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Microfibrous solids derived from SiO and from other main group oxide vapours

Apisit Songsasen and Peter L. Timms*

School of Chemistry, University of Bristol, Bristol, UK BS8 1TS.
E-mail: Peter.Timms@bristol.ac.uk

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The composition of "Monox", the microfibrous or particulate solid formed by condensing gaseous silicon monoxide in inert gas streams, has been shown to be close to SiO if the solid was collected and analysed in the total absence of oxygen, but the solid oxidised quickly in air to the previously reported composition, Si_4O_5. Heating mixtures of Si, SiO_2 with lithium or calcium silicates to 1800 °C, allowed co-liberation of SiO with Li or Ca vapours which gave microfibres of high aspect ratio when condensed in argon, an effect believed to be due to promotion of fibre growth by SiO_2/Li_2SiO_3 or $SiO_2/CaSiO_3$ eutectics. Novel silicon-free microfibrous solids have been prepared by condensation of the vapours liberated at 1700–1800 °C when calcium gallate is reduced by carbon under argon, or when aluminium and gallium oxides are reduced by boron in hydrogen; in each case fibre growth is thought possible because of the formation of both metal and oxide phases in the hot condensate.

Silicon monoxide vapour condensed at high temperatures in flowing inert gas streams forms a brown powder containing an intimate mixture of silica and silicon known as "Monox".[1] When prepared under suitable conditions, Monox is composed of an intertwined mass of microfibres typically 200 nm long with an aspect ratio of 10–20.[2] In a previous paper, it was shown that if the condensation of SiO was carried out in the presence of the vapours of various compounds of main group elements, the morphology of the microfibres underwent major changes due to the presence of the additives, leading to fibres with a much higher aspect ratio in some cases.[3] In this paper, we describe developments of this work in three ways: first, a study to check the true composition of condensed silicon monoxide; second, a quest for new additives which strongly affect the growth behaviour of microfibres formed by condensing SiO; third, a quest for other oxide vapour systems which exhibit a similar propensity to form microfibres on condensation to that shown by SiO.

Results and discussion

Further studies on SiO condensation

Condensate composition. Previous work on chemical analysis of either the microfibrous products or more particulate products formed by condensation of SiO at high temperatures in oxygen-free, flowing gas streams, indicated that the composition of the solid was always close to Si_4O_5 (corresponding to Si 21.8%, SiO_2 78.2%) and that this remained unchanged over long periods of exposure to air.[1–3] To resolve the uncertainty as to whether this observed Si_4O_5 composition was a result of air oxidation of the condensate or the result of transport of SiO_2 along with molecular SiO, an attempt was made to collect and analyse the solid in the total absence of oxygen.

As described before,[3] SiO was prepared batchwise by rapidly heating an intimate mixture of silicon and silica to 1800 °C in a graphite crucible and driving out the liberated SiO with argon into a cooler stream of argon (the "quench gas") where condensation occurred. When SiO production was at a maximum, part of the condensate was sucked into and trapped by a filter unit of known weight which could be subsequently sealed and reweighed. To analyse the solid on the filter, the unit was flooded very rapidly with a large excess of an O_2-free, 0.2 M solution of $AgClO_4$ in 2 M HF. This reagent oxidised and dissolved the condensate forming solid silver which was filtered off, dissolved and estimated volumetrically. The oxidisable Si content measured repeatedly under these conditions was $31.3 \pm 0.7\%$, close to the 31.86% Si expected in a 1 : 1 Si : SiO_2 mixture, showing that all previous condensates collected and then analysed in air had undergone partial air oxidation.

Further fibre enhancing additives for condensation with SiO. The tentative conclusion from the previous work on increasing the aspect ratio of SiO microfibres by the addition of additives was that those additives which were most successful were those which lowered the melting point of silica.[3] Such additives had the effect of allowing microfibres to grow more rapidly over a wider temperature range than for pure SiO. Further evidence in support of this idea has come from experiments in which SiO was produced from mixtures of Si/SiO_2 with lithium or calcium silicates.

With lithium silicate, the most effective mixture in the crucible contained Li_2SiO_3, Si and SiO_2 in proportions corresponding to a mole ratio Li : Si : SiO_2 of 1 : 5 : 5. The condensate obtained with this additive was a brown solid containing many fibres of higher aspect ratio than those from condensing SiO alone (see Fig. 1). The surface area was 42 $m^2 g^{-1}$ and the lithium content 4.90% by weight. A quite similar product was obtained when Li_2SiO_3 was replaced by LiF, but the effluent gas stream was very acidic due to the presence of SiF_4 which suggests that conversion of LiF to a lithium silicate by reaction with excess SiO_2 was occurring in the crucible.

No crystalline lithium phases were detectable in the product by powder XRD but evidence for the presence of oxidisable lithium species was obtained in the following way. Treating the product with $AgClO_4/HClO_4$ to liberate silver proportional to the free silicon gave an apparent value of *ca.* 26% Si, 4–5% higher than normal for condensed SiO (after exposure to air). However, if the products were treated first with 0.5 M $HClO_4$ to dissolved any easily oxidised lithium species before adding the $AgClO_4$ solution, the amount of silver metal obtained

Fig. 1 Condensate obtained from the vapours liberated by a Li_2SiO_3/Si/SiO_2 mixture in Ar at 1800 °C.

indicated a silicon content of 22.7%, only slightly higher than normal.

With $CaSiO_3$ as part of the crucible charge, the most fibrous condensate was obtained using a Ca : Si : SiO_2 ratio of 6 : 7 : 7, *i.e.* much more calcium needed to be added than in the corresponding system with lithium as an additive. This mixture gave a condensate with a high proportion of long fibres (Fig. 2). This product contained 19% by weight Ca and analysis by powder XRD showed crystalline silicon and weaker peaks corresponding to Ca_2SiO_4 and Ca_2Si in the sample. Using a significantly lower or higher proportion of $CaSiO_3$ with the Si/SiO_2, or using other calcium salts co-condensed with SiO under a variety of conditions, failed to give fibrous products. Practical problems with use of the optimised $CaSiO_3$/Si/SiO_2 mixture were that the total yield of condensate was quite low and the residue in the graphite crucible was very hard to remove.

Addition of sodium or potassium salts to the Si/SiO_2 mixture in the crucible, or co-condensation of SiO with sodium or potassium salts evaporated from independent crucible sources, resulted mainly in a loss in fibre character of the condensates. Similarly, attempts to incorporate magnesium or barium vapours or vapours of their compounds in the condensing SiO generally gave products less fibrous than those from pure SiO.

The species leaving the crucible when lithium or calcium silicates were used as additives to Si/SiO_2 mixtures are believed to have been Li or Ca atoms plus SiO. A comparison of the free energies for the two reactions shown below at 2100 K (1827 °C)[4] makes apparent why it was necessary to have lithium silicate only as a minor component but calcium silicate as a major component compared to the amount of Si/SiO_2 in the crucible, in order to have the right amount of each of the metal vapours transported along with the SiO:

$$Li_2O(l) + Si(l) = 2Li(g) + SiO(g)\, \Delta G(2100\ K) = -16\ kJ\ mol^{-1}$$

$$CaO(s) + Si(l) = Ca(g) + SiO(g) \Delta G(2100\ K) = +121\ kJ\ mol^{-1}$$

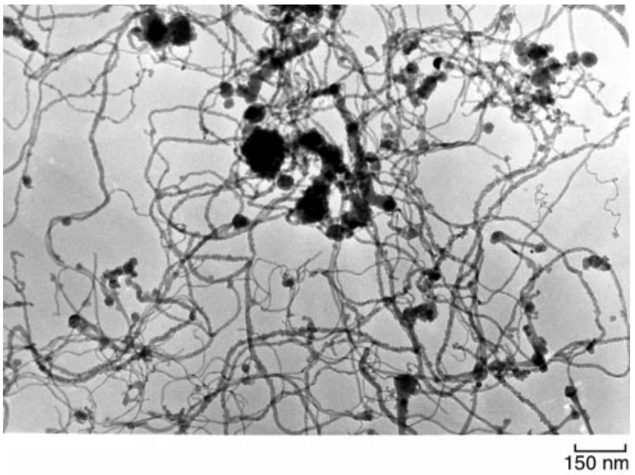

Fig. 2 Condensate obtained from the vapours liberated by a $CaSiO_3$/Si/SiO_2 mixture in Ar at 1800 °C.

Nucleation and condensation of SiO gas would have occurred mainly at temperatures[3] of 1400–1600 °C and, as there is no thermodynamically stable solid phase SiO,[5] condensation would have been accompanied by disproportionation to Si (liquid or solid) and SiO_2 (viscous glassy solid). Reaction of lithium or calcium vapours with excess SiO_2 liberated as the SiO condenses and disproportionates would yield the metal silicate and silicon in thermodynamically favorable reactions. Reaction of the metal vapours with silicon would give metal silicides. However, as described by Füglein and Schubert in their study of the reaction of condensed SiO with magnesium,[6] such silicides could react with SiO_2 to give metal oxides/silicates but the rapid cooling of the solids in the argon stream may have prevented this reaction going to completion. The phase diagram for the Li_2O/SiO_2 system is quite complex but the presence of lithium lowers the melting point of silica by up to 700 °C. The melting point lowering is much less for CaO/SiO_2 but this system has a eutectic at about 1440 °C. The longer fibres observed by condensing SiO in the presence of lithium or calcium must arise because the liquid range of the silica phase has been extended and its viscocity reduced by the presence of lithium or calcium silicates respectively. It may seem surprising that using sodium or magnesium silicates as additives to Si/siO_2 mixtures proved counter-productive with loss of much of the fibre character. However, this fact reinforces the idea that the growth of SiO fibres depends on a delicate balance of physical and chemical factors and it is very easy to disturb this balance with an additive so that less fibre formation occurs.

Silicon-free fibre forming systems

The Ca/Ga/O system. The success obtained in modifying SiO fibres with addition of calcium prompted a similar investigation of the effect of calcium on condensing Ga_2O which disproportionates into Ga and Ga_2O_3. Gallium has been used previously[3] as an additive to give extended fibres from SiO but condensation of the Ga_2O vapour from heating mixtures of Ga and Ga_2O_3 gives no fibres. Unlike SiO_2, Ga_2O_3 is not semi-fluid much below its melting of 1795 °C and so it cannot flow to form microfibres. However, the CaO/Ga_2O_3 system forms glasses and has liquid phases over a wide range of compositions and temperatures (down to *ca.* 1250 °C).[7–9]

A composition for the crucible charge was sought which would allow co-liberation of Ga_2O and calcium vapours. After some trials, the best mixture was found to be $CaGa_2O_4$, $CaCO_3$ and C in a 1 : 2 : 7 mole ratio, heated rapidly to *ca.* 1700 °C in an argon stream with argon as the quench gas. The $CaCO_3$ in the crucible charge was necessary to boost the amount of calcium vaporised along with the more readily liberated Ga_2O. Under these conditions, a dark grey condensate was obtained which had a microstructure consisting of tapering fibres of diameter *ca.* 25 nm and length 200–500 nm attached to spherical heads of 50–100 nm diameter (Fig. 3); the specific surface area of the product was measured as 27.8 $m^2\ g^{-1}$. Like SiO based fibrous materials, there was no visible change in the solid on exposure to air. However, evidence from analysis, given below, indicated that there was an initial interaction with air after which the solid still contained much oxidisable material and when ignited it glowed and burned without a flame to leave a white residue.

The analysis of these fibres has proved quite difficult and there are still some unanswered questions. The composition of

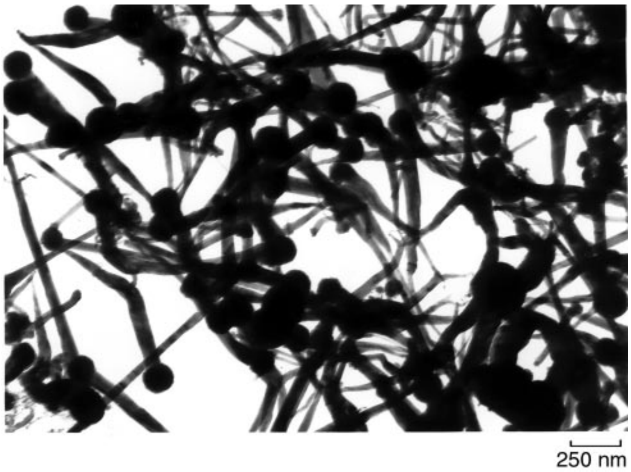

Fig. 3 Condensate obtained from the vapours liberated by a $CaGa_2O_4$/$CaCO_3$/C mixture in Ar at 1800 °C.

the fibres, based on the Ca and C content determined by elemental analysis and the Ca : Ga ratio by EDAX microanalysis (calibrated with $CaGa_2O_4$ as a standard), assuming the balance as oxygen, was $CaGa_{1.74}O_{2.45}C_{0.30}$. The powder XRD spectrum of the solid was very weak but showed lines which could be assigned to Ga_2O_3 and $CaGa_2O_4$. After the sample had been heated and further oxidised in air, the powder XRD spectrum showed the same lines with much greater intensity and all the additional lines consistent with the presence of Ga_2O_3 and $CaGa_2O_4$. As with the $Si/SiO_2/Ga_2O_3$ system described previously,[3] no Ga (or any of the possible intermetallic Ca/Ga phases) was detected by powder XRD. Nevertheless, treatment of the solid with aqueous Ag^+ in the presence of HF liberated silver. Each 100 mg of fibres gave 2.373 mmol of silver, an amount equivalent to an elemental Ga content of 55.0%, or to a CaGa alloy content of 52.1% (assuming each Ca atom liberates 2Ag and each Ga atom 3Ag).

The only well defined bands in the infrared spectrum (Nujol mull) were at 877 and 711 cm^{-1} suggesting the presence of calcium carbonate. The $CaCO_3$ was evidently poorly crystalline as it was not detected by powder XRD analysis, so it is very unlikely to have arisen by mechanical transport of a reactant from the crucible to the condensate but rather by subsequent reaction of atmospheric CO_2 with Ca or CaO dispersed in the condensate. The XPS spectrum (Table 1) gave one peak for Ca $2p_{3/2}$ consistent with $CaCO_3$ and/or $CaGa_2O_4$, and also indicated the presence of Ga metal and Ga_2O_3.

The mechanism of formation of the fibres shown in Fig. 3 may be similar to those of comparable SiO fibres involving disproportionation and phase separation, but there are important differences in the condensation behaviour of SiO and Ga_2O. The latter is much more volatile, so condensation from a vapour stream carrying Ga_2O at a partial pressure of 5×10^3 Pa would not be expected at temperatures above 1100 °C, compared to *ca.* 1600 °C for SiO condensation at the same partial pressure. Based on the model of the Si/SiO_2 system, fibre formation requires extrusion of a semi-liquid oxide phase away from a metal-rich fibre head. For the Ga/Ca/O system, a semi-liquid oxide phase could exist only above 1250 °C. It may be that primary condensation in the system is due to a reaction

$$\mathrm{Ca(g) + Ga_2O(g) \rightarrow CaO(s) + 2Ga(1)}$$

followed by

$$\mathrm{CaO(s) + 3Ga_2O(g) \rightarrow CaGa_2O_4 + 4Ga(1)}$$

or overall

$$\mathrm{CaO(g) + 4Ga_2O(g) \rightarrow CaGa_2O_4 + 6Ga}$$

The formation of calcium gallate allows condensation of $Ga_2O(g)$ at temperatures at which the oxide phases are mobile enough to form fibres. The presence of Ga_2O_3 in the products suggests that the calcium may promote condensation and disproportionation of Ga_2O to an even greater extent than indicated by the equations above. The possibility remains that the large amount of elemental gallium liberated may have alloyed with calcium, giving a metallic phase which promoted the material transport necessary for fibre growth. It is likely, but not proved by these studies, that the spherical head region of the fibres of Fig. 3 is richer in the metallic phase(s) and that the tail region is richer in oxide phases. Analysis of the bulk solid showed its composition to be richer in oxygen than required by the above equations, indicating that, like SiO, this solid had undergone partial oxidation on exposure to air.

No microfibrous condensate could be obtained by replacement of calcium by magnesium or of gallium by indium in the experiments above.

The Al/B/Ga/O/H and Al/B/In/O/H systems. A quite different approach to silicon-free microfibre forming systems was tried, building on previous experience of co-evaporating SiO and boron oxides in a hydrogen stream.[3] It was known that condensation of GeO, Ga_2O or In_2O did not yield microfibres, but it seemed worthwhile to find out if their behaviour could be changed by co-condensation with boron oxide species. Accordingly, GeO, Ga_2O and In_2O were generated by heating mixtures of GeO_2, Ga_2O_3 and In_2O_3 (or preferably $InBO_3$) respectively with boron using hydrogen as the gas passed through the crucible and argon as the quench gas. In each case, there was quite a vigorous reaction in the crucible at a temperature above 1400 °C and some vapour was ejected very quickly, but the condensates were not fibrous. In an effort to reduce the vigour of the reduction of the oxides by boron, Al_2O_3 was added to the mixtures in the crucible as an "inert diluent". The addition of Al_2O_3 to the B/GeO_2 mixtures caused

Table 1 Identification of components of some condensates by XPS after the solids had been exposed to air

System	Measured peak[a]/eV	Ident. E_b(lit.)[a]/eV	Ref.
Ca/Ga/O	347.7	$CaCO_3$, Ca $2p_{3/2}$, 347.2	13
	1116.8	Ga metal, Ga $2p_{3/2}$, 1116.3 ± 0.2[b]	14
	1118.6	Ga_2O_3, Ga $2p_{3/2}$, 1118.1 ± 0.2[b]	14
$Al/B/Ga/O(H_2)$	75.5	Al_2O_3, Al 2p, 74.8	15
	193.6	$B(OH)_3$, B 1s, 193.2	16
	1117.3	Ga metal, Ga $2p_{3/2}$, 1116.3 ± 0.2[b]	14
	1119.1	Ga_2O_3, Ga $2p_{3/2}$, 1118.1 ± 0.2[b]	14

[a] Referenced against C 1s at 285.0 eV unless noted otherwise. [b] Referenced against C 1s at 284.8 eV.

Fig. 4 Condensate obtained from the vapours liberated by a Al_2O_3/B/Ga_2O_3 mixture in H_2 at 1800 °C.

no detectable development of fibre character among the spherical particles of the condensed products. However, the Al_2O_3/B/Ga_2O_3 and Al_2O_3/B/$InBO_3$ systems proved more interesting.

Heating a mixture of Al_2O_3, B and Ga_2O_3 in a 1 : 8 : 1 mole ratio to 1800 °C at 10^5 Pa pressure in a stream of hydrogen with argon as quench gas, gave a product which showed distinct development of microfibrous character. The same mixture gave a more fibrous product (Fig. 4) when the overall pressure in the system was lowered to an optimum value of 5×10^4 Pa (this was an unexpected result as studies on the condensation of SiO have shown that the variations of system pressure within the range 1.5×10^5–5×10^4 Pa caused no detectable change in the fibre character although loss of fibrosity was observed[10] below 1×10^4 Pa). Average fibres in this grey coloured product were about 35 nm in diameter and 350 nm long, *i.e.* the aspect ratio was about 10, although there were also some relatively large spherical particulates formed and the surface area was only 5.8 $m^2\ g^{-1}$, much less than values of 50–100 $m^2\ g^{-1}$ observed for fibrous Monox.

Using a combination of chemical and X-ray analysis, the Al : B : Ga mole ratio in the solid was found to be close to 1 : 1 : 2. The infrared spectrum of the fibrous solid after it had been exposed to air showed strong peaks of $B(OH)_3$ and a band at 760 cm^{-1} assigned to B_2O_3 so imbedded in the solid that it did not hydrolyse rapidly. The power XRD spectrum of the solid showed only weak features with the peaks assignable to $B(OH)_3$ most clearly visible. From the XPS spectra of the solid (see Table 1), evidence was obtained for the presence of Al_2O_3, H_3BO_3, Ga and Ga_2O_3. However, there was reproducibly a *ca.* 0.5 eV shift in the peak positions assigned to the $2p_{3/2}$ electron levels for Ga and Ga_2O_3 in this sample compared to the values obtained with the Ca/Ga/O samples described above, but this may be the effect of the quite different matrix in the two types of samples.

A somewhat fibrous product could be obtained using a crucible charge of Al_2O_3, B and $InBO_3$ in a 1 : 3 : 1 mole ratio in the presence of hydrogen under an optimum pressure of 10^5 Pa (see Fig. 5). The powder XRD spectrum was dominated by lines for indium metal with weaker lines of boric acid. There was no evidence of crystalline Al_2O_3 and analysis indicated an Al : B : In mole ratio of about 1 : 4 : 5, *i.e.* this product contained a much lower proportion of Al than the more fibrous gallium product.

The observed transport of aluminium in the above experiments was a surprise so experiments were carried out in which a mixture of B and Al_2O_3 in a 4 : 1 mole rato was used as the crucible charge and was heated to 1800 °C in argon or hydrogen streams. It was found that when argon was passed through the crucible, the weight loss from the crucible charge after 5 min heating was only 1% and very little condensate was obtained. When hydrogen was passed through the crucible at the same temperature for the same time, 22% of the charge was vaporised and the condensate contained 11.1% by weight of Al.

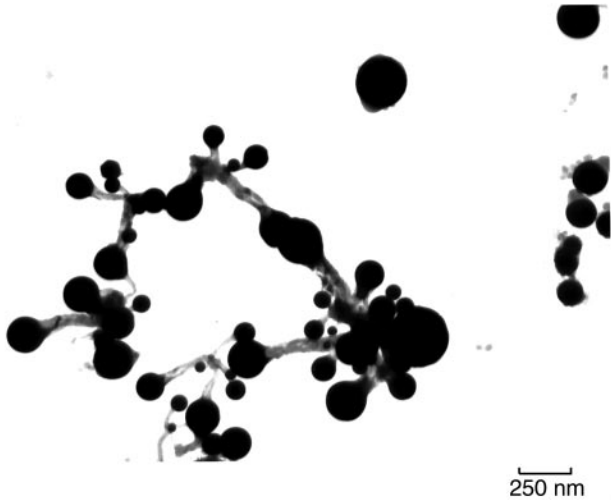

Fig. 5 Condensate obtained from the vapours liberated by a Al_2O_3/B/In_2O_3 mixture in H_2 at 1800 °C.

The forms in which B and Al were transported in this case are not known. It is likely from published data on the B/O/H system at high temperatures[11] that the main species carrying boron was $(HBO)_3$. Partial replacement of boron by aluminium to give a vapour species $H_3AlB_2O_3$ seems possible. It is known[12] that :AlOH is more stable than the isomeric HAlO but in a planar boroxine ring, the –O–Al(H)–O– moiety should be somewhat stabilised.

With the ternary mixture Al_2O_3/Ga_2O_3/B in the crucible in the presence of hydrogen, all three elements Al, B and Ga were transported to appear in the final condensate. Some gallium must have been transported as Ga_2O, but the possibility that part of the gallium was transported with boron or with boron and aluminium as cyclic species, such as $H_3B_2GaO_3$ or $H_3AlBGaO_3$, cannot be ruled out.

The system Al_2O_3/B_2O_3/Ga_2O_3 is partly liquid at temperatures down to *ca.* 800 °C giving wide scope for condensation and growth of the oxide rich part of the fibres. The growth tip was almost certainly gallium rich but its ability to allow transport of material into the fibre tail may have been modified by some alloying with aluminium and/or boron. With the indium-based fibres shown in Fig. 5, a major concentration of indium-rich material in the fibre heads is evident from the high contrast between the head and tail regions of the fibres.

In conclusion, this work has demonstrated that the possibility of forming microfibrous solids by condensation of oxide vapours is not unique to SiO. Nevertheless, based on earlier work on understanding SiO condensation,[3] it is likely that the requirements for fibre growth are always rigorous. The condensation must be accompanied by disproportionation or other reactions which initially give a two-phase condensate, with a molten metallic phase and a fluid oxide phase which are immiscible. The molten metallic part of a tiny hot particle may act as a growth tip on which other tiny particles can aggregate with continuous separation of metallic and oxide phases which allows for strongly asymmetric growth of the particle, forming an oxide-rich tail and a metal-rich head. Apart from SiO, other simple suboxide systems in which condensation is accompanied by disproportionation do not give fibres because the physical states of both the metallic phase and the oxide phase during particle aggregation are not compatible with the above criteria for fibre growth. However, our exploration of more complex oxide mixtures has shown that through a fortuitous balance of

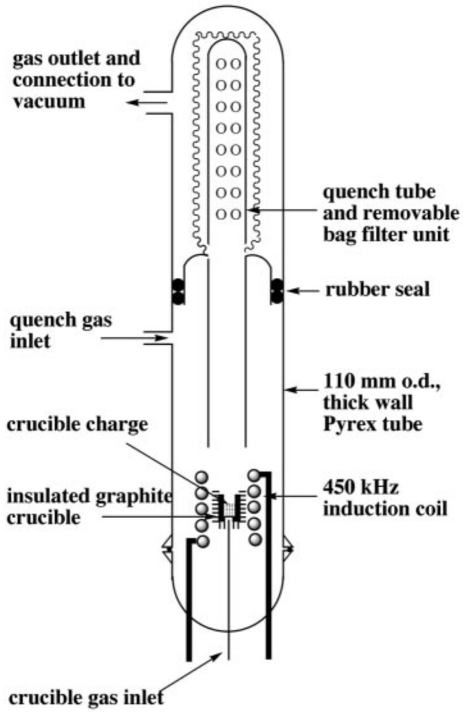

Fig. 6 Apparatus used for the formation and condensation of vapours at high temperatures at pressures of 10^4 to 2×10^5 Pa.

factors the Ca/Ga/O and Al/B/Ga/O/H systems will give microfibres comparable to those from SiO.

Experimental

Apparatus

The experiments on the stoichiometry of condensed SiO and initial experiments on the effect of added lithium and calcium were carried out in apparatus similar to that described in ref. 3, but the apparatus of Fig. 6 was used for all other experiments.

Silicon monoxide or other gaseous species were formed from solids contained in a graphite crucible, 52 mm long, 28 mm o.d. and 16 mm i.d., lightly insulated with graphite felt and supported on a 6 mm o.d. graphite tube. The crucible was heated by a water cooled copper work coil connected to a 6 kW, 450 kHz Radyne radiofrequency generator. With a power input of 2.8–3 kW, the crucible reached a temperature of *ca.* 1500 °C in 1 min and reached a plateau temperature close to 1800 °C in *ca.* 2 min. The furnace assembly was contained within a cylindrical heavy-wall Pyrex vessel so that experiments could be run at pressures in the range 10^4 to 2×10^5 Pa. The vessel could be evacuated before each experiment to a pressure < 1 Pa to remove water and oxygen. Vapours generated within the crucible were driven out by a stream of argon or hydrogen passed upwards through the crucible. The rising vapour stream merged with the quench gas, a further stream of relatively cold argon, within the quench tube and the resulting cooling triggered condensation. The solid formed was collected in a paper filter at the top of the quench tube and was normally removed from the filter for analysis in air.

Product analysis

Instrumentation and procedures for analysis of the products by IR and XPS spectrometry, by electron microscopy, by powder XRD and by chemical treatment with silver ions, were exactly as described under "Product analysis" in reference 3. Collected data for XPS measurements are shown in Table 1.

In samples of condensate containing Si, O and either lithium or calcium, analysis for Li and Ca was achieved by treating a weighed sample of material with HF/HNO_3 to oxidise and then remove as fume the silicon and silica, followed by further treatment with NH_4F, to leave LiF or CaF_2 as residues which could be weighed. Calcium and aluminium were also determined by atomic absorption spectroscopy and Ca/Ga, Al/Ga and Al/In ratios were measured using the EDAX system on a JEOL 100 CX electron microscope. Boron was determined as boric acid by titration in the presence of mannitol.

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