

Figure 4 An example of the observation of dislocation-type contrast in association with the stabilized matrix region/ $\Sigma 9$  triple junctions. (a) A matrix dark-field micrograph showing a series of triangularly prismatic matrix regions in association with the  $\Sigma 9$  grain boundary. (b) A twin dark field micrograph showing strain field contrast at the triple junctions.

similar twin variants leads to the stabilization of matrix regions as a series of triangular prisms. In general, these prisms are only observed when one

twin variant impinges on the coherent plane of a dissimilar twin variant.

### Acknowledgements

The authors are grateful to Professor R. W. K. Honeycombe for the provision of laboratory facilities. Valuable discussions with Dr A. R. Jones and financial support from the Science Research Council and the Ministry of Defence are gratefully acknowledged.

### References

1. K. T. AUST and J. W. RUTTER, *Trans. Met. Soc. A.I.M.E.* **218** (1960) 1023.
2. D. G. BRANDON, B. RALPH, S. RANGANATHAN and M. WALD, *Acta. Met.* **12** (1964) 813.
3. D. VAUGHAN, *Phil. Mag.* **22** (1970) 1003.
4. P. J. GOODHEW, "Grain boundaries" (Institution of Metallurgists, Jersey, 1976) A40.

Received 16 September  
and accepted 1 November 1977.

P. R. HOWELL

J. V. BEE

Department of Metallurgy and Materials Science,  
University of Cambridge, UK

### Vibrational spectra of sulphur-doped borate glasses

One of us has recently pointed out [1] that the blue chromophore in boro-ultramarine should be assigned to the  $S_3^-$  ion, and not to  $S_2^-$  as suggested by Paul *et al.* [2], but the additional presence of  $S_2^-$  was not excluded. The detection of  $S_2^-$  in the presence of  $S_3^-$  by Raman spectroscopy, has been elegantly demonstrated by Clark and Franks [3] for ultramarine blue. We describe here an investigation of the infra-red and Raman spectra of boro-ultramarine designed to confirm the presence of  $S_3^-$  and/or  $S_2^-$ . The Raman spectra were obtained using a variety of laser excitation wavelengths and, together with the infra-red spectra, were compared with similar spectra for Reckitt's blue\*.

Holzer *et al.* [4] have demonstrated by resonance Raman (RR) spectroscopy of sulphur-doped

alkali halides that the stretching frequency of  $S_2^-$  occurs at about  $590\text{ cm}^{-1}$  and is associated with an optical absorption band at about 400 nm. Similarly, they showed that the totally symmetric stretching vibration of  $S_3^-$ , which has  $C_{2v}$  symmetry, occurs in the range  $523$  to  $555\text{ cm}^{-1}$  (depending on the host lattice) and is associated with an optical absorption band at about 600 nm. The antisymmetric stretching mode of  $S_3^-$  occurs at about  $580\text{ cm}^{-1}$  in the infra-red spectrum while  $S_2^-$  is, of course, infra-red inactive. RR spectra are obtained when a molecule is excited with a laser line whose frequency falls within the envelope of an allowed electronic transition. Such spectra are characterized by an enhancement in the intensity of a totally symmetric vibration of the scattering molecule and by high intensity overtone progressions.

The Raman spectra were recorded on a Jarrell—Ash model 25-100 double monochromator cali-

\*Reckitt's blue was a commercial sample manufactured in England by Reckitt and Son Ltd.

brated with indene. Quoted line positions are accurate to  $\pm 1 \text{ cm}^{-1}$ . The detection system consisted of an ITT model FW 130 phototube and an SSR model 1105 photon counter made by Princeton Applied Research Corporation. Excitation at 632.8 nm was provided by a Spectra-Physics model 125 helium-neon laser. The three other exciting lines used were obtained from a Coherent Radiation CR3 argon-ion laser. Appropriate interference filters were used to isolate each line. The power available at the sample for the 457.9, 488.0, 514.5, and 632.8 nm excitation was about 35, 150, 300, and 25 mW respectively. Samples were mounted in a 6 cm diameter ring which was rotated at about 1000 r.p.m. to prevent thermal decomposition.

Infra-red spectra were obtained using a Perkin-Elmer model 580 ratio-recording spectrophotometer with attached computer for data handling. To improve the signal-to-noise ratio of these weak spectra, ten separate scans of each sample were obtained and averaged. The resolution was about  $3 \text{ cm}^{-1}$ . Samples were prepared as CsI discs using about 15 mg Reckitt's blue or boro-ultramarine and 200 mg of CsI.

Several methods for the preparation of sulphur-doped borate glasses were attempted. We were unable to obtain a satisfactory blue colour from melting 2 g of an equimolar mixture of  $\text{K}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3$  with 0.002 g of sulphur and boric acid in a platinum crucible at about  $850^\circ \text{C}$  [5]. Paul *et al.* have also reported lack of success with this method. This was probably due to loss of sulphur by vaporization since we found that substitution of sulphur by  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  gave a blue glass. A series of blue glasses were prepared by melting, with stirring, varying compositions of TABLE I Composition and colour of alkali-borate glasses melted with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  or sulphur

Composition (g)			Colour
$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	NaOH	$\text{H}_3\text{BO}_3$	
—	1.4	8.6	Colourless
0.3	0.68	9.3	Mid-blue
0.3	1.4	8.6	Very dark blue
0.3	2.2	7.8	Amber
0.3	3.0	7.0	White, opaque
0.2	2.0 <sup>a</sup>	4.7	Blue
0.04 <sup>b</sup>	1.4	8.6	Deep blue

<sup>a</sup>Equimolar  $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$  mixture.

<sup>b</sup>Elemental sulphur.

$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , sodium hydroxide and boric acid together in a 10 ml platinum crucible at about  $900^\circ \text{C}$  (Table I). The melt was poured into an indentation in a sheet of aluminium and allowed to cool.

The deepest blue sulphur-doped glass was used for the spectral measurements and the spectra obtained were compared with the corresponding spectra of Reckitt's blue and of a colourless

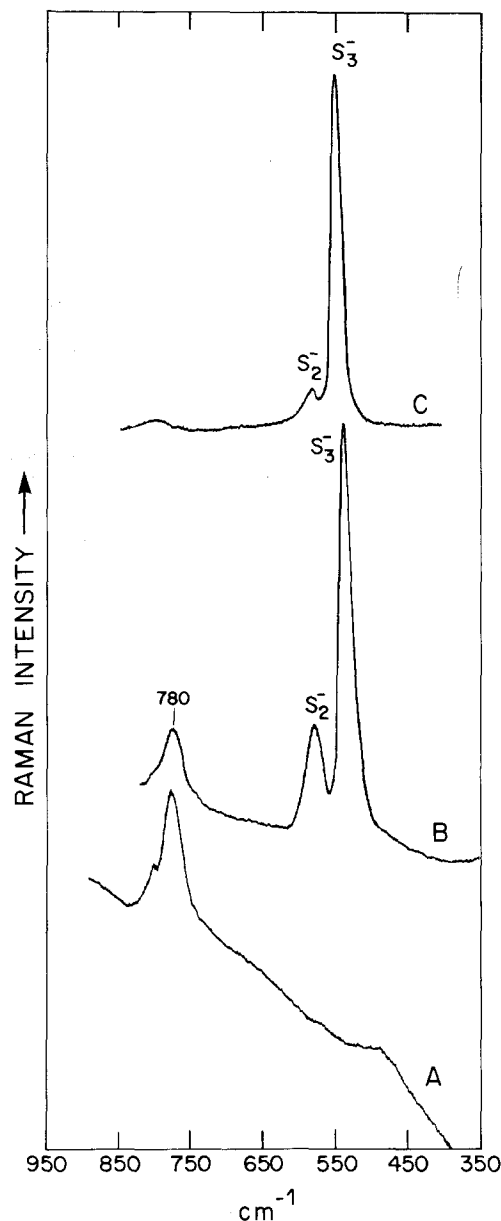


Figure 1 Resonance Raman spectra of (A) sulphur-free borate glass (B) sulphur-doped borate glass and (C) Reckitt's blue obtained with 514.5 nm excitation.

sulphur-free glass. The infra-red spectrum of Reckitt's blue showed a band at  $585\text{ cm}^{-1}$  (cf. ultramarine blue,  $580\text{ cm}^{-1}$  [6]) attributed to the antisymmetric stretching mode of  $S_3^-$ . This band could not be detected in the infra-red spectra of sulphur-doped borate glasses, although it should be emphasized that the ground-up glass is a much paler blue than Reckitt's blue and thus probably contains a correspondingly lower concentration of  $S_3^-$  than Reckitt's blue. The presence of  $S_3^-$  in boro-ultramarine has been demonstrated by ESR measurements [5, 7] and visible absorption spectra ( $\lambda_{\text{max}} 590\text{ nm}$ ) [1, 2, 5]. The Raman spectra, described below, confirm the existence of  $S_3^-$  in boro-ultramarine and reveal the additional presence of  $S_2^-$ .

In Table II the Raman spectral data of boro-ultramarine are compared with those for Reckitt's blue and with the corresponding data obtained by Clark and Franks [3] for natural ultramarine. The Raman spectrum of boro-ultramarine shows peaks at  $581\text{ cm}^{-1}$  and  $537\text{ cm}^{-1}$ , corresponding to the symmetrical stretching modes of  $S_2^-$  and  $S_3^-$ , respectively (see Fig. 1). As the frequency of the laser excitation moves closer to the visible absorption band of  $S_2^-$  ( $\lambda_{\text{max}} 400\text{ nm}$ ) the intensity of the Raman band for  $S_2^-$  increases relative to that for  $S_3^-$ . A similar increase in relative intensities is observed for Reckitt's blue, but the effect is not as dramatic as reported by Clark and Franks, who found a ten-fold increase in the relative areas of the  $S_2^-/S_3^-$  bands in synthetic ultramarine on changing from 514.5 to 457.9 nm excitation. Holzer and co-workers have previously observed a similar increase in the ratio of the scattering cross-sections of  $S_2^-$  and  $S_3^-$  in KI as a function of excitation wavelength [8]. The possibility that the intensity of the  $581\text{ cm}^{-1}$  line is enhanced by a

contribution from the antisymmetric stretch of  $S_3^-$  is ruled out by the fact that several literature reports [9–11] of the Raman spectra of  $S_3^-$ , *in the absence of  $S_2^-$* , reveal that a band at about  $580\text{ cm}^{-1}$  ( $\nu_{\text{as}}S_3^-$ ) is not observed in the Raman spectrum of  $S_3^-$  even when the band at about  $535\text{ cm}^{-1}$  ( $\nu_sS_3^-$ ) is quite strong.

In the Raman spectra of boro-ultramarine the presence of a weak, broad band at  $487\text{ cm}^{-1}$  and a strong band at  $780\text{ cm}^{-1}$  makes the measurement of  $S_2^- : S_3^-$  relative intensities more difficult, since the latter band causes the base line to slope upwards. This band is also present in the Raman spectrum of colourless, sulphur-free borate glasses and is probably associated with the glass matrix.

The fact that blue borate glasses can be obtained using either sulphide ( $S^{2-}$ ) or elemental sulphur ( $S^0$ ) as a source of the chromophore supports the earlier suggestion [1, 12] that polysulphur radical anions  $S_x^-$  ( $x = 2, 3$ ) are formed in these systems via polysulphides  $S_y^{2-}$  ( $y = 2$  to 6). Polysulphide ions can be produced from elemental sulphur by nucleophilic degradation of the  $S_8$  ring and from sulphide by oxidation. The radical anions  $S_2^-$  and  $S_3^-$  would then be formed from polysulphides either through dissociation or by disproportionation [9, 12]. Although the strong band at about 400 nm observed for sulphur-doped borate glasses [2, 5] could be due to polysulphides [13], in addition to  $S_2^-$ , there is no evidence from the Raman spectra that polysulphides are present. Sharp, strong bands in the  $400$  to  $500\text{ cm}^{-1}$  region are expected for polysulphides [14, 15]. Thus it appears that the amount of sulphur (or sulphide) converted to polysulphides in boro-ultramarine is quite small and the polysulphides formed completely dissociate or disproportionate to  $S_3^-$  (and  $S_2^-$ ) in the glassy matrix. This is similar to the

TABLE II Resonance Raman spectral data for boro-ultramarine, Reckitt's blue and natural ultramarine

Exciting line (nm)	Boro-ultramarine <sup>a</sup>	Reckitt's blue <sup>b</sup>	Ultramarine blue <sup>c</sup>
647.1	—	—	0.01
632.8	0.25	0.09	—
514.5	0.26	0.073	0.027
488	0.24	0.084	0.037
457.9	0.33	0.11	0.27

<sup>a</sup>Ratio of peak heights  $S_2^-$  ( $581\text{ cm}^{-1}$ ) :  $S_3^-$  ( $537\text{ cm}^{-1}$ ). Estimated uncertainty  $\pm 0.02$  ( $\pm 0.03$  for  $632.8\text{ nm}$  exciting line); slit widths were 8 to  $9\text{ cm}^{-1}$  (11 to  $12\text{ cm}^{-1}$  for  $632.8\text{ nm}$  exciting line).

<sup>b</sup>Ratio of peak heights  $S_2^-$  ( $586\text{ cm}^{-1}$ ) :  $S_3^-$  ( $549\text{ cm}^{-1}$ ). Estimated uncertainty  $\pm 0.01$  ( $\pm 0.02$  for  $632.8\text{ nm}$  exciting line); slit widths were 5 to  $6\text{ cm}^{-1}$  (11 to  $12\text{ cm}^{-1}$  for  $632.8\text{ nm}$  exciting line).

<sup>c</sup>Data from [3]. Ratio of peak areas  $S_2^-$  ( $586.5\text{ cm}^{-1}$ ) :  $S_3^-$  ( $548.9\text{ cm}^{-1}$ ).

situation found for dilute solutions of sulphur in hexamethylphosphoramide [9], whereas for solutions of sulphur in primary amines, Raman spectra reveal the presence of several polysulphides in addition to  $S_3^-$  [11].

### Acknowledgement

We thank the National Research Council of Canada for financial support.

### References

1. T. CHIVERS, *J. Mater. Sci.* **12** (1977) 417.
2. A. PAUL, A. WARD and S. GOMOLKA, *ibid.* **9** (1974) 1133.
3. R. J. H. CLARK and M. L. FRANKS, *Chem. Phys. Lett.* **34** (1975) 69.
4. W. HOLZER, W. F. MURPHY and H. J. BERSTEIN, *J. Mol. Spectroscopy* **32** (1969) 13.
5. W. GIGGENBACH, *Inorg. Chem.* **10** (1971) 1308.
6. K. -H. SCHWARZ and U. HOFMANN, *Z. Anorg. Chem.* **329** (1964) 102.
7. S. D. McLAUGHLAN and D. J. MARSHALL, *J. Phys. Chem.* **74** (1970) 1359.
8. W. HOLZER, S. RACINE and J. CIPRIANI, *Adv. Raman Spectroscopy* **1** (1972) 393.
9. T. CHIVERS and I. DRUMMOND, *Inorg. Chem.* **11** (1972) 2525.
10. H. H. EYSEL and D. NOTHE, *Z. Naturforsch.* **31B** (1976) 411.
11. F. P. DALY and C. W. BROWN, *J. Phys. Chem.* **77** (1973) 1859.
12. T. CHIVERS, *Nature* **252** (1974) 32.
13. W. GIGGENBACH, *Inorg. Chem.* **10** (1971).
14. H. H. EYSEL, G. WIEGHARDT, H. KLEIN-SCHMAGER, and G. WEDDIGEN, *Z. Naturforsch.* **31B** (1976) 415.
15. G. J. JANZ, J. R. DOWNEY, Jr., E. RODUNER, G. J. WASILCZYK, J. W. COUTTS, and A. ELVARD, *Inorg. Chem.* **15** (1976) 1759.

Received 19 September  
and accepted 1 November 1977.

T. CHIVERS  
E. GILMOUR  
R. A. KYDD  
*Department of Chemistry,  
The University of Calgary,  
Calgary, T2N 1N4, Alberta, Canada*

### Domain structure of amorphous Nd—Co thin films

Domain structure and magnetic anisotropy of rare earth—cobalt films were investigated by several authors. Investigations concerned mostly amorphous thin films of Gd—Co alloys [1–5]. In this work domain structure in evaporated Nd—Co thin films is investigated.

The films were obtained by vacuum evaporation of two different alloys. The alloys were obtained by melting the stoichiometric quantities of pure metals in atomic ratios of Nd:Co of 2:7 and 2:17 in a vacuum furnace. Compositions of the obtained alloys were controlled by chemical methods. Impurities of other metals were smaller than 0.3%. Glass and mica were used as the substrates, and evaporation was carried out at 300 K.

Some of the films were investigated immediately after deposition and the rest of films after a one month annealing process at room temperature. Investigations made by means of an electron microscope showed that the as-deposited films

were amorphous and had a smooth surface. The domain structure of the films was investigated by the Lorentz microscopy and the Kerr effect methods. The thickness of the films was about 100 nm.

The surface of the film was oriented perpendicular to the electron beam during the domain structure observations by the Lorentz microscopy method. The influence of the external demagnetizing field direction oriented in the plane of the films on the domain patterns was observed. This observation brought us to certain conclusions about the type of the magnetic anisotropy of the films. The domain patterns of the as-deposited films were characteristic for both compositions of the films, and are shown in Fig. 1. The direction of magnetization was determined on the basis of the contrast in areas between the domains, and from contrast observed in investigations made by means of the Kerr effect method. It was ascertained that the domains were separated by  $180^\circ$  walls. The domain patterns of the films enriched with Co did not depend on the direction of the demagnetizing field. In these films zigzag-