# Microwave-assisted Solid-state Reactions involving Metal Powders†

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The ability of metal powders to couple to microwave radiation at 2450 MHz has been used to accelerate a range of solid-state reactions. Although metal objects cause extensive arcing within a microwave cavity, metal powders couple in a more conventional manner with the microwave radiation and experience high heating rates. This property has been utilised for the synthesis of metal chalcogenides and metal cluster compounds of the Group 5 and 6 elements.

In recent years there have been a number of examples of solid-state reactions which have been accelerated using microwave power. The loss tangents of certain metal oxides in particular have proved to be sufficiently large to couple with the microwaves and thereby provide sufficient thermal energy to permit the reaction to proceed rapidly.[1–3] Reaction temperatures in excess of 900 °C have been achieved as a result of the thermal runaway properties associated with one of the components of the reaction mixture.[4] In contrast, prior to our preliminary report in 1992,[5] there had been no reports of metal powders being used in microwave-induced chemical reactions, either as the microwave absorbing material or as a reagent alongside other high-loss-tangent materials.[6] This may reflect a widespread belief that metals invariably cause plasma discharges within a microwave cavity and are therefore an unsuitable component for microwave-assisted syntheses. It is well known that the presence of solid metal samples or continuous metal films in high microwave fields results in large electric field gradients and may cause very visible and at times dramatic electric discharges. In contrast to bulk samples, however, metal powders can couple effectively with microwave fields at 2.45 GHz[7] and heat up to temperatures in excess of 1000 °C in very short periods of time without causing visible electric discharges. This paper describes how the microwave properties of metal powders have been used to accelerate the syntheses of a wide range of metal chalcogenides and as reducing agents in the formation of low-oxidation-state metal cluster compounds. Although there may be additional contributions from localised plasma effects,[8] the microwave heating properties associated with metal powders result primarily from conduction mechanisms. Attenuation of microwave radiation in a conductive medium arises from the creation of currents resulting from charge carriers being displaced by the electric field. The charge carriers are subject to resistance in the medium in which they travel due to collisions with the lattice phonons, which leads to Ohmic heating. Since the conduction electrons in a metal are extremely mobile, the time required for the complete polarisation of a metal particle is very small, typically of the order of $10^{-18}$ s. In a microwave cavity the time required for the applied electric field to be completely reversed is far longer than this, $\approx 2 \times 10^{-10}$ s at 2.45 GHz. The large potential differences which result if the metal particles are large or the metal forms a continuous strip or macroscopically large object give rise to dramatic discharges if they are large enough to break down the electrical resistance of the medium separating the metal particles or objects. However, small metal particles do not generate sufficiently large potential differences for this phenomenon to occur. In this paper the microwave dielectric heating of metal particles is utilised in two classes of solid-state reactions.

## Results and Discussion

*Synthesis of Metal Chalcogenides.*—Transition-metal chalcogenides have been comprehensively studied by a number of workers and, in general, their conventional syntheses require straightforward but time-consuming procedures. Typical synthetic routes include binary combination of the elements and the reaction of $H_2S$ with either the metal, metal oxide, or metal chloride. Synthesis by direct combination of the elements, the method of interest in this work, usually involves three stages. The initial reaction of the elements at relatively low temperatures is followed by high-temperature treatment to improve homogeneity, and almost invariably annealing at progressively lower temperatures to achieve the phase required in a crystalline form. Owing to these stages, many syntheses require a week or more to complete and therefore represent ideal systems with which to assess the advantages of microwave heating for syntheses involving metal powders. Elemental sulfur (resistivity, $\rho = 2 \times 10^{27}$ μΩ cm) and selenium ($\rho = 2 \times 10^{13}$ μΩ cm) are insulators and possess no dipoles and consequently they have extremely small loss tangents, and would not be expected to contribute to microwave heating effects. It is therefore reasonable to ascribe all the *initial* heating effects in these reactions to the metal reagent. A summary of the chalcogenide syntheses which were carried out in microwave cavities operating at 2450 MHz is given in Table 1.

Previous work on microwave-assisted solid-state reactions has been successfully performed using a variety of containment methods,[16] many of which allow control of the reaction atmosphere. Syntheses involving elemental chalcogens, on the other hand, require the use of sealed evacuated ampoules in order to contain the chalcogen vapour. Microwave irradiation gives rise to visible discharges in low-pressure gases,[17] and it is therefore extremely important that consideration is given to the nature and pressure of the gas in the ampoule. Some gases (notably argon), although chemically inert, are prone to violent electrical discharges over large pressure ranges in microwave fields. The extreme efficiency with which this may occur not only diverts microwave power from the sample, but may also cause dangerous overheating of the silica ampoule. Preliminary

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† *Non-SI units employed:* Torr ≈ mmHg ≈ 133 Pa.

**Table 1** Chalcogenide syntheses involving metal powders (X = S, Se or Te)

| | Mass/g | | | | |
|---|---|---|---|---|---|
| Product | Metal | X | Reaction time/min | Annealing time/h | Ref. |
| CrS | 2.08 | 1.28 | 8.5 | 17 | 9 |
| $Cr_7S_8$ | 2.08 | 1.50 | 8.5 | 10 | 9 |
| $Cr_2S_3$ | 2.08 | 1.94 | 8.5 + 20 | 1 | 9 |
| CrSe | 2.60 | 3.95 | 5 | 5.5 | 10 |
| $Cr_3Se_4$ | 2.60 | 5.27 | 5 + 5 | 8 | 10 |
| $Cr_2Se_3$ | 2.08 | 4.78 | 5 | 3 | 10 |
| $Cr_2Te_3$ | 1.73 | 6.35 | 10 | 14 | 11 |
| MnS | 2.74 | 1.60 | 1 | 10 min | 12 |
| $Fe_7S_8$ | 2.79 | 1.60 | 1 + 10 | 1 | 12 |
| $TaS_2$ | 4.52 | 1.60 | 20 | 12 + 12 | 13 |
| $SnS_2$ | 2.37 | 1.60 | 3 | 10 min | 14 |
| $FeCuS_2$ | Fe 1.40<br>Cu 1.575 | 1.60 | 5 + 5 + 5 | — | 15 |

tests established that nitrogen, as well as being sufficiently inert for these reactions, cannot support a discharge below a pressure of *ca.* 0.1 Torr at 600 W applied power. The reagents were therefore sealed in silica ampoules of a suitable size (internal diameter 1.5 cm × 10 cm) under nitrogen at a pressure of $< 10^{-2}$ Torr. The use of larger ampoules was found to be disadvantageous since, as described later, some chalcogen was always lost from the reaction site, and the larger volume only served to exacerbate this problem.

The reactions were initiated by placing the ampoule on a firebrick in the microwave cavity, and applying microwave power. Initially, reactions were performed in an unmodified 500 W domestic microwave oven (Swan), and it was not possible to control the applied power. Subsequent reactions were carried out in either a domestic oven with modified power control (Sharp R5V11), or in an industrial oven with variable power (Microwave Heating Ltd.). Details of the modifications have been described previously.[16] In a typical reaction with chromium powder (2 g, −100 mesh), the optimum applied power was found to be approximately 200 W, although it should be noted that much of this power is dissipated in the walls, *etc.*, and does not contribute to the sample heating. With ovens equipped with continuously variable power output it is also possible to anneal the samples under microwave irradiation, an important subsequent step in many of these syntheses.

*Synthetic Details.*—Chromium sulfides and selenides were synthesised by direct combination of the elements in much less time than is required by conventional methods, whilst giving products of comparable quality. In a typical synthesis the metal reaction sites are raised extremely rapidly to red heat, and although this gives rise to some loss of chalcogen, which condenses on the cool walls of the ampoule, the reaction occurs so rapidly that most of the chalcogen combines with the metal within a few seconds. Although the initial heating effects are solely due to the metal particles, subsequent heating effects, as the metal is used up, are due also to the conducting/semiconducting properties of the products, thus enabling a smooth reaction with one microwave absorbent component replacing another as the reaction proceeds. The sulfide $Cr_2S_3$ was synthesised by two routes. The direct combination of the elements has already been mentioned, but it was also possible to use the dielectric loss tangent of CrS in order to effect a reaction between this and elemental sulfur. This is a further demonstration of the role which is played by the product in these syntheses. Initial heating effects are certainly due to the metal powder, but at later stages of the reaction an increasingly large proportion of the heating effects arises from the dielectric properties of the products.

The synthesis of $TaS_2$ proved to be very straightforward. This material has a large number of polytypes and a mixture of phases were synthesised. The 2H polytype, which is only stable below 600 °C, is of particular interest for intercalation reactions,[13] and it was possible to prepare a crude sample of this material through an extended annealing process. This sample remained unsuitable for intercalation reactions, but this work indicates that the possibility exists to refine this method to produce polytypically pure samples.

In addition to single metal chalcogenides, the mixed-metal chalcogenide $FeCuS_2$ (chalcopyrites) was synthesised. This synthesis was more difficult to perform and gave a poorly defined product, but is particularly important since the phase decomposes above 390 °C. With more sophisticated applicators and suitable temperature monitoring it is not unreasonable to suppose that more reliable heating could be carried out to give a correspondingly better-quality product. Following our original report of this work,[5] other workers have successfully synthesised similar chalcopyrites phases using microwave dielectric heating techniques.[18]

In each of the syntheses, including those of tellurides, a small amount of the chalcogen is observed to condense on the walls of the ampoule during the course of the reaction. In contrast to the conventional synthesis, the chalcogen cannot be directly heated once condensed, and it is necessary to recombine the reactants by allowing the reactants to cool before shaking the tube and reheating the contents. The reaction may be driven to completion in this way, although it took up to five of these reaction–recombination–reaction cycles in some cases. The higher reaction time needed for the sulfide syntheses is a direct consequence of the lower boiling point of sulfur, since more chalcogen is lost from the reaction than in corresponding selenide syntheses.

Most of the reactions were complete after approximately 5 min, although the synthesis of highly crystalline samples required an annealing stage. This stage is only possible when the product has a relatively large loss tangent[15] such that microwave heating of the product is possible. It must be emphasised that although there is a decrease in the time required for the syntheses, this does not represent an increase in the actual *rate* of the reaction, since many of these reactions are exothermic. The decrease in reaction time is brought about using microwaves because it is possible rapidly to heat the metal sample without either heating the reaction vessel or generating high vapour pressures. This is very difficult to emulate with conventional methods since the extremely high heating rate induced by coupling of the metal particles with microwaves has no thermal analogue. As a result, much of the chalcogen reacts with the metal reagent in the first few seconds of the synthesis, and relatively little is found to condense on the walls.

The optimum synthetic route for sulfide and selenide syntheses was found to be a combination of microwave and conventional heating. A great deal of time may be saved from the conventional route by first heating the reactants with microwaves, such that the reaction is almost complete. Some chalcogen will condense on the ampoule walls, and this may then be incorporated into the product by conventional methods. In this way, it was possible to reduce synthesis times for chromium chalcogenides from 6 to 3 d, whilst obtaining a comparable quality sample.

In all of the syntheses involving sulfur or selenium a bright blue microwave-induced plasma was seen to fill the ampoule within a few seconds of the reaction commencing. Since this was not observed in telluride syntheses, and as the colour was markedly different in the cases of sulfur and selenium, the existence of the plasma was ascribed to the presence of chalcogen vapour. The plasma was found to disappear when the reaction was complete, thus providing a convenient end-point indicator.

*Reaction temperatures and heating rate.* Reactions with sulfur or selenium as the chalcogen reagent displayed extremely efficient heating profiles. Portions of the reactants in these

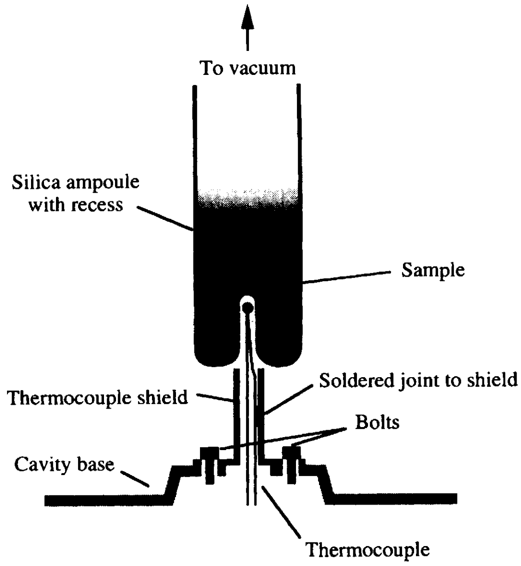

**Fig. 1** Shielded thermocouple

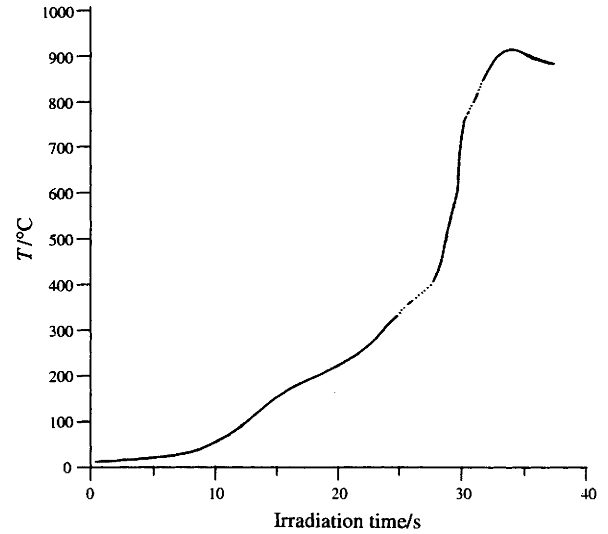

**Fig. 2** Temperature gradient in the microwave synthesis of CrS. Where electrical discharges have affected the data the curve has been interpolated (dotted lines)

syntheses become red hot within 10 s of applying the microwaves, and the maximum measured heating rate was found to be $\approx 100$ °C $s^{-1}$. Precise temperature measurement in the presence of microwaves presents a major challenge to the experimentalist,[19,20] and this is especially true when high temperatures are generated rapidly, since the presence of strong electric fields usually precludes the use of metal instruments such as thermocouples. However, in these reactions, it was found that a thermocouple could be placed into a silica recess in the core of the sample providing that (*a*) it was suitably shielded from microwaves up to the entry point in the ampoule, and (*b*) one of the thermocouple leads was held at the same potential as that of the microwave cavity (Fig. 1). Measurements were carried out on the Cr–S system, principally for reasons of convenience. Whilst this method does not totally remove the effects of induced voltages, the amplified thermocouple signal for a Cr–S system (1 : 1 molar ratio) could be plotted on a chart recorder (Fig. 2). The results indicate that the maximum rate of heating is of the order of 100 °C $s^{-1}$. Whilst this method may give an adequate approximation of the heating rate, precise temperature measurement is limited by the presence of the silica wall between the sample and the thermocouple. Short-lived or very localised high temperatures, for example, would not be registered using this technique. In contrast to the conventional syntheses (where low heating rates are necessary to prevent high vapour pressures of unreacted chalcogenides) this represents an extremely large temperature gradient, which is only possible because the microwave heating is specific to the metal powder and generates a high temperature and more reactive reaction site. Any chalcogen which is lost from the heated portion of the tube condenses in a cool region of the ampoule and no significant vapour pressure is built up. This presents problems in maintaining the stoichiometry of the reaction products, but as discussed above these may easily be overcome.

Other methods used to estimate the maximum temperature of the reaction could only provide measurements indirectly. In preliminary experiments, fine silica tubes containing salts with a variety of melting points were placed into the reaction, and the effect of heat from the reaction observed. The salts used were both anhydrous and had low dielectric loss tangents so the results were not invalidated by direct microwave heating effects. The reaction was run for 20 s before being quenched, and the silica tubes removed. The results indicated a reaction temperature of between approximately 850 and 1100 °C. This figure is supported by consideration of the chromium sulfide phase diagram in ref. 9. Microwave syntheses run with no control of the applied power inevitably give rise to quenched reaction products since the applied power is either 'high' or 'off'. The X-ray powder diffractions of products formed by quenched reactions from a range of chromium : sulfur ratios indicated the presence of a continuous solid solution which, by reference to the Cr–S phase diagram,[9] suggests a reaction temperature in excess of 1050 °C.

Measurements taken with a hand-held infrared pyrometer also indicated a temperature after 10 s of heating in the approximate range 850–975 °C. The accuracy of the technique is quite severely limited since the sample is small, has unknown emissivity, and is held within a silica ampoule. It was, however, possible crudely to calibrate the pyrometer by heating a sample to a known temperature in a conventional furnace and measuring the temperature with the pyrometer. Although these results also vary quite widely, they support those obtained by the other temperature-sensing techniques.

The heating rates observed with tellurium as the co-reactant were much less than those observed with either sulfur or selenium. Red heat in the reaction was only achieved after approximately 10 min at 650 W. The effect is predominantly due to the metallic nature of tellurium ($\rho = 2 \times 10^6$ μΩ cm); an intimate mixture (2 : 3 molar ratio) of tellurium with chromium is correspondingly conductive ($\rho \approx 0.5 \times 10^5$ μΩ cm), but the resulting surface is relatively reflective to microwaves. Although some heating is observed initially, principally from electrical discharges between metal particles, it is only as product begins to form that the reaction begins to proceed effectively. If the reaction is halted after some product has formed and allowed to cool to room temperature it may be restarted more easily than from the elemental mixture, indicating that a major contribution to the total dielectric heating effect arises from the product phase. This was also found to be true in a number of the other syntheses, particularly those of the chromium sulfides.

*Product purity.* Energy dispersive X-ray analysis (EDXA) studies demonstrated that the incorporation of silicon from the ampoule into the samples became a problem when low sulfur to chromium ratios were used ($< 4:5$). In these cases a proportion of the chromium was invariably recovered as a sintered mass. Quantitative analysis using EDXA[21] allowed the amount of incorporation of silicon to be plotted as a function of starting composition (Fig. 3), and clearly shows the limiting composition required for obtaining samples free from silicon. The phase diagram indicates that above a 1 : 1 Cr : S ratio a

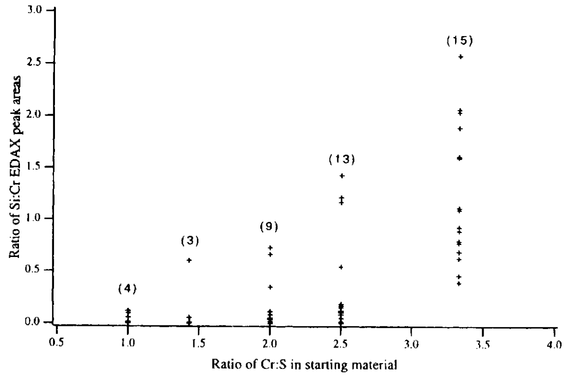

**Fig. 3** Incorporation of silicon into chromium sulfide samples. The EDXA analyses were performed on 15 crystallites for each starting ratio, and the ratio of Si:Cr peak areas measured in those crystallites where silicon was present. Figures indicate the number of crystallites found to contain Si

binary Cr–CrS phase exists, and as a result, when Cr:S ratios greater than 1:1 are used, the high-temperature unreacted chromium reacts with ampoule materials to incorporate silicon into the final product mixture.

X-Ray diffraction patterns have established that the metal chalcogenides in Table 1 crystallise in the same morphologies as those established for conventional thermal syntheses. Electron microscopy studies have also established that the samples are homogeneous, although in contrast to studies by other workers no differences in morphology were detected between microwave and conventional syntheses.

*Analysis of the plasmas.* An extremely striking property of the syntheses involving sulfur or selenium, and to a very limited degree those of tellurium also, was that within seconds of initiating a reaction the evacuated space in the ampoule is wholly or partially filled with a blue discharge. This was present irrespective of the vacuum pressure in the ampoule, and was attributed to the vaporised chalcogen, since analogous reactions involving tellurium showed no propensity for discharge formation. This effect is particularly important since, if this interpretation is correct, the discharge gives a reliable indication that there is free chalcogen remaining. Disappearance of the discharge therefore provided a reliable indication that the reaction was complete. Evidence for the validity of this interpretation was obtained by analysis of the discharge emission spectra.

It was significant that plasmas were observed in the reactions only after heating had caused some evaporation of chalcogenide, and that they could no longer be observed after completion of the reaction. The distinct colour differences between the plasmas formed during sulfide and selenide syntheses, together with the absence of a discharge during the telluride syntheses, indicated that the emission was at least partially due to the vaporised chalcogen.

By using a tunable re-entrant cavity fed by a coaxial microwave source (Electro-medical Supplies Ltd., Microtron 200 Mk. 3) it proved possible to arrange small-scale syntheses of chromium sulfides and selenides in the sample cavity of an emission spectrophotometer (Spex Emission Spectrometer), and to analyse the resulting emission spectrum of the discharge. The schematic arrangement is shown in Fig. 4. The tunable cavity and microwave source was originally designed for the creation of microwave-induced plasmas, and may deliver power levels of up to 200 W. In this work 20 W was found to be sufficient to create and maintain a discharge for sufficiently long periods for spectra to be obtained. If the plasma would not ignite, or when the plasma occasionally died away, it was possible to re-ignite it by introducing an electric spark from a tesla coil. The cavity is designed with an observation slit of dimensions 3 × 15 mm and was positioned such that power was fed to the reaction, whilst ensuring that the observation slit lay over a portion of the discharge. Background light was reduced as much as possible by blacking out windows, *etc.*

Atomic emission lines are extremely narrow, and it was necessary to run the spectrometer at its maximum resolution in order to detect them reproducibly. However, the scan time that this required ensured that only a very small portion of the spectrum could be analysed before either the discharge failed, or overheating of the ampoule created a safety hazard. Despite this limitation, the spectra obtained (Fig. 5) clearly showed the presence of emission lines at wavelengths corresponding to the $\mathrm{S^{I}}$ spectral lines (*i.e.* those due to neutral sulfur) at 674.36, 674.88 and 675.72 nm and of selenium emission lines from the $\mathrm{Se^{I}}$ series at 473.08, 473.90 and 474.20 nm. There were, by contrast, no detectable emission lines due to the $\mathrm{N^{I}}$ series (at 484.74 or 818.49 nm) nor of the $\mathrm{Cr^{I}}$ series (at 473.07, 473.74 or 746.20 nm). The emission lines in the selenium spectrum displayed intensity ratios in good agreement with those of published data (500:400:300), although those of the sulfur spectrum (published ratio 160:285:450) did not.[22] This was attributed to the extreme narrowness of the lines which were only observed at the limit of the spectrometer resolution which renders precise measurement of the maximum intensity impossible. It is interesting that there were no emission lines corresponding to the $\mathrm{S^{II}}$ and $\mathrm{Se^{II}}$ spectral series (*i.e.* those due to the $\mathrm{S^{+}}$ and $\mathrm{Se^{+}}$ ions), indicating that there are relatively few singly ionised chalcogen ions present in the discharge. It is only with higher levels of applied microwave power that these species would become numerous enough for detection.

*Synthesis of Solid-state Chloride Cluster Compounds.*—There has been a remarkable growth in the area of metal cluster compounds in recent years, particularly those of second- and third-row transition metals where the larger atomic sizes aid the formation of metal–metal bonds. Although much of this work has been in the area of organometallic chemistry, metal cluster systems are also found in oxide, alkoxide and halide systems.[23] The octahedral clusters of Mo, W, Nb and Ta were chosen for this work as they may be synthesised by reduction of high-oxidation-state halides of the metals using a variety of metals as reducing agents over an extended period.[24–33] Although other synthetic routes exist, the syntheses performed here involve high-temperature reactions which create the respective $[\mathrm{M_6Cl_n}]^{m+}$ cations which are linked in the solid state through chloride bridges which makes the compounds insoluble in water and organic solvents. However, they may be converted into the corresponding $[\mathrm{M_6Cl_{12}}]\mathrm{Cl_2}$ (M = Nb or Ta) or $[\mathrm{M_6Cl_8}]\mathrm{Cl_4}$ (M = Mo or W) anionic salts by the addition of aqueous or methanolic halide solutions.

A range of cluster compounds was synthesised using a variety of metal powder reducing agents as shown in Table 2. The non-metal starting materials are all extremely poor conductors at room temperature, and consequently have poor microwave heating characteristics. Therefore, in common with the syntheses of metal chalcogenides, the initial microwave heating is due solely to the heating effect associated with the metal powders. Two basic types of reaction were attempted, direct reduction of the higher chloride by aluminium to form the 'dichloride' (better formulated as $[\mathrm{M_6Cl_m}]\mathrm{Cl_n}$), and reactions involving formation of an intermediate compound containing the metal cluster cation. In both methods it was found simplest to purify the product by dissolving in water and recrystallising the cation as the 'dichloride' hydrate.

Unfortunately, from a synthetic point of view, the reaction products from a simple reduction or conproportionation (*i.e.* the lower-oxidation-state metal halides) appear to have very small dielectric loss tangents. Once a proportion of the metal reagent has reacted the microwave heating mechanism is reduced and the reaction slows down. As a result, the use of stoichiometric quantities of metal powder in such reactions renders high-yield microwave syntheses impossible, a typical

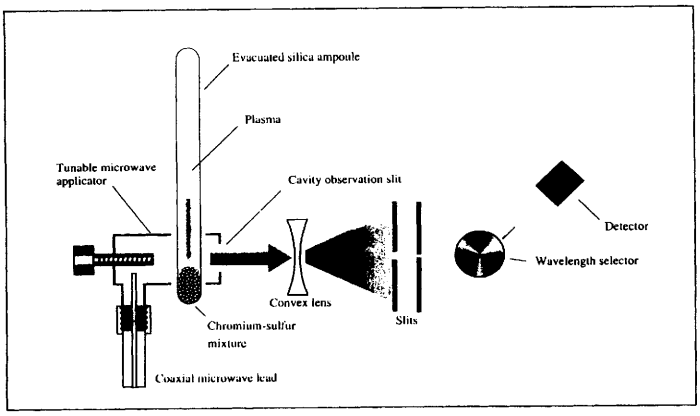

**Fig. 4** Schematic arrangement for obtaining microwave plasma–emission spectra

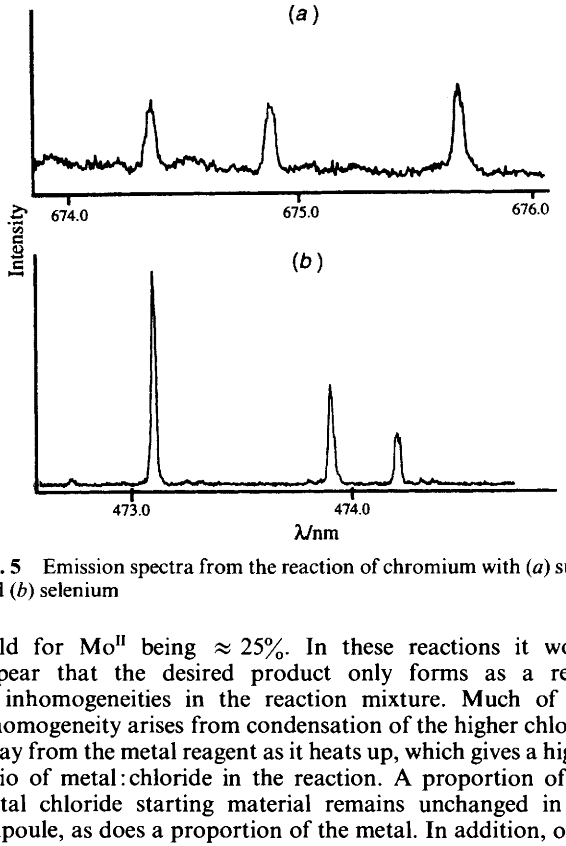

**Fig. 5** Emission spectra from the reaction of chromium with (*a*) sulfur and (*b*) selenium

yield for Mo$^{II}$ being ≈ 25%. In these reactions it would appear that the desired product only forms as a result of inhomogeneities in the reaction mixture. Much of this inhomogeneity arises from condensation of the higher chloride away from the metal reagent as it heats up, which gives a higher ratio of metal:chloride in the reaction. A proportion of the metal chloride starting material remains unchanged in the ampoule, as does a proportion of the metal. In addition, other intermediate chlorides are formed. In the synthesis of $[W_6Cl_8]Cl_4 \cdot 7H_2O$, for example, needles of $WCl_4$ were seen to condense on the ampoule wall. By increasing the quantity of metal used it was possible to obtain an increase in the yield of metal(II) species from these reactions (approximately 35% for molybdenum), although this then gives rise to other problems. It was found that increasing the amount of metal reagent much beyond 150% of the stoichiometric quantity caused the reaction to become very unpredictable. A two-fold excess of aluminium with $WCl_6$ in the synthesis of '$WCl_2$', for example, led to a 'thermal runaway'-induced ampoule failure. In this case the aluminium vaporised the starting material extremely rapidly, leaving a metal–metal chloride mixture which showed increasingly efficient microwave coupling properties. The rapid heating rate, and high temperatures which this produced, resulted in an explosive pressure of the metal halide vapour. By extremely careful application of low power levels, however, this procedure provides a rapid synthesis of the metal cluster species, albeit in relatively low yield.

In contrast to the reactions discussed above, syntheses which produced the metal clusters directly as salts displayed relatively good microwave heating characteristics. A sample of $Na_4[Nb_6Cl_{12}]Cl_6$ (2 g), for example, could be melted in under a minute using 300 W microwave irradiation. It is therefore possible to continue heating the reaction to completion using microwaves. Reactions of this type also have the advantage that they involve relatively high-temperature melts which reduce the vapour pressure in the ampoule, and result in a correspondingly safer procedure. When performing these reactions allowance must be made for the extreme variation in the dielectric losses of the reactants. Initially, it was found that the metal requires a short burst of very high power input (> 600 W) to initiate heating. Once heating commences and the reactants melt a higher density of metal powder results. It was found that this higher density powder generally requires lower power levels (*ca.* 150 W) to heat the metal safely and without arcing. As the reaction progresses, creation of the products decreases the dielectric heating effect, and correspondingly higher power levels were required for a sustainable melt (250 W). After the creation of the melt the syntheses progress smoothly, and although short bursts of arcing are occasionally observed these did not appear to affect the outcome of the reaction.

## Conclusion

The ability of metal powders to couple efficiently with microwave radiation leads to very high heating rates and does not cause major arcing problems. This property can be combined with the remote and selective nature of microwave dielectric heating to induce a range of solid-state reactions. Specifically we have described the applications of this phenomenon to the synthesis of metal chalcogenides and metal cluster compounds. The technique is particularly effective when the reaction is exothermic and one of the products of the reaction also couples effectively with microwave radiation. Indeed the fact that the metal atom is being heated directly and the second component, *e.g.* sulfur and selenium, is transparent to microwaves leads to a situation where the reaction occurs very rapidly at the metal sites and large pressures in the reaction vessel are not induced. In a subsequent paper we shall describe the application of this property to the acceleration of the reactions of metal powders with gases.

## Experimental

The following sections describe details of the syntheses discussed in this paper. Literature values for powder X-ray diffraction patterns were obtained from a published library of powder diffraction data.[34]

*Syntheses.*—CrS. In a typical reaction, chromium powder (−100 mesh, 2.08 g) was mixed with ventilated sulfur powder

**Table 2** Synthesis of solid-state cluster compounds under microwave irradiation

| Product | Reagents | Mass/g | | Reaction time/min | Yield (%) |
|---|---|---|---|---|---|
| | | Chloride | Metal | | |
| $[Mo_6Cl_8]Cl_4\cdot7H_2O$ | $MoCl_6$ + Mo | 7.50 | 8.00 | 1 | 11 |
| | $MoCl_6$ + Al + $AlCl_3$ + NaCl | 4.55 | 0.46 | 20 + 60 | 56 |
| $[W_6Cl_8]Cl_4\cdot7H_2O$ | $WCl_6$ + Al + $AlCl_3$ + NaCl | 3.97 | 0.40 | 60 + 60 | 48 |
| $[Ta_6Cl_{12}]Cl_2\cdot8H_2O$ | $TaCl_5$ + Al | 5.00 | 0.70 | 2 + 2 + 2 | 40 |
| $[Nb_6Cl_{12}]Cl_2\cdot8H_2O$ | $NbCl_5$ + Nb + NaCl | 7.56 | 12.0 | 5 + 5 + 5 | 45 |
| | $NbCl_5$ + Al | 5.00 | 2.50 | 1 | 35 |

(1.28 g). The mixture was placed in a silica ampoule (internal diameter 1.5 cm x 15 cm), and sealed under vacuum with a final pressure of $10^{-2}$ mmHg. The ampoule was placed on a firebrick in a 500 W domestic microwave oven (Swan) at full power setting for 8.5 min. During this time the application of power was intermittently halted and the ampoule allowed to cool to room temperature before being shaken to recombine the condensed sulfur with the partially completed reaction mixture. The product was removed from the ampoule, ground, and resealed in a second ampoule before being annealed in a variable-power oven (Microwave Heating Ltd.) at approximately 200 W applied power. Selected *d* spacings/Å (relative intensity): 3.17 (99), 3.00 (100), 2.62 (25), 2.38 (33), 2.10 (50) and 1.75 (41) [lit., 3.17 (100), 3.02 (55), 2.62 (30), 2.38 (70), 2.10 (60) and 1.74 (60)].

The following compounds were prepared similarly.

$Cr_7S_8$. From chromium (2.08 g) and sulfur (1.50 g). The product was annealed by heating in a variable-power microwave oven at 200 W for 10 h Selected *d* spacings/Å (relative intensity): 2.999 (52), 2.663 (84), 2.078 (100) and 1.730 (47) [lit., 2.995 (30), 2.657 (50), 2.077 (100) and 1.731 (50)].

$Cr_2S_3$. *Method* 1. From chromium (2.08 g) and sulfur (1.94 g). The reaction was carried out for total of 20 min, with frequent breaks to allow recombination of the reactants. Selected *d* spacings/Å (relative intensity): 5.59 (29), 2.99 (19), 2.653 (64), 2.032 (100) and 1.713 (33) [lit., 5.55 (16), 2.96 (16), 2.613 (80), 2.024 (100) and 1.713 (50)].

*Method* 2. As above without annealing, and the product was intimately mixed with a slight excess of sulfur (0.6 g) before being sealed in an ampoule under vacuum. The reactants were heated for total of 20 min, with frequent breaks to allow recombination of the reactants. The product was removed from the ampoule and washed with $CS_2$ to remove any unreacted sulfur before annealing in a variable-power microwave oven at 200 W for 3 h. Selected *d* spacings/Å (relative intensity): 5.58 (24), 2.97 (36), 2.623 (58), 2.034 (100), 1.714 (37) and 1.570 (21) [lit., 5.55 (16), 2.96 (16), 2.613 (80), 2.024 (100), 1.713 (50) and 1.569 (25)].

$Cr_2Se_3$. From chromium (2.08 g) and selenium (4.78 g). The reaction was carried out for a total of 5 min, with occasional breaks to allow recombination of the reactants. The product was annealed for 3 h. Selected *d* spacings/Å (relative intensity): 2.89 (6), 2.75 (100), 2.12 (46), 1.80 (34), 1.53 (7), 1.50 (11) and 1.38 (7) [lit., 2.89 (10), 2.75 (100), 2.13 (40), 1.81 (50), 1.64 (20), 1.53 (10), 1.51 (30) and 1.38 (30)].

CrSe. From chromium (2.60 g) and selenium (3.95 g). The reaction was carried out for total of 5 min, with one break to allow recombination of the reactants. The product was annealed for 8 h. Selected *d* spacings/Å (relative intensity): 2.81 (100), 2.18 (50), 1.83 (45), 1.540 (10) and 1.412 (10) [lit., 2.81 (100), 2.17 (100), 1.83 (100), 1.536 (50) and 1.399 (50)].

$Cr_3Se_4$. From chromium (2.60 g) and selenium (5.27 g). The reaction was carried out for total of 5 min, with one break to allow recombination of the reactants. The product was annealed for 8 h. Selected *d* spacings/Å (relative intensity): 2.98 (9), 2.79 (100), 2.17 (28), 1.82 (42), 1.67 (13), 1.43 (6) and 1.39 (7) [lit., 2.92 (10), 2.77 (90), 2.16 (20), 1.81 (100), 1.67 (40), 1.45(60) and 1.39(20)].

$Cr_2Te_3$. From chromium (1.73 g) and tellurium (6.35 g). The reaction was carried out for total of 1 min. Despite a very small amount of tellurium vaporisation, no recombination of the reactants was judged necessary. The product was annealed for 14 h. Selected *d* spacings/Å (relative intensity): 3.02 (16), 2.96 (100), 2.26 (30), 1.74 (14), 1.65 (9) and 1.64 (12) [lit., 3.02 (10), 2.97 (100), 2.26 (30), 1.73 (20), 1.65 (10) and 1.64 (10)].

α-MnS. From manganese powder (2.74 g, −100 mesh) and sulfur (1.60 g). The reaction was carried out for total of 1 min. The product was improved by a short annealing period in a variable power oven at 200 W. Selected *d* spacings/Å (relative intensity): 2.98 (80), 2.64 (80), 1.866 (10) and 1.492 (30) [lit., 3.02 (14), 2.61 (100), 1.847 (50) and 1.509 (20)].

$Fe_{1-x}S$. From iron powder (2.79 g, −100 mesh) and sulfur (1.60 g). The reaction was carried out for 1 min then halted. The ampoule was cooled, broken open, and the contents ground together before being sealed in a second ampoule and reheated. The product was improved by annealing for 1 h. Selected *d* spacings/Å (relative intensity): 5.91 (23), 2.975 (63), 2.638 (70) 2.064 (100) and 1.720 (59) [lit., 5.72 (40), 2.978 (90), 2.647 (80), 2.067 (100) and 1.721 (80)].

$TaS_2$. From submicron tantalum powder (4.52 g) and sulfur (1.60 g). The reaction was carried out for total of 20 min. The product was annealed for two periods of 12 h, being reground to improve homogeneity between each. Selected *d* spacings/Å (relative intensity): 6.02 (100), 3.01 (11), 2.863 (22), 2.796 (3) and 2.33 (6) [lit., for 2 H polytype, 6.05 (100), 3.02 (6), 2.871 (32), 2.793 (7) and 2.339 (4)].

$SnS_2$. From granular tin (2.37 g, 20 mesh) and sulfur (1.60 g). The reaction was carried out for total of 3 min. The product was improved by a short annealing period. Selected *d* spacings/Å (relative intensity): 5.92 (100), 3.22 (8), 2.953 (5), 2.800 (91), 2.158 (2), 1.967 (6) and 1.825 (2) [lit., 5.90 (6), 3.16 (25), 2.94 (10), 2.78 (45), 2.15 (4), 1.96 (62) and 1.82 (100)].

$FeCuS_2$. Iron powder (1.40 g, −100 mesh), copper powder (1.575 g, −100 mesh) and sulfur (1.60 g) were ground together before being sealed under nitrogen at $10^{-2}$ mmHg. The reaction was carried out for 3 x 5 min periods, as for the synthesis of CrS. No attempt was made to anneal the product. Selected *d* spacings/Å (relative intensity): 3.04 (100), 2.64 (78), 1.87 (23) and 1.59 (10) [lit., 3.03 (100), 2.64 (30), 1.87 (40) and 1.59 (60)].

$[Mo_6Cl_8]Cl_4\cdot7H_2O$. *Method* 1. Molybdenum pentachloride (7.5 g) and submicron molybdenum metal powder (8.0 g) were sealed in an evacuated silica ampoule under $10^{-2}$ mmHg pressure of nitrogen. The reaction was heated at 600 W applied power initially, which was rapidly lowered to approximately 200 W on the first signs of heating. Heating was halted after 1 min to avoid ampoule failure. The product was dissolved in hot concentrated HCl and filtered through Celite. It crystallised on cooling the solution, and was filtered off, washed with cold concentrated HCl and diethyl ether, and dried overnight. Analysis was carried out on the anhydrous chloride, prepared by heating the product under vacuum. Yield: 0.57 g (11%). UV/VIS 314 and 356 nm (lit.,[35] 317 and 359 nm) (Found: Cl, 41.15. Calc. for $MoCl_2$: Cl, 42.5%).

*Method* 2. The pentachloride (4.55 g), aluminium powder (0.46 g, 100 mesh), $AlCl_3$ (4.45 g) and NaCl (2.75 g) were ground together and sealed in an evacuated silica ampoule.

Microwave power (200 W) was applied for 20 min, and the sample allowed to cool to room temperature for inspection. Power was then applied for 60 min. The product was worked up in a similar manner to that in Method 1. Analysis was carried out on the anhydrous chloride, prepared by heating the product under vacuum. Yield: 1.57 g (56%). UV/VIS 318 and 360 nm (Found: Cl, 42.40%).

$[W_6Cl_8]Cl_4 \cdot 7H_2O$. Tungsten hexachloride (3.97 g), aluminium powder (0.40 g, 100 mesh), $AlCl_3$ (2.67 g) and NaCl (1.8 g) were ground together, sealed in an evacuated silica ampoule and treated as for the previous synthesis. Power was applied for two 60 min periods. Yield: 1.36 g (48%). Mass spectrum: *m/z* 1602.2 $[W_6Cl_{14}]^-$ and 1566.7 $[W_6Cl_{13}]^-$. UV/VIS 281, 316 and 355 nm (lit.,[36] 280, 318 and 357 nm) (Found: H, 1.5; Cl, 25.1. Calc. for $H_{18}Cl_{12}O_8W_6$: H, 1.1; Cl, 25.4%).

$[Ta_6Cl_{12}]Cl_2 \cdot 8H_2O$. Tantalum pentachloride (5.0 g) and aluminium powder (0.7 g, 100 mesh) were sealed in an evacuated silica ampoule, and heated for three 2 min periods at 200 W applied power, as for the synthesis of $[Mo_6Cl_8]Cl_4 \cdot 7H_2O$. The product was extracted in copious amounts of hot deionised water, precipitated with concentrated HCl and filtered off before being washed with cold concentrated HCl, ether and drying. Yield: 1.51 g (40%). UV/VIS (in water) 748, 638, 398 and 330 nm (lit.,[37] 755, 637, 398 and 329 nm) (Found: H, 1.2; Cl, 28.2. Calc. for $H_{16}Cl_{14}O_8Ta_6$: H, 0.9; Cl, 28.8%).

$[Nb_6Cl_{12}]Cl_2 \cdot 8H_2O$. This reaction was performed as for $[Ta_6Cl_{12}]Cl_2 \cdot 8H_2O$. Niobium pentachloride (5.0 g) was ground with aluminium powder (2.50 g, 100 mesh), sealed in an evacuated silica ampoule, and heated for 1 min at 200 W applied power. The solid obtained was worked up as for $[Ta_6Cl_{12}]Cl_2 \cdot 8H_2O$. Yield: 1.32 g (35%). UV/VIS (in water) 396 and 273 nm (lit., 397 and 274 nm) (Found: H, 1.3; Cl, 41.5. Calc. for $H_{16}Cl_{14}Nb_6O_8$: H, 1.2; Cl, 42.1%).

Alternatively, $NbCl_5$ (7.56 g), niobium powder (12.0 g, 100 mesh) and NaCl (2.34 g) were ground together and sealed in an evacuated silica ampoule. Microwave power was applied for three 5 min periods, first at 150 W and then at 300 W. The solid product, analysed as $Na_4[Nb_6Cl_{12}]Cl_6$ by powder X-ray diffraction, was treated as for the previous synthesis to yield the final product. Yield: 5.32 g (45%). UV/VIS 748, 638, 398 and 330 nm (lit.,[38] 755, 637, 398 and 329 nm) (Found: H, 1.1; Cl, 41.9%).

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