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Sol–gel approach to preparing germanium disulphide

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A sol–gel route to germanium disulphide reported in the literature, via dihydrogen sulphide treatment of germanium tetra-ethoxide, has been re-examined. It has been found that the reported X-ray diffraction pattern of the product previously obtained coincides with germanium dioxide and not disulphide. A repetition of the synthesis, and investigation of the product by infrared spectroscopy and X-ray diffractometry, shows that germanium disulphide is indeed formed but contamination by oxide is difficult to avoid.

1. Introduction

Although enormous progress has been made over the last 20 years in the technology of optical communications, present systems are fully optical only to the extent of signal transmission. Truly optical switching for signal routing, although not currently available, may be achieved by utilizing non-linear materials whose optical transmission at high incident intensities is not proportional to the incoming beam intensity [1].

Nasu and Mackenzie [2] have shown that the semiconducting chalcogenides should exhibit large non-linear refractive indices suitable for switching. A composite glass of chalcogenide-doped silica would not only have the advantage of compatibility with current silica-based fibre systems but also very fast switching may be achievable as demonstrated for the quantum dot structured cadmium sulphoselenide-doped silicate glasses [3].

Conventional melting to produce chalcogenide-doped silica would be unsuccessful due to the volatility of chalcogenides at the high melting temperature of silica. Chemical vapour deposition of chalcogenide materials has not yet been demonstrated. Low-temperature sol–gel routes to obtain silica are now well developed [4] and a sol–gel preparation of germanium disulphide has been described by Melling [5]. As a first step towards producing GeS_2-doped SiO_2 the reported sol–gel preparation of GeS_2 was repeated and forms the subject of this communication.

To prepare GeS_2 Melling [5] treated solutions of germanium tetra-ethoxide ($Ge(OEt)_4$) with gaseous H_2S. Using X-ray diffractometry it was shown that the products so formed ranged from crystalline to totally amorphous depending upon the concentration of $Ge(OEt)_4$ employed. However, re-examination by us of the reported X-ray pattern of the crystalline product has shown that it resembles that of GeO_2 rather than GeS_2. This product will be termed product "A (lit)".

2. Experimental procedure

During the preparations of both the germanium tetra-ethoxide ($Ge(OEt)_4$) precursor and product A, described below, very dry conditions were maintained.

In order to produce $Ge(OEt)_4$ precursor, freshly cleaved metallic sodium (BDH) was added to excess anhydrous ethanol to produce a solution of Na(OEt). Following the method of Johnson and Fritz [6], $GeCl_4$ (stored in a sealed ampoule under Ar) was added dropwise at room temperature to the ethanolic Na(OEt). After refluxing the solution, the NaCl by-product was removed by filtration under an inert atmosphere and excess ethanol was distilled away to leave liquid $Ge(OEt)_4$.

Product A was prepared by passing H_2S over $Ge(OEt)_4$ in dried toluene (50% vol/vol) stirred at room temperature. After 1 h the solution gelled over a period of about 1 min. The gel was pale yellow and granular in appearance; further passage of gas caused cracking and solvent loss to leave a pale yellow powder cake, termed product A.

In a separate experiment, for comparison purposes, an ethanolic solution of $Ge(OEt)_4$ was cooled in an ice-bath and allowed to react with a slight excess of water in the absence of H_2S. A cloudy white, smooth gel formed immediately. Solvent was removed by oven drying the gel at 110 °C to leave product B which was a white powder.

Products A and B were investigated by means of infrared spectroscopy using the KBr disc method

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(1% wt/wt sample/KBr) in the range 1000–300 cm^{-1} on a Perkin Elmer 683 spectrophotometer. Powder X-ray diffractometry was carried out using CuK_α radiation.

The effect of water exposure on product A was monitored by means of infrared spectroscopy. Thus part of product A was placed in a large excess of deionized water which was stirred at room temperature. Small samples of the wet solid were withdrawn after various times and dried, firstly on filter paper and then for a few minutes at 50 °C, and subsequently analysed by infrared spectroscopy.

To prepare vitreous GeS_2, Ge (99.999% purity) and sulphur (99.999% purity) were sealed into a silica ampoule evacuated to 10^{-5} torr (1 torr = 1.333 $\times 10^2$ Pa). Prior to batching the ampoule was heated at 1000 °C for 1 h to remove adsorbed moisture. The batch was melted at 900 °C for 24 h, quenched and annealed. The glass was characterized by means of infrared spectroscopy.

3. Results

3.1. Product B

The infrared spectrum of product B is shown in Fig. 1d and the position of absorption peaks in the region 1000–300 cm^{-1} are compared in Table I with those reported by Mukerjee and Sharma [7] for crystalline hexagonal GeO_2 and for gel-derived GeO_2. The spectrum of product B contains a major absorption peak and shoulder at 879 and 957 cm^{-1}, respectively, as expected for GeO_2. Mukerjee and Sharma [7] noted that the sharp triplet of strong peaks at 515, 545 and 585 cm^{-1} for hexagonal GeO_2 are indicative of crystallite development and these are replaced by a broad band at 570 cm^{-1} in the spectrum of the GeO_2 gel. The former set of sharp peaks are also present in the spectrum of product B, suggesting that it is crystalline. However, Mukerjee and Sharma [7] report a band at 780 cm^{-1} characteristic of their aqueous derived GeO_2 gel, which was dried at 25 °C, and was proposed by them to be due to (Ge–(OH)). This band is also evident in the spectrum of product B.

The XRD pattern of product B matches well that of hexagonal GeO_2 (compare Fig. 2b with d). Although product B was prepared by H_2O treatment of $Ge(OEt)_4$, its XRD pattern is almost identical to that reported previously for product A(lit) [5], formed by H_2S treatment of $Ge(OEt)_4$ (compare Fig. 2b with c).

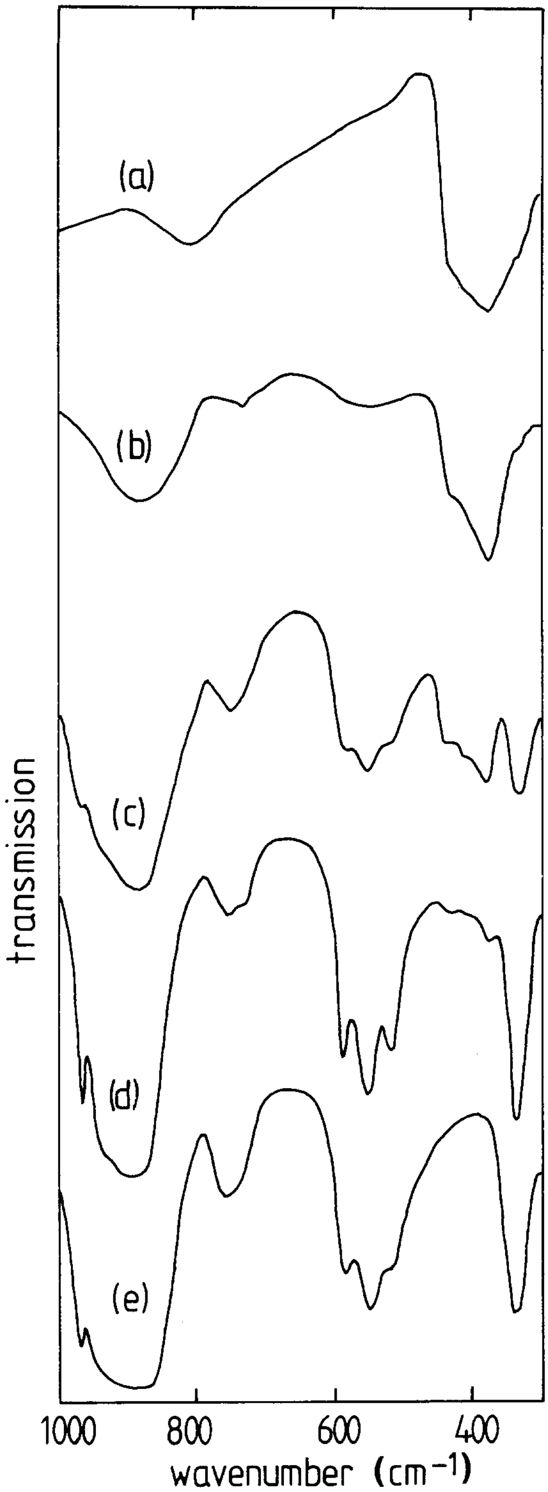

Figure 1 Infrared absorption spectra of (a) vitreous GeS_2; (b) product A, (c) similar preparation to product A but $Ge(OEt)_4$ precursor was exposed to ambient atmosphere prior to H_2S treatment, (d) product B, (e) product A after soaking in water at room temperature for 48 h and drying at 50 °C.

3.2. Product A

The infrared absorption spectrum of product A (Fig. 1b) may be compared with that of vitreous GeS_2 (Fig. 1a). The absorption peak at 375 cm^{-1} flanked by weakly defined shoulders at 350 and 430 cm^{-1} found in the spectrum of vitreous GeS_2 are present for product A at 378, 337 and 434 cm^{-1}, respectively. The strong triplet set of peaks expected for hexagonal GeO_2 at 515, 545 and 585 cm^{-1} are almost completely absent for product A other than a weak band at 550 cm^{-1}. Similarly the 780 cm^{-1} absorption characteristic of GeO_2 gel is extremely weak. In summary, the vibrational absorption peaks present in the region 800–300 cm^{-1} suggest that a substantial part of product A is sulphide in character although a quantitative assessment of sulphide/oxide would require a knowledge of extinction coefficients.

The strong absorption peak at 885 cm^{-1} for hexagonal GeO_2 is assigned by Mukerjee and Sharma [7] to (Ge–O–Ge) anti-symmetric stretching. Kawamoto and Tsuchihashi [8] have studied the infrared spectra of mixtures of GeO_2 and GeS_2 glasses. They report the

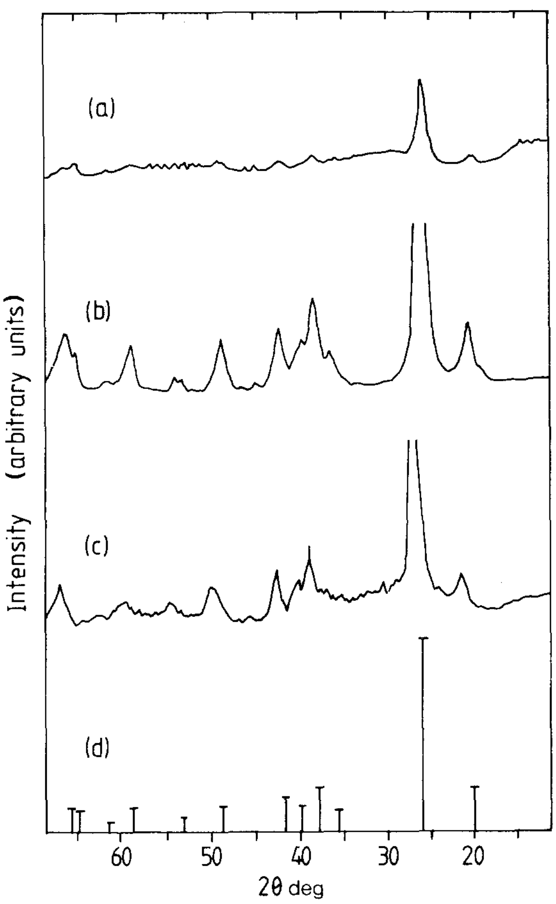

Figure 2 Powder XRD patterns of (a) product A, (b) product B, (c) product A (lit) [5] reproduced by permission of the American Ceramic Society, (d) crystalline hexagonal GeO_2 (schematic drawing).

TABLE I Infrared absorption bands in the region 1000–300 cm^{-1} of product B, crystalline hexagonal GeO_2 and gel-derived GeO_2 dried at 25 °C [7]

Product B	Crystalline hexagonal GeO_2 [7]	Gel-derived GeO_2 [7]
334 vs	333 vs	
	355 sh	
520 s	515 s	570 m, br
543 s	555 s	
582 s	587 vs	
754 m		780 m
879 vs, br	885 vs	880 vs
957 sh	957 sh	960 sh

vs = very strong; s = strong; m = medium; sh = shoulder; b = broad.

(Ge–O–Ge) absorption at 864 cm^{-1} for glassy GeO_2. The analogous (Ge–S–Ge) vibrational absorption peak for glassy GeS_2 was about 100 cm^{-1} lower. However, if the latter glass contained only 1 wt % oxide in admixture, then this absorption peak was shifted upwards again to 832 cm^{-1}. Thus this peak's position is sensitive to the presence of oxide contamination in GeS_2. Product A possesses an absorption band at 864 cm^{-1} which lies closer in wave number to that found here for product B (879 cm^{-1}) than to that for vitreous GeS_2 (804 cm^{-1}) hence indicating the presence of oxide in product A.

From XRD, product A is more amorphous than product B but the observed diffraction peaks again match hexagonal GeO_2 (Fig. 2a, b and d). In addition there is a broad, embryonic peak at about 15° 2θ which is possibly due to GeS_2 (monoclinic GeS_2 has its most intense XRD peak at 15.5° 2θ).

After 15 min exposure of product A to water at room temperature, infrared spectroscopy showed that the product was unaffected. However, after 48 h continuous exposure the infrared spectrum altered, becoming identical to that of product B (Fig. 1b, e and d).

4. Discussion

XRD and infrared spectroscopic evidence have confirmed that product B is crystalline hexagonal GeO_2 with some hydroxide contamination. Its preparation may be represented by a two-step reaction scheme of hydrolysis and subsequent condensation similar to the mechanism of silicate sol–gel syntheses

$$Ge(OEt)_4 + 4H_2O \rightarrow Ge(OH)_4 + 4EtOH\uparrow \quad (1)$$

$$Ge(OH)_4 \rightarrow GeO_2 + 2H_2O\uparrow \quad (2)$$

Product B was dried at 100 °C to encourage the removal of water (Equation 2) but some hydroxide remained according to infrared spectroscopy.

The XRD pattern of product A(lit) [5] is reproduced in Fig. 2c (by kind permission of the American Ceramic Society) and may be seen to closely resemble the pattern of product B. Hence product A(lit) is also largely hexagonal GeO_2, despite the presence of H_2S during its preparation.

When the preparative route employed for product A(lit) [5] was repeated here, product A was formed. XRD suggests that the latter is fairly amorphous and partially consists of hexagonal GeO_2. However, there is strong evidence from infrared spectroscopy that a substantial part of product A is GeS_2.

Melling [5] has proposed a reaction scheme analogous to Reactions 1 and 2 above for the production of GeS_2

$$Ge(OEt)_4 + 4H_2S \rightarrow Ge(SH)_4 + 4EtOH\uparrow \quad (3)$$

$$Ge(SH)_4 \rightarrow GeS_2 + 2H_2S\uparrow \quad (4)$$

Just as Reaction 1 tends to lead to (Ge–OH) contamination of the final oxide product, so Reaction 3 might be expected to lead to the presence of uncondensed (Ge–SH) in the sulphide product. The absence of any (S–H) vibrational absorption (expected at 2500 cm^{-1} [9]) in the infrared spectrum of product A, however, is perhaps not unexpected. Removal of H_2S to leave the disulphide, as in Reaction 4, will be achieved more easily than the dehydration of Reaction 2 because of the gaseous nature of H_2S at ambient temperatures and its lower propensity for hydrogen bonding relative to water.

Melling [5] showed that it was possible to form entirely amorphous material by varying the solvent ratio during the synthesis. It is tempting to suggest that the degree of non-crystallinity is a measure of sulphide content of the product; however, Mukerjee and Sharma [7] have shown that aqueous derived GeO_2 can also be amorphous.

The fact that both Melling's product and our product A contain oxide is probably due to irreducible water contamination in the reaction zone which will tend to hydrolyse the $Ge(OEt)_4$ precursor in a manner described by Reactions 1 and 2. Should this be true, then future syntheses would encounter more success if the entire operation were carried out in a dry atmosphere-controlled glovebox.

A possible alternative cause of the oxide formation is a competing reaction involving bond cleavage at the GeO–Et site, rather than Ge–OEt, producing oxide as below

$$Ge(OEt)_4 + 4H_2S \rightarrow Ge(OH)_4 + 4EtSH\uparrow \quad (5)$$

$$Ge(OH)_4 \rightarrow GeO_2 + 2H_2O\uparrow \quad (6)$$

By the above scheme GeO_2 is an unavoidable by-product of GeS_2.

However, when we allowed $Ge(OEt)_4$ to be exposed to ambient atmosphere prior to treatment with H_2S, infrared spectroscopy of the product showed an enhanced ratio of oxide to sulphide (compare Fig. 1c with b). This supports the suggestion that the oxide source is water contamination.

Subsequent exposure of product A to water was seen to hydrolyse the sulphide to oxide rather slowly at room temperature i.e.

$$GeS_2 + H_2O \rightarrow GeO_2 + H_2S\uparrow \quad (7)$$

Removal of H_2S drives Reaction 7 to the right-hand side.

5. Conclusions

It is concluded that the successful preparation of GeS_2 via H_2S treatment of $Ge(OEt)_4$ relies on the prevention of hydrolysis of the latter.

In the proposed mixed GeS_2/SiO_2 sol–gel preparation from germanium and silicon alkoxides, the water required to produce silica would tend to prevent formation of germanium disulphide. However, GeS_2 itself has been shown to be hydrolysed fairly slowly, hence if it were prepared initially in isolation then it might survive subsequent exposure to water required to convert the alkoxy-silane to silica. However, because of the difficulty in drying silicate gels it is more likely that GeO_2/SiO_2 would prevail.

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