polytypes.

For the polytypic crystals examined, powder lines of notable intensity from higher polytypes are usually overlapped by strong 2H reflections, the only exception being the 1 0 . 1 reflection from the 4H structure. This is probably why only one SnS_2 polytype other than the basic 2H modification has ever been reported from powder studies alone, this latter being the 4H polytype observed by Guenter and Oswald [3]. Ishizawa and Fujiki [4–6] have also examined polytypes of SnS_2 by powder and Weissenberg techniques and infer in their work that single crystal X-ray examination is to be preferred if reliable structure analysis is to be achieved. Terhell and Lieth [7] have reported structural alterations similar to those described above in their studies of GaSe layer crystals.

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Optical absorption of transition metals in alkali lime germanosilicate glasses

The absorption loss in alkali lime germanosilicate optical fibres, made by the double crucible method, is due in general to the presence in the glass of OH groups and transition metals, in concentrations in the p.p.m. and p.p.b. range respectively [1, 2]. In the course of an investigation aimed at lowering the loss of these optical fibres, the absorption spectra of the different transition metal ions in alkali lime germanosilicate glass were measured.

Typical core glasses of molar composition 0.44 SiO_2 0.29 GeO_2 0.02 Al_2O_3 0.10 CaO 0.14 Na_2O 0.1 K_2O with 0.05% As_2O_3 acting as a fining agent were melted in Pt–10% Rh crucibles in a resistance furnace. Very pure starting materials* with transition metal impurities below 0.01 p.p.m. were used. Transition metal compounds were added to the batch to give a concentration of 20 p.p.m. (V, Cr, Co, Ni, and Cu) or 200 p.p.m. (Ti, Mn and Fe). The melt was bubbled for one hour at 1400° C after which the melt was allowed to stand for one hour at 1300° C for fining. The bubble free melt was poured into graphite moulds and annealed at 620° C for one hour. This melting procedure was chosen because it had previously proved possible to minimize the absorption loss of optical fibres by using pure glasses prepared in this manner in fused silica crucibles [2]. The absorption spectra were recorded from 350 to 1500 nm with a Cary 17 spectrophotometer on 5 to 10 cm polished rods. This range incorporates the wavelengths at which it is proposed to use optical fibres (800 to 1300 nm)

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*SiO_2, $CaCO_3$, Na_2CO_3, K_2CO_3 and As_2O_3 (Merck, FO Optipur), GeO_2 (Hoboken-Belgium extra pure) and Al_2O_3 (J. T. Baker, Ultrex).

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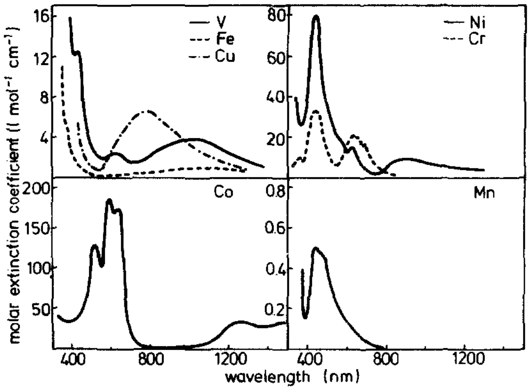

Figure 1 Absorption spectra of transition metals in alkali lime germanosilicate glass.

[3]. Below 500 nm a weak absorption band was observed which was ascribed to Rh^{3+} ions [4]. Consequently an undoped glass was used as a reference for calculating the absorption coefficient.

The absorption spectra obtained are shown in Fig. 1. In most cases the spectra are comparable with those found by Bamford [5] for transition metals in sodium silicate glasses melted under oxidizing conditions. Therefore only differences observed between those results and the results reported in this paper will be noted. Furthermore the molar extinction coefficients ϵ given by Bamford [5] will be used in the discussion of the spectra. Details concerning the identification of the different absorption bands using ligand field theory can be found in a review by Bates [6].

The following observations concerning the spectra shown in Fig. 1 can be made:

Titanium: No Ti^{3+} absorption band at 590 nm is observed indicating that Ti^{4+} ions are predominantly present.

Vanadium: Three absorption bands are observed at 1020, 620 and 430 nm) which can be ascribed to V^{4+} ions in a distorted octahedral oxygen coordination in which one 0 is nearer to the V^{4+} ion ($V0^{2+}$) [7, 8]. The value of the crystal field parameter of this ion is 16 100 cm^{-1} as compared with 16 400 cm^{-1} in sodium silicate glasses. The relatively low extinction coefficient of the bands indicates that V^{5+} ions are also present [5]. No absorption band of V^{3+} is observed [7].

Chromium: The threefold split band with maxima at 640, 658 and 698 nm and the band at 440 nm are typical for Cr^{3+} ions in octahedral coordination [5]. The crystal field parameter for this ion is 15 200 cm^{-1} as compared with 15 400 cm^{-1} in sodium silicate glass. The weak band at 355 nm (2 l mol^{-1} cm^{-1}) can be ascribed to the charge transfer and of Cr^{6+} ions [5]. The value of ϵ for this band in sodium silicate glasses is 4×10^3 l mol^{-1} cm^{-1}, giving a Cr^{3+}/Cr^{6+} ratio of 2×10^3.

Manganese: In sodium silicate glasses tetrahedrally coordinated Mn^{2+} produces a sharp, weak double band at 430 nm with $\epsilon = 0.3$ l mol^{-1} cm^{-1} [9], and octahedrally coordinated Mn^{3+} gives a band at 490 nm with $\epsilon = 10$ l mol^{-1} cm^{-1} [5]. The intensity of the absorption band at 490 nm and the tail up to 800 nm therefore indicates that both Mn^{2+} and Mn^{3+} ions occur but that the former ion predominates.

Iron: The broad absorption band with maximum at 1050 nm is produced by octahedrally coordinated Fe^{2+} ions. The relative weakness of this band and the shouder at the UV absorption edge at 380 nm caused by the Fe^{3+} ions both indicate that predominantly Fe^{3+} ions are present [10]. From the intensity of the 1050 nm band, assuming a molar extinction coefficient of Fe^{2+} at 1050 nm of 30 l mol^{-1} cm^{-1} [5], a Fe^{3+}/Fe^{2+} ratio of 40 is obtained.

Cobalt: The spectrum indicates that predominantly tetragonally coordinated Co^{2+} ions are present. In both alkali lime germanosilicate and sodium silicate glasses identical extinction coefficients if the bands of Co^{2+} are observed [5]. This justifies the assumptions made previously that the molar extinction coefficients of the different transition metal ions in these two glasses are comparable.

Nickel: The spectrum shows that Ni^{2+} ions in both octahedral and tetrahedral coordination are present [5]. The intensities of the different bands, however, indicate that, as compared with sodium silicate glass, relatively more octahedrally coordinated Ni^{2+} ions are present.

Copper: One broad band is observed at 780 nm (8 l mol^{-1} cm^{-1}) produced by Cu^{2+} ions in a tetrahedrally distorted octahedral coordination. In sodium silicate glasses a similar band at 790 nm with equal ϵ is observed [5], indicating that predominantly Cu^{2+} ions are present.

The low dopant concentration allows for extrapolation of these data to determine the contri-

TABLE I Contribution in dB km^{-1} p.p.m.$^{-1}$ of transition metal impurites to the loss in alkali lime germanosilicate optical fibres.

	850 nm	1050 nm	1300 nm
Ti	<5	<5	<5
V	150	220	80
Cr	90	40	<5
Mn	<5	<5	<5
Fe	30	40	30
Co	40	370	1460
Ni	430	350	240
Cu	270	140	30

bution of 1 p.p.m. of a transition metal in the glass, to the total loss of the fibre (Table I). The values are given at 850, 1050 and 1300 nm, wavelengths at which it is proposed to use optical fibres for long distance optical communication purposes [3]. Comparable data for other glass systems used for making optical fibres are given by Schultz for fused silica [11], by Ikeda *et al.* for T1 containing sodium borosilicate glass [12] and by Newns *et al.* for sodium lime silicate glass [13]. Concerning Table I the following concluding remarks can be made:

(1) In the case of alkali lime germanosilicate optical fibres a concentration of a few p.p.b. of Ni, Cu, V or Co is sufficient to cause measurable losses in the fibre at the proposed wavelengths. Therefore glasses have to made in which these impurities are present in concentrations below 1 p.p.b.

(2) The contribution of the absorption produced by Cr, Ni and Cu, which together with Fe are the most common impurities, to the loss of the optical fibre, decreases at longer wavelengths.

(3) Fe in alkali lime germanosilicate glasses melted under oxidizing conditions is predominantly present as Fe^{3+}. Consequently the susceptibility of the loss of the optical fibre to the presence of the most common impurity both in the starting material and the environment (such as ambient air and furnace lining), is relatively small.

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Direct observations of debonding at crack tips in glass bead-filled epoxy

Glass bead-filled polymers are often much tougher than the unfilled matrix polymer. In studying the origin of the increased toughness various workers [1–4] have examined fractured samples after unloading but there are no reports of direct observations of crack tip processes in these materials during fracture. The results of observing cracks directly as they grow in a glass bead–epoxy resin composite are reported, together with the implications of these observations for the origins of the increase of toughness.

Plate-like specimens (35 mm × 35 mm × 3 mm) of an epoxy resin* containing approximately 25%

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*XD927, Ciba Geigy Ltd.

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