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The blue chromophore in sulphur-doped borate glasses (boro-ultramarine)

Paul *et al.* [1] have recently attributed the blue colour of sulphur-doped borate glasses to the S_2^- ion. That assignment is erroneous and I will establish here that the correct identity of the species is S_3^-, the trisulphur radical anion, and point out that the authors should have considered this possibility. I will also comment on their proposed mechanism of formation of polysulphur radical anions from elemental sulphur in borate glasses.

An interest in the fascinating and ubiquitous blue chromophore formed by sulphur in a wide variety of basic or reducing media [2] brought the paper under consideration to my attention. Although the manuscript was submitted in December 1973, the literature review of the controversy concerning the identity of the blue species considered references only up to 1970, and several important studies prior to 1970 were omitted.

Paul *et al.* correctly stated that Giggenbach [3] assigned the blue species to the S_2^- ion on the basis of spectroscopic and magnetic measurements of solutions of alkali polysulphides in dimethylformamide (DMF), but they mistakenly reported that Merritt and Sawyer [4] came to the same conclusion from their studies of the electrochemical reduction of elemental sulphur in dimethyl sulphoxide. In fact, these authors first attributed the blue species to the S_8^- ion, but on re-investigation [5], which revealed an error in the coulometer reading, they concurred with the assignment of S_3^- to the blue species, suggested by other workers (*vide infra*). Although Paul *et al.* discuss the blue colour of sulphur-doped alkali halides they omit reference to the important paper by Holzer *et al.* [6]. In 1969, these authors were able to assign visible absorption bands at 400 and 610 nm to S_2^- and S_3^-, respectively, by an elegant application of Raman spectroscopy. During the period 1970–73, the blue colour of (a) ultramarine [7, 8], (b) sulphur solutions in an LiCl–KCl eutectic [9], (c) solutions of alkali polysulphides in hexamethylphosphoramide [10] or DMF [11, 12] was attributed to the S_3^- ion. French workers [13], who studied the electrochemical reduction of elemental sulphur at an inert electrode in DMF or DMSO, originally proposed S_6^{2-} for the blue species, but in a full account of their work published recently [14], they agree with the assignment of S_3^-. Thus in

1973, as pointed out in a review [15], there was reason to doubt Giggenbach's proposed identity of S_2^- for the blue species, and other alternatives, particularly S_3^-, should have been considered. In fact, very recent theoretical calculations [16] are in accord with the assignment of S_3^- to the blue chromophore.

To turn to the specific question of sulphur-doped borate glasses. The fact that the visible absorption spectrum of these glasses (λ_{max} 590 nm) is similar to that found for ultramarine blue [7, 8] or sulphur solutions in LiCl–KCl eutectics [9] strongly suggests that the same blue sulphur species is involved. Following the earlier work of Hofmann [17], Matsunaga [18] first reported the esr spectrum of boroultramarine. In 1970, Marshall and McLaughlan found values of $g_1 = 2.008 \pm 0.002$, $g_2 = 2.035 \pm 0.001$, and $g_3 = 2.046 \pm 0.002$ for boro-ultramarine at room temperature and suggested that these resonances arise from S_3^-. The following year, Giggenbach [19] published details of the visible absorption, emission and esr spectra of sulphur-doped borate glasses. A relatively sharp three-line esr absorption was observed with $g_1 = 2.050$, $g_2 = 2.031$ and $g_3 = 2.003$ at 90 K in good agreement with the values obtained for S_3^- in sulphur-doped alkali halide crystals, $g_x = 2.049$, $g_y = 2.035$ and $g_z = 2.001$ [20]. Giggenbach concluded that S_3^- was present in addition to the species which absorbs at 590 nm, which he attributed to S_2^-, but is now known to be due to S_3^- (*vide supra*). The strong absorption band at ~400 nm in sulphur-doped borate glasses has been attributed to polysulphide ions [19] and/or S_2^- [1].

In summary, the available visible absorption and esr spectroscopic evidence is consistent with the assignment of S_3^- to the blue chromophore in boro-ultramarine. The additional presence of S_2^- seems likely from the emission and excitation spectral data [1, 21]. Confirmation of the existence of S_2^- in the presence of S_3^- can best be obtained by Raman spectroscopy, cf. ultramarine blue [22].

At the temperature of the molten glass, various sulphur allotropes, S_x (but not atomic sulphur as suggested in the mechanism proposed by Paul *et al.*) will be present [15]. The fact that dissolved water in the glass [1] or the presence of water vapour or hydroxides in LiCl–KCl eutectics [19] facilitates the formation of S_3^- suggests that nucleophilic degradation of S_x by hydroxide ion to give polysulphides S_y^{2-} is involved. Dissociation or disproportionation of S_y^{2-} will produce polysulphur radical anions [9–12]. Indeed the formation of the blue S_3^- ion from elemental sulphur and OH^- has been reported for other systems, e.g. in acetone solution [23, 24] and at catalytic surfaces [25].

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On phase relations in the system As_2Se_3–Sb_2Se_3

Preliminary X-ray diffraction analysis of crystalline $(1-x)As_2Se_3$–xSb_2Se_3 materials showed evidence of terminal solid solubility. However, results of an investigation on the phase relation in this system, subsequently published by Berkes and Myers [1], showed no solid solubility between As_2Se_3 and Sb_2Se_3. In view of the disparity between our findings and those of Berkes and Myers it seems necessary to further clarify the controversy. This investigation was performed by X-ray diffraction and liquid metal solution calorimetry with specimens of crystalline As_2Se_3–Sb_2Se_3, in the range of 0 to 0.5 g atomic fraction of Sb_2Se_3. The calorimetric results on the heats of formation of these alloys are also of interest. It was not our intention to prove or disprove Berkes and Myers' findings, but to assemble data needed for interpreting electrical, optical and crystallization characteristics of these materials [2–5].

Amorphous specimens of $(1-x)As_2Se_3$–xSb_2Se_3 ($x = 0.05$, 0.10, 0.20, 0.30, 0.40, 0.45, 0.50) were prepared from As_2Se_3 and Sb_2Se_3, which were initially prepared from high purity As, Sb and Se (99.999 + %). For each of the As_2Se_3 and Sb_2Se_3 compounds, nominally stoichiometric amounts were placed in a quartz ampoule which was repeatedly evacuated, flushed with argon, and finally evacuated to 10^{-6} Torr before sealing. Each sealed ampoule was heated for about 5 h at 623 K, whereupon the temperature was raised to 1023 K and maintained for about 5 h. The resulting As_2Se_3 and Sb_2Se_3 were in turn placed, in the desired proportions, in a quartz ampoule, which was again flushed, evacuated and sealed. To ensure vigorous mixing the ampoule with the molten material was rotated by a motor shaft while in the furnace (125 rpm). The ampoule was held at 1023 K for 1 h, then withdrawn from the furnace and quenched in air while still in rotation. This technique, described in more detail elsewhere [6], allows the preparation of homogeneous materials. Electron micro-probe analysis revealed no detectable variation in chemical composition and confirmed the stoichiometry of the prepared materials. The amorphous state of these alloys was confirmed by standard metallographic and X-ray diffraction techniques.

Crystalline samples were prepared by annealing amorphous materials in sealed, evacuated, vycor-capsules for 40 h at 400 K, followed by annealing for 80 h at 523 K. Under such conditions these amorphous materials are entirely crystallized within a few hours. However, to approach closer to thermodynamic equilibrium, a much longer annealing time was employed. During annealing, special precautions were taken to avoid any temperature gradient in the specimen tube. This eliminated the possibility of phase separation by vapour transport, due to the vapour pressure difference between As_2Se_3 and Sb_2Se_3. In addition, because the ampoules were small in size and were sealed, the specimens retained identical overall chemical composition before and after annealing. Standard metallographic and X-ray diffraction techniques did not reveal the existance of amorphous phase in the annealed materials.

The heats of formation of crystalline $(1-x)As_2Se_3$–xSb_2Se_3 based on crystalline As_2Se_3 and Sb_2Se_3 were measured by liquid metal solution calorimetry with bismuth as solvent. The calorimetric procedure and the method of calculation have been described by Bever et al. [7] elsewhere. The specimens were added from 273 K to the bath at 623 K. Successive additions consisted of crystalline $(1-x)As_2Se_3$–xSb_2Se_3 samples and corresponding mechanical