses having different Na_2O/B_2O_3 ratios are reported. Our EPR results are quite different from those in phosphate glasses described above; the observed features have been explained in terms of the usual crystal field theory [15].

2. Experimental details

All the batch materials (Na_2CO_3, H_3BO_3, $Na_2B_4O_7 . 10H_2O$) were of AnalaR quality. Chromium was added to the batch as ammonium dichromate. 10 g batches of glass were melted at 1000 ± 10°C in a Pt + 2% Rh crucible in an electric furnace with a controlled atmosphere ($p_{O_2} = 10^{-2}$ to 10^{-6} atm depending upon the composition of the glass) for 4 h. For a particular glass the oxygen potential was adjusted to obtain the maximum possible trivalent chromium so that the optical absorption maxima due to Cr^{3+} could be identified accurately with minimum influence from the chromium(VI)-absorption tail. To achieve this, lower oxygen potentials were required with increasing Na_2O content of the glass. Difficulty was experienced with the glass containing ~ 11 mol% Na_2O where with $p_{O_2} \leqslant 10^{-4}$ atm, Cr^{2+} formed in the glass [9]. Glasses of this series were melted with $p_{O_2} = 10^{-2}$ atm only; these glasses contained about 70% of the total chromium in the hexavalent state. The absorption envelopes were not clearly resolved, thus the ligand field parameters could not be estimated accurately.

After melting, the glass was cast as rectangular slabs and thoroughly annealed. The slabs were polished and the optical absorption spectra were measured with a Cary-14 spectrophotometer. Finally, the glass slabs were coarsely powdered for EPR measurements and chemical analysis.

All EPR spectra were recorded at room temperature (20°C) with a Varian V-4502 EPR spectrometer, operating at x-band microwave frequency (~ 9.5 GHz) and provided with a 100 kHz field modulation. DPPH with $g = 2.0036$ was used as the standard field marker. The magnetic field at DPPH resonance was measured by proton resonance using a Varian model F-8A fluxmeter and a Hewlett-Packard 524-C counter. In some selected cases, EPR spectra were also recorded at liquid nitrogen temperature, and no significant difference from that at room temperature was observed.

All glasses were chemically analysed: the total and hexavalent chromium was estimated colorimetrically with diphenyl carbazide [10], and the trivalent chromium was estimated from the difference. Na_2O and B_2O_3 were estimated with conventional acid-base titrations [11].

3. Results

The compositions of the glasses and their chromium concentrations together with relevant ligand field and EPR parameters are given in Table I. A typical absorption spectrum of Cr^{3+} in a borate glass is shown in Fig. 2 where different electronic transitions are marked on the spectrum. The ligand field strengths, Δ_{oct}, reported in Table I are the self consistent values calculated from the spin-allowed and spin-forbidden transition energies. Fig. 3 shows a typical EPR spectrum of Cr^{3+} in a borate glass in which the positions of $g_\parallel$ and $g_\perp$ have been marked.

4. Discussion

The optical absorption spectra of all glasses of the present investigation are very similar in nature, and are characteristic of Cr^{3+} in a slightly distorted octahedral environment. Indeed, the ligand field stabilization for octahedral

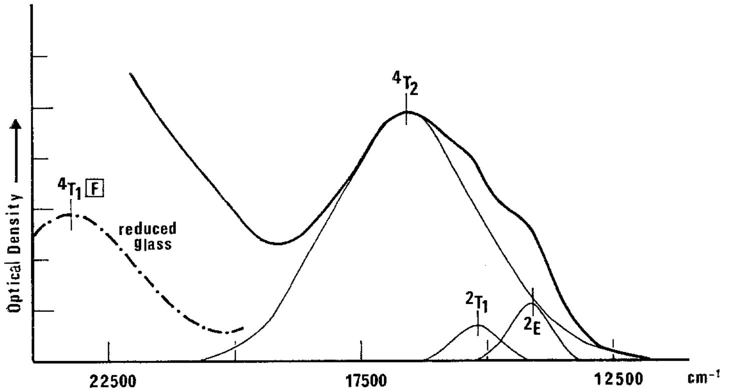

Figure 2 Typical absorption spectrum of Cr^{3+} in a borate glass.

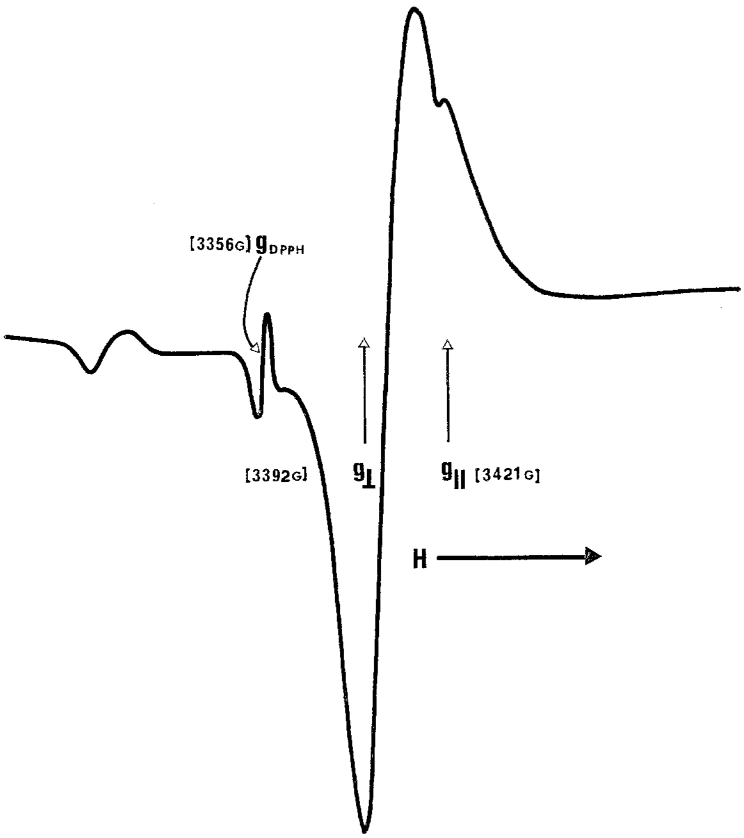

Figure 3 Typical EPR spectrum of Cr^{3+} in a borate glass.

Cr^{3+} relative to any other configuration is so large that the occurrence of Cr^{3+} in four-fold co-ordination is not expected [12]. The average ligand field strength, Δ_{oct}, in borate glasses (16 000 cm^{-1}) is about 5 and 10% larger than that in alkali silicate (15 300 cm^{-1}) and alkali phosphate (14 500 cm^{-1}) glasses respectively [8, 13].

Our EPR observations on Cr^{3+}-doped borate glasses are entirely different from results previously reported [7, 8] on phosphate glasses; we have not observed any effect of total chromium concentration (up to 2 wt%) on the EPR spectrum in a borate glass of a particular composition (see Table I), although some of the glasses (1D and 2D) having a high chromium concentration were translucent, as they contained precipitated crystals. Furthermore, we have

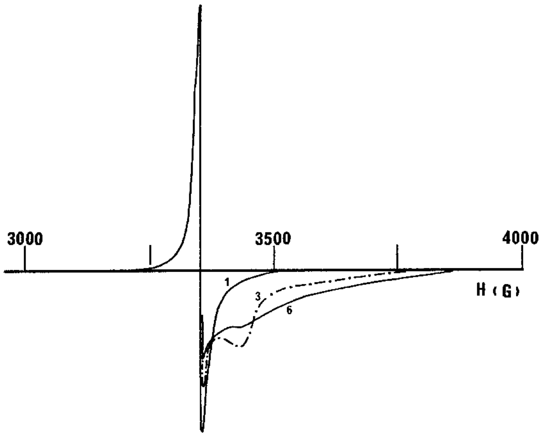

Figure 4 EPR spectra of Cr^{3+} in different borate glasses.

observed only one kind of Cr^{3+}-complex* which shows a change in symmetry with changing Na_2O/B_2O_3 ratio of the glass. For low-alkali glasses (Na_2O = ~ 11 and ~ 14 mol%) a single symmetrical line on the high-field side of DPPH marker was obtained with $g_\parallel = g_\perp = 1.984 \pm 0.001$. This means that in these glasses, the Cr^{3+}-complex is in perfect octahedral symmetry. As the alkali content increases above ~ 17 mol%, the EPR line starts to become asymmetric (Fig. 4) and $g_\parallel$ is no longer equal to $g_\perp$. The characteristic two-peaked pattern of an axial complex in a powdered sample is then observed. Therefore, the Cr^{3+} site in these glasses no longer has the perfect octahedral symmetry, but is axially distorted. The axial distortion lifts the degeneracy of the $S = 3/2$ ground manifold leading to two doublets $\pm 3/2$ and $\pm \frac{1}{2}$, separated by $2|D|$, giving the usual Cr^{3+} spectrum. In single crystals one would observe three allowed transitions ($\Delta M = \pm 1$) in the EPR of such a complex. However, in glasses, as in powders [14], the outer two lines corresponding to the transitions $\pm 3/2 \leftrightarrow \pm \frac{1}{2}$ will average out because of the random orientations of the paramagnetic centres leaving only the averaged central transition ($+\frac{1}{2} \leftrightarrow -\frac{1}{2}$) peaked at field

TABLE I EPR and ligand field parameters of Cr^{3+} in different sodium borate glasses

Glass no.	Na_2O (mol %)	B_2O_3 (mol %)	Total chromium (calc. as Cr, wt %)	$g_\parallel$	$g_\perp$	$\frac{1}{3}(g_\parallel + 2g_\perp)$	Δ_{oct} (cm^{-1})
1A	11.12	88.85	0.021	1.984 ± 0.002	1.984 ± 0.002	1.984 ± 0.002	
B	11.15	88.73	0.017	1.984 ± 0.001	1.984 ± 0.001	1.984 ± 0.001	16 260
C	11.29	88.17	0.530	1.984 ± 0.001	1.984 ± 0.001	1.984 ± 0.001	
D†	11.81	86.11	2.072	x	x	x	
2A	14.30	85.67	0.021	1.984 ± 0.001	1.984 ± 0.001	1.984 ± 0.001	
B	14.33	85.56	0.103	1.984 ± 0.001	1.984 ± 0.001	1.984 ± 0.001	16 260
C	14.45	85.03	0.512	1.984 ± 0.001	1.984 ± 0.001	1.984 ± 0.001	
D†	14.87	83.12	2.000	x	x	x	
3A	17.26	82.71	0.020	1.945 ± 0.003	1.986 ± 0.001	1.972 ± 0.002	
B	17.28	82.61	0.099	1.945 ± 0.001	1.986 ± 0.001	1.972 ± 0.001	16 180
C	17.38	82.12	0.494	1.945 ± 0.001	1.986 ± 0.001	1.972 ± 0.001	
D	17.73	80.33	1.933	1.945 ± 0.001	1.986 ± 0.001	1.972 ± 0.001	
4A	20.03	79.94	0.019	1.938 ± 0.003	1.986 ± 0.001	1.970 ± 0.002	
B	20.04	79.85	0.096	1.938 ± 0.001	1.986 ± 0.001	1.970 ± 0.001	16 000
C	20.12	79.39	0.478	1.938 ± 0.001	1.986 ± 0.001	1.970 ± 0.001	
D	20.40	77.72	1.870	1.938 ± 0.001	1.986 ± 0.001	1.970 ± 0.001	
5A	25.03	74.94	0.018	1.932 ± 0.003	1.986 ± 0.001	1.968 ± 0.002	
B	25.05	74.84	0.090	1.932 ± 0.003	1.986 ± 0.001	1.968 ± 0.002	15 870
C	25.08	74.45	0.448	1.932 ± 0.001	1.986 ± 0.001	1.968 ± 0.001	
D	25.25	72.98	1.756	1.932 ± 0.001	1.986 ± 0.001	1.968 ± 0.001	
6A	33.33	66.65	0.017	1.932 ± 0.003	1.986 ± 0.003	1.968 ± 0.003	
B	33.33	66.58	0.086	1.932 ± 0.003	1.986 ± 0.001	1.968 ± 0.002	15 500
C	33.32	66.23	0.429	1.932 ± 0.002	1.986 ± 0.001	1.968 ± 0.002	
D	33.33	64.98	1.685	1.932 ± 0.002	1.986 ± 0.001	1.968 ± 0.002	

†These glasses were opaque due to precipitation of some unidentified crystals.

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*"Complex" is used to denote the grouping of the Cr^{3+} ion with its nearest neighbour oxygen atoms (usually six in number).

values corresponding to $g_{\parallel}$ and $g_{\perp}$ of the complex. This is, in fact, what was observed in glasses with a higher alkali content.

Furthermore, the g-values are given by the equations [14]:

$$g_{\parallel} = g_S - \frac{8\lambda}{\Delta_0} \text{ and } g_{\perp} = g_S - \frac{8\lambda}{\Delta_1}$$

where the symbols have their usual meaning, and $g_S = 2.0023$. For cubic symmetry $\Delta_0 = \Delta_1$ and hence $g_{\parallel} = g_{\perp}$. The g-value is isotropic and less than g_S as observed in glasses of series 1 and 2 (see Table I).

With high-alkali glasses, Δ_0 decreases (as shown by the optical data) and hence so does $g_{\parallel}$. The fact that $\Delta_0 \neq \Delta_1$ and hence $g_{\parallel} \neq g_{\perp}$ as observed, is also due to axial distortion (see Table I). However, the spin-orbit coupling constant, λ and the contribution to orbital moment also reduce from their free-ion values, owing to bonding of the Cr^{3+} ion with the surrounding ligands in the glass. Thus a straightforward correlation between the observed g-values and estimated Δ_{oct} from optical spectra is not possible.

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