Microwave-assisted Solid-state Reactions involving Metal Powders

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The high dielectric loss tangents of metal powders at 2450 MHz have been utilised to accelerate the syntheses of a wide range of metal chalcogenides in the solid state.

In recent years the acceleration of a wide range of chemical reactions using microwave dielectric heating techniques has been reported.[1–4] The great majority of these reactions have been in the solution phase where the high dielectric loss tangents of the polar solvents have been used to couple with the microwave energy. There have also been examples of solid-state reactions where the loss tangents of certain metal oxides have proved to be sufficiently large to couple with the microwaves and thereby provide sufficient thermal energy to raise the temperature of the reaction mixture to *ca.* 1000 °C and permit the reaction to proceed.[5–7] There have been very few reports, however, of microwave-assisted solid-state reactions involving metal powders. This may reflect a widespread belief that metals within a microwave cavity cause plasma discharges and are therefore an unsuitable component for microwave-assisted syntheses. Solid metal samples and continuous metal films lead to large electric field gradients within a microwave cavity and cause dramatic electric discharges. In contrast metal powders can couple effectively with microwave fields at 2450 MHz[8] and heat up to temperatures in excess of 1000 °C in very short periods of time without causing visible electric discharges.[9] In this communication we describe how the high dielectric loss tangents of metal powders can be used to accelerate the syntheses of a wide range of metal chalcogenides. The high loss tangents result primarily from conduction mechanisms although there may be additional contributions from localised plasma effects.[9]

In a typical reaction the chalcogenides S, Se or Te (1–5 g) were mixed with metal powders Cr, Mn, Sn, Fe and Ta (1–5 g) (<100 mesh) and sealed in 10 cm silica tubes under vacuum. When the silica tube was placed on a firebrick in a multimode microwave cavity operating at 2450 MHz (continuous power) and 650 W (Matsui 170TC) the temperature rose rapidly to between 800 and 1000 °C, and the reaction leading to the metal chalcogenide was complete in less than 10 min. The chalcogenide compounds (Table 1) were synthesised as pure phases in this manner using the appropriate metal:chalcogenide ratio. Although more than 40 reactions have been completed there were no examples of tube failure despite the high temperatures. Analytical electron microscopy studies have demonstrated that the incorporation of silicon in the samples was only a problem when very low sulfur to chromium ratios ($<2:5$) were used.

The volumetric nature of the microwave dielectric heating sets a lower limit on the amount of metal powder required to provide the 'thermal runaway' necessary to drive the reaction. For the reactions involving sulfur this lower limit is *ca.* 1.00 g, because of the low loss tangent of sulfur. For Se and Te which have higher loss tangents smaller quantities of metal may be used.

The total reaction time is not determined primarily by the rate of heating of the metal powder, which may be as high as 100 °C s^{-1}, but the volatility of the chalcogenide which leads to its sublimation to cooler parts of the tube away from the metal particles. Those reactions involving sulfur which is the most volatile chalcogenide take the longest time because the sample has to be cooled after an initial exposure to the microwaves at full power for 30 s and then the tube is shaken to redistribute the metal and sulfur. This process is repeated several times leading to a total reaction time of *ca.* 30 min. This is still much shorter than conventional procedures which require several days heating. The fact that the metal powders heat up so rapidly in the microwave cavity enables the reaction to occur at metal particle sites prior to the occurrence of significant amounts of sublimation away from the metal powder. Interestingly, the presence of unreacted sulfur is indicated by a blue plasma in the silica tube and therefore the loss of this plasma provides an excellent guide to when the reaction is complete. In conventional heating, low heating rates are necessary to prevent tube explosions resulting from the pressure build-up associated with the unreacted chalcogenides. For the reactions involving selenium and tellurium the reactions are more efficient and the total reaction times are less than 5 min.

The 'thermal runaway' associated with the microwave dielectric heating leads to a reaction sequence which effectively leads to very rapid melting for a short period of time followed by a rapid quenching of the reaction after the removal of the microwave power. These conditions which are difficult to emulate using conventional resistive heating techniques result in samples which are generally sufficiently crystalline to obtain X-ray diffraction patterns of a sufficiently high quality to characterise the phases unambiguously. The crystallinity was improved considerably by annealing the sample using a variable microwave power multimode oven (Microwave Heating Ltd.) which monitors the reaction temperature using an infrared pyrometer. This procedure is particularly effective for the majority of the metal chalcogenides in Table 1 which have appreciable loss tangents in their own right.[16]

The X-ray diffraction patterns established that the metal chalcogenides in Table 1 crystallise in the same space groups as those found in conventional thermal syntheses. Electron microscopy studies also revealed that the samples are homogeneous. Physical measurements are in hand to establish whether the

Table 1 Summary of metal chalcogenides synthesised by microwave techniques

Compound	Mass of metal/g	Mass of chalcogen/g	Reaction time/min	Annealing time/h	Unit cell	Ref.
CrS	2.08	1.28	8.5	17	Monoclinic	10
Cr_7S_8	2.08	1.50	8.5	10	Hexagonal	10
Cr_2S_3	2.08	1.94	8.5 + 20	1	Hexagonal	10
CrSe	2.60	3.95	5	5.5	Hexagonal	11
Cr_3Se_4	2.60	5.27	5 + 5	8	Monoclinic	11
Cr_2Se_3	2.08	4.78	5	3	Monoclinic	11
Cr_2Te_3	1.734	6.35	<1	14	Hexagonal	12
α-MnS	2.74	1.60	1	10 min	Cubic	13
Fe_7S_8	2.79	1.60	1 + 10	1	Hexagonal	13
TaS_2	4.52	1.60	20	12 + 12	Hexagonal	14
SnS_2	2.37	1.60	3	10 min	Hexagonal	15

samples made by this route have physical properties identical to those made conventionally, or whether differences in grain boundary structures, *etc.* have resulted in significant differences.

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