JOURNAL OF MATERIALS SCIENCE 9 (1974) 1133–1138

Origin of the blue colour in alkali-borate glasses containing sulphur

A. PAUL, A. WARD, S. GOMOLKA
Department of Glass Technology, University of Sheffield, UK

The optical, absorption, emission and excitation spectra of blue binary alkali-borate glasses containing sulphur have been studied. The presence of dissolved water in glass was found to help the formation of blue sulphur chromophore, the chromophore being unstable in glasses containing less than 10 mol % R_2O or more than 30 mol % R_2O. The blue colour is suggested to be due to the S_2^- (hypersulphide) ion, and optical absorption and emission transitions due to this ion have been assigned.

1. Introduction

Sulphur in glass has been reported to produce different colours, namely blue, green, yellow, amber and even red depending upon the composition and melting conditions of the glass [1]. The present investigation was undertaken to study the origin of the blue colour in sulphur containing glasses.

Geitner [2] reported in 1864 that when sulphur is heated at 180°C together with water and traces of some basic salt, a deep blue colour develops which disappears on cooling. Since then, various workers have reported the blue solution of sulphur in liquid ammonia [3], in molten alkali halides [4] and sulphates [5] in organic aprotic solvents like dimethyl formamide (DMF), [6] etc. In most of the cases the blue colour appears only at high temperature and vanishes when the solvent is cooled.

It is well known that molten potassium thiocyanate develops a deep blue colour when heated above 300°C [7]; the intensity of blue colour increases by adding elemental sulphur or K_2S_4 to the melt, while the blue colour bleaches on the addition of KCN or K_2S [8]. All these blue solutions in aqueous and non-aqueous solvents exhibit a strong absorption band around 16 000 cm^{-1} together with a series of other bands of varying relative intensity at higher energies. Hoffmann [9] has reported a similar set of absorption bands in boro-ultramarine containing sulphur. In most of the cases the blue colour was attributed to the formation of uncharged sulphur particles such as S_2, S_4, or colloidal sulphur. However, recent electrochemical reduction studies by Merritt *et al.* [10] on elemental sulphur in dimethyl sulphoxide (DMSO), and spectroscopic and magnetic studies by Giggenbach [6] in organic polysulphide solutions suggest that these blue solutions are caused by the hypersulphide ion, S_2^-.

In this investigation we have studied the optical absorption, fluorescence and excitation spectra of the blue sulphur chromophore in binary alkali borate glasses as functions of glass composition, water content of the glass, and the degree of reduction.

2. Experimental

All the batch materials were of AnalaR quality. Alkali oxides were introduced as carbonates or hydroxides, boric oxide as orthoboric acid and sulphur as elemental sulphur. The composition of the batch and of the final glass (after chemical analysis) is given in Table I. Batch materials to yield 10 g of glass were weighed, thoroughly mixed and melted in vitreous silica crucibles at 950 ± 10°C for 1 h with mechanical stirring for homogeneity. The melt was cast on a mild steel plate and annealed at appropriate temperatures to remove strain. The slabs were polished and optical absorption measured on a Cary 14 spectrophotometer. Emission and excitation spectra of representative samples were measured as follows.

Samples 2 mm thick were excited using a tungsten-halogen lamp and a Jarrel-Ash 0.25 m Ebert monochromator to select the appropriate exciting frequency. The fluorescence collected at right angles to the incident radiation

TABLE I Composition and colour of alkali-borate glasses melted with sulphur

Series	After Chemical Analysis				Batch materials	Colour
	*Base glass (mol %)		Weight percent			
	R_2O	B_2O_3	Water	Sulphur		
A	7.10 Na_2O	92.90	0.40	1.21	Powdered glass + sulphur	Colourless
	11.14	88.86	0.13	1.37		Colourless
	14.32	85.68	0.11	1.42		Colourless
	17.38	82.62	0.08	1.47		Colourless
	20.04	79.96	0.09	1.34		Faint blue
	25.05	74.95	0.12	1.40		Faint blue
	33.20	66.80	0.32	1.70		Brown
	20.01 Li_2O	79.99	0.07	1.10		Colourless
	28.90 K_2O	71.10	0.32	1.69		Faint green
B	14.32 Na_2O	85.68	0 15	1.01	10 g glass powder + sulphur + 100 mg carbon	Colourless
	20.04	79.96	0.06	1.13		Faint blue
	25.05	74.95	0.07	1.11		Faint blue
	33.20	66.80	0.21	1.10		Brown
	20.01 Li_2O	79.99	0.02	0.97		Colourless
	28.90 K_2O	71.10	0.32	1.69		Faint green
C	7.00 Na_2O	93.00	5.10	0.40	ROH + boric acid + sulphur	Colourless
	12.16	87.84	4.32	0.31		Blue
	18.41	81.59	3.74	0.37		Blue
	22.61	77.39	3.98	0.39		Blue
	26.49	73.51	4.66	0 41		Blue
	27.96	72.04	3.57	0.47		Grey (Blue + Brown)
	33.30	66.70	6.65	0.49		Brown
	20.00 Li_2O	80.00	2.11	0.36		Colourless
	28.57 K_2O	71.43	3.20	0.57		Green

*Base glass composition is calculated so that moles of alkali oxide + moles of boric oxide = 100.

was monitored by a second monochromator. The fluorescence was recorded using phase-sensitive detection and a photomultiplier. The emission spectra (corrected for instrument response) were plotted in units of energy per unit wavenumber interval as shown in Fig. 2. The excitation spectra shown in Fig. 2 are uncorrected. After optical and fluorescence measurements the same piece of glass was finely powdered and chemically analysed for alkali oxide and boric oxide by the conventional acid-base titrations, total sulphur by the V_2O_5 fusion method [11], and dissolved silica from the crucible by the molybdic acid method [12]. The amount of dissolved water was estimated by the method of subtraction and its relative accuracy was checked against infra-red absorption of thin films of these glasses around 3 to 5 μm [13].

Three methods were adopted for making these glasses. In series A, alkali carbonates and boric acid were melted in a platinum crucible at 1000°C for 4 h; dry nitrogen gas was bubbled through the melt to reduce water content of the melt. The melt was then cast, finely powdered. 10 g portions of this powdered base glass were then mixed with different amounts of sulphur and remelted in silica crucibles at 950 ± 10°C for 1 h with stirring. In series B, 10 g portions of the base glass powder were mixed with different amounts of sulphur and 100 mg of fine graphite powder and remelted in silica crucibles at 950 ± 10°C for 1 h with stirring. In series C, alkali hydroxides and orthoboric acid were mixed with sulphur and melted in silica crucibles at 950 ± 10°C for 1 h with stirring. As can be seen from Table I, glasses of series C contained the maximum amount of water, and that of series B contained the least; in a particular series, however, the amount of dissolved water varied with composition of the glass.

3. Results

The optical absorption spectra of representative glasses are shown in Fig. 1. In the $Na_2O–B_2O_3$

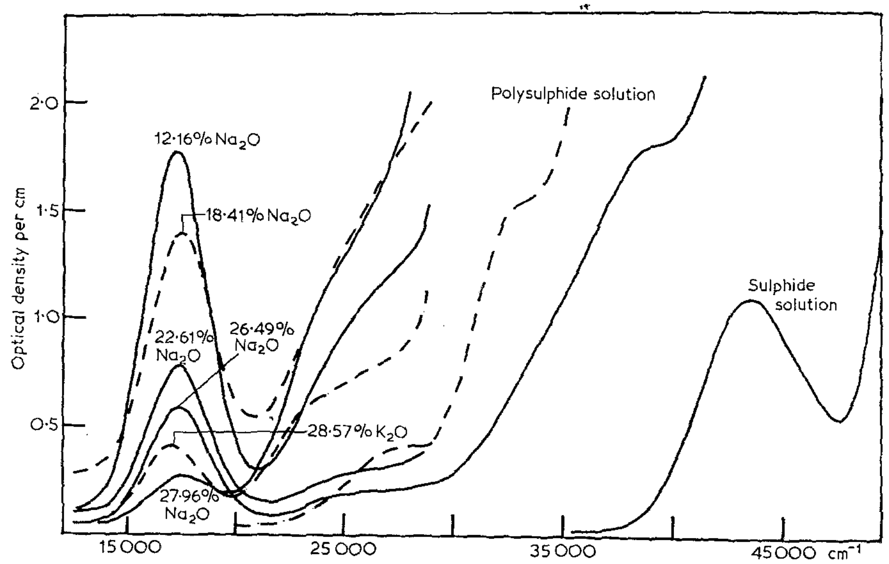


Figure 1 Optical absorption spectra of blue glasses containing sulphur and of sulphide and polysulphide solutions.

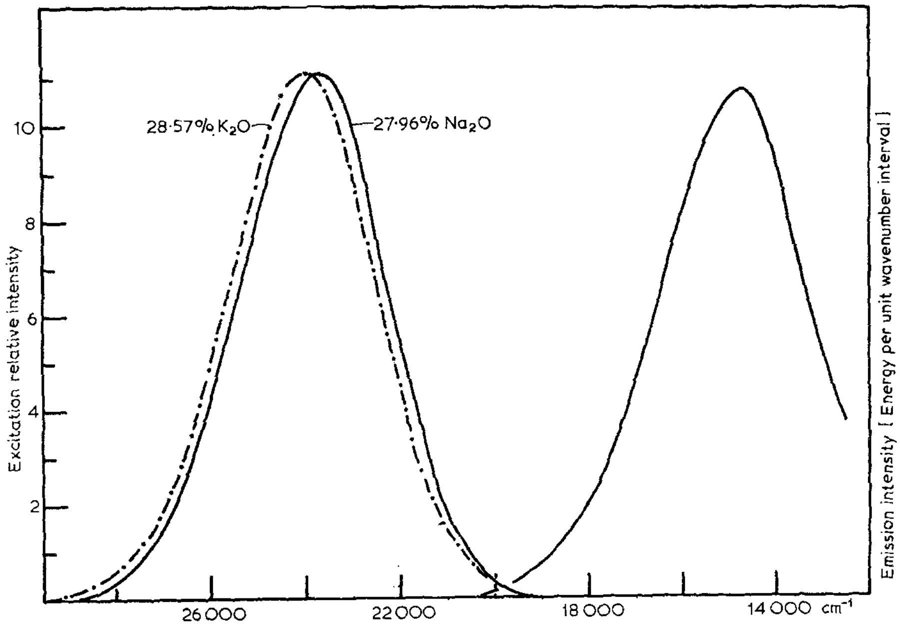


Figure 2 Emission and excitation spectra of some sulphur containing blue glasses.

glasses, the colour of the glass changes from blue to grey to amber when the soda content is increased from 28 to 34 mol%; the position of the absorption band at 17 000 cm^{-1} remains unshifted although its relative intensity changes considerably; and the band at 24 000 cm^{-1} becomes stronger relative to the intensity of the 17 000 cm^{-1} band, and thus the shade of colour changes from blue to grey and finally to amber. From Table I it can be seen that glasses melted with alkali carbonates instead of hydroxides did not produce satisfactory blue colour; and the addition of a reducing agent (graphite powder) did not produce any stronger blue colour. The glasses containing 33 mol% Na_2O in series A and B produced only a brown colour without any sign of absorption bands at 17 000 cm^{-1}.

Glasses melted with KOH were distinctly green; the absorption band around 17 000 cm^{-1} has shifted slightly to lower energies, but the band around 25 000 cm^{-1} has moved considerably to lower energies shifting the position of maximum transmission to the green region of the spectrum.

Fig. 1 also contains the absorption spectra of Na_2S in 1N NaOH and that of sodium "polysulphide" solution in 1N NaOH. These absorption spectra of aqueous solutions were measured using 0.10 cm path length quartz cell.

Emission and excitation spectra of some representative glasses are shown in Fig. 2. All the blue glasses show orange fluorescence when excited around 24 000 cm^{-1}; no emission could be detected by exciting at 17 000 cm^{-1}. Even glasses having the faintest blue colour produced reasonably strong fluorescence and concentration quenching could not apparently be observed. On the other hand, neither alkaline sulphide solution nor the polysulphide solution showed any fluorescence when excited around 24 000 cm^{-1}, whereas a green solution which was obtained by mixing 20 vol % of the polysulphide solution with 80 vol% DMF produced green fluorescence when excited at 24 000 cm^{-1}.

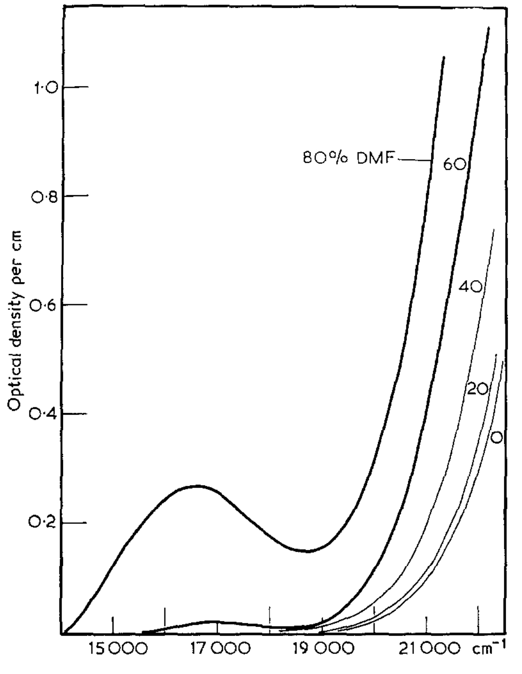
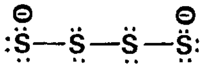


Figure 3 Optical absorption spectra of polysulphide and hypersulphide in different water-DMF mixtures.

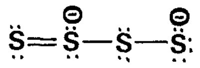
4. Discussion

Aqueous solutions of alkali polysulphides have been studied extensively, and it has been found that only the tetra- and pentasulphides form stable solutions, whereas di- and trisulphides disproportionate into monosulphide and mixtures of tetra- and pentasulphides [14]. The absorption spectra of aqueous solutions of yellow polysulphide, which has been prepared by saturating 1N NaOH solution of Na_2S with elemental sulphur at room temperature is very similar to that reported for tetrasulphide ion, S_4^{2-}. On addition of DMF to this solution, a gradual shift of the entire spectrum to lower energies has been observed (Fig. 3). A mixture containing 25 vol% DMF is still yellow, further addition of DMF changes the colour to green and a new band appears at 16 200 cm^{-1}. The intensity of this band depends reversibly on the DMF content of the mixture. This has usually been explained as follows: The tetrasulphide ion in solution can assume different electronic arrangements:



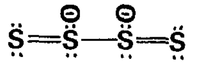
$$:\overset{\ominus}{\ddot{S}}-\ddot{S}-\ddot{S}-\overset{\ominus}{\ddot{S}}:$$

(A)



$$\ddot{S}=\overset{\ominus}{S}-\ddot{S}-\overset{\ominus}{\ddot{S}}:$$

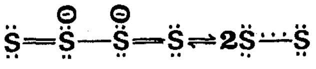
(B)



$$\ddot{S}=\overset{\ominus}{S}-\overset{\ominus}{S}=\ddot{S}$$

(C)

In water, state A is stabilized through hydrogen bonding which keeps the charges at the end of the chain; the interaction of free electron pairs of aprotic polar solvents like DMF favour a more uniform distribution of the electronic charges on the tetrasulphide ion as in cases B and C. When the concentration of DMF in the solvent is very high, the accumulation of negative charges on the two inner sulphur atoms will weaken the middle bond and finally lead to the dissociation of the tetrasulphide ion into two hypersulphide ions:



$$\ddot{S}=\overset{\ominus}{\ddot{S}}-\overset{\ominus}{\ddot{S}}=\ddot{S} \rightleftharpoons 2\ddot{S}\cdots\ddot{S}$$

The electronic configuration arising from the 3p electrons of the ground state of this hypersulphide ion is: $[\delta_g]^2\ [\Pi_u]^4\ [\Pi_g]^3$, which corresponds to a $^2\Pi_g$ state. The most probable excited state is the $^2\Pi_u$ state with the configuration: $[\delta_g]^2\ [\Pi_u]^3\ [\Pi_g]^4$. The band at 16 200 cm^{-1} is, therefore, assigned to a $^2\Pi_g \rightarrow {}^2\Pi_u$ transition.

In alkali borate glasses with small amounts of water (series A and B), faint blue colour was developed only with 20 and 25 mol% Na_2O; glass containing 33 mol% Na_2O was distinctly brown (polysulphide colour), and glasses containing less than 20 mol% Na_2O did not produce any colour at all. On the other hand, glasses rich in water (series C) produced a blue colour (the absorption band at 17 000 cm^{-1}) in almost all the glasses; however, glasses containing less than 15 mol% Na_2O were pale blue, and in glasses containing 33 mol% Na_2O, the brown colour was more prominent than the faint blue hue in it. In analogy to the alkali polysulphides in aqueous solutions, the sulphur reactions in glass melts at high temperature may be suggested as follows:

$$4S + 4R_2O \rightleftharpoons R_2SO_4 + 3R_2S \qquad (1)$$

$$3S + R_2S \rightleftharpoons R_2S_4 \qquad (2)$$

$$R_2S_4 \rightleftharpoons 2S_2^- + 2R^+ . \qquad (3)$$

Equations 1 to 3 explain the dependence of the S_2^- concentration on the composition of the glass. It is known that with very high R_2O activity in the melt, sulphur exclusively dissolves as sulphate without producing any sulphide [15]:

$$S + R_2O + \tfrac{3}{2}\,O_2 \rightleftharpoons R_2SO_4 .$$

In glasses containing 33 mol% R_2O probably enough R_2S and R_2S_4 are formed, but high concentration of R^+ does not allow significant dissociation of R_2S_4 as in Equation 3. Thus this glass appears brown characteristic of tetrasulphide group. On the other hand, with very low R_2O activity in the melt, sulphur does not dissolve and presumably escape as SO_2 from the melt:

$$S + O_2 \rightleftharpoons SO_2 .$$

Thus sulphide and correspondingly tetrasulphide is formed within a limited range of R_2O activity in the melt.

From our results (Table I) it is clear that dissolved water in glass plays a decisive role in producing the blue colour with sulphur. Similar observations have been made in molten alkali halides where it was impossible to obtain a blue colouration by the addition of sulphur to a highly purified alkali halide melt; however, in the presence of traces of water vapour or hydroxides in the melt sulphur easily dissolved with a deep blue colour.

Water in borate glasses produces hydroxyl and hydrogen-bonded hydroxyl groups [16]. The mechanism of sulphur-glass-water interactions cannot be deduced from our experiments. As discussed before, in alkaline water, tetrasulphide ion is stable due to hydrogen bonding; when aprotic polar solvents like DMF is added, the tetrasulphide group dissociates producing hypersulphide group. It can be that water in the glass melt helps the formation of a tetrasulphide ion which subsequently dissociates to the blue hypersulphide group. In the absence of water (hydroxyl group) tetrasulphide ion is not formed in glass. However, to understand this aspect further work with controlled p_{S_2} and p_{H_2O} in contact with glass melts have to be done.

The emission and excitation spectra of some typical blue glasses are shown in Fig. 2. The yellow polysulphide solution did not show any fluorescence. The green hypersulphide solution exhibits green fluorescence on excitation at 25 000 cm^{-1}. Similarly, blue glasses exhibit orange fluorescence on excitation at 25 000 cm^{-1}; no fluorescence could be detected by exciting around 17 000 cm^{-1}. From Fig. 1 it can be seen that both polysulphide and hypersulphide absorbs around 25 000 cm^{-1}; although absorption at 17 000 cm^{-1} can be solely ascribed to the hypersulphide ion, the absorption at 25 000 cm^{-1} may be due either to the hypersulphide ion or to any of the polysulphide ions. Similar orange fluorescence has been reported in ultramarine and in alkali halides doped with sulphur at room temperature. It should be pointed out that these alkali halides containing sulphur are deep blue at high temperature, but when cooled to room temperature become pale yellow, characteristic of polysulphide, and no traces of blue colour could be seen although they exhibit strong fluorescence. On the other hand the aqueous solutions of alkali polysulphides do not exhibit any fluorescence, but when DMF is added to this solution, the colour becomes green and a green fluorescence appears on excitation around 25 000 cm^{-1}. Thus the most probable origin of the orange or green fluorescence seems to be the hypersulphide ion although the possibility of other intermediate polysulphides can not be ruled out from our measurements.

If the orange fluorescence is due to the hypersulphide ion, then together with the excitation band at 24 000 cm^{-1}, the observed transitions may be explained in the following qualitative way: The absorption band at 17 000 cm^{-1} is due to the allowed transition from the $^2\Pi_g$ ground state of the S_2^- ion to its first excited state, $^2\Pi_u$. The weak band around 24 000 cm^{-1} may be attributed to a parity-forbidden transition from $^2\Pi_g$ to some unknown state, ^2X_g. It is this state which is thought to be the origin of the fluorescence observed in both solution and in glasses which contained the hypersulphide ion. This conclusion is based on the fact that glasses containing the hypersulphide ion do not fluoresce when excited at 17 000 cm^{-1}. Further the fluorescence observed in solutions, has a higher energy than that of the $^2\Pi_g$ state; this state, therefore, can not be the origin of the green fluorescence.

Concentration quenching of the orange fluorescence was not observed even in the deep blue glasses. However, it should be noted that if the fluorescence in these glasses is detected through a large thickness of sample, most of the fluorescence is reabsorbed which can lead to the erroneous conclusion that the fluorescence is concentration quenched.

References

1. (a) W. A. WEYL, "Coloured Glasses" (Society of Glass Technology, 1967) p. 237.
   (b) C. GENISSON, A. MICHAUD and J. HERBERT, "Coloured Glasses" (Jablonec, 1965) p. 136.
2. C. F. GEITNER, *Pharm. Annls.* **129** (1864) 350.
3. (a) H. MOISSAN, *C.P. Lebd. Seanc. Acad. Sci., Paris* **132** (1901) 510.
   (b) O. RUFF and E. GEISEL, *Ber. dth. chem. Ges.* **38** (1905) 2659.
4. G. DELARUE, *Bull. Soc. Chim. Fr.* (1960) 1654.
5. R. MOLINA, *ibid* (1961) 1001.
6. W. GIGGENBACH, *J. Inorg. Nucl. Chem.* **30** (1968) 3189.
7. (a) C. NOLLNER, *Pogg. Ann.* **98** (1856) 189.
   (b) E. PATERNO and A. MAZZUCHELLI, *Gazz. Chim. Ital.* **38** (1908) 137.
   (c) J. GREENBERG, B. R. SUNDHEIM and M. GRUEN, *J. Chem. Phys.* **29** (1958) 461.
8. H. LUX and H. ANSLINGER, *Chem. Ber.* **94** (1961) 1161.
9. J. HOFFMANN, *Z. Anorg. Allg. Chem.* **138** (1929) 37.
10. M. V. MERRITT and D. T. SACOYER, *Inorg. Chem.* **9** (1970) 211.
11. P. N. SMITH, Tech. Note No. 86, BGIRA, Sheffield (1965).
12. I. R. MORRISON and A. L. WILSON, *Analyst* **88** (1963) 100.
13. H. SCHOLZE, *Glastech. Ber.* **32** (1959) 81, 142, 278.
14. G. SCHWARZENBACH and A. FISCHER, *Helv. Chim. Acta* **43** (1960) 1365.
15. J. B. FINCHAM and F. D. RICHARDSON, *Proc. Roy. Soc. (London)* **A223** (1954) 40.
16. H. FRANZ, *J. Amer. Ceram. Soc.* **49** (1966) 473.

Received 12 December 1973 and accepted 16 January 1974.