Plasma-promoted dielectric heating in the microwave synthesis of spinels

David J. Brooks,[a] Richard E. Douthwaite*[a] and Lisa J. Gillie[b]

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Comparison between the rates of synthesis of the spinel phases (MAl_2O_4, M = Mg, Zn, Ni; and MFe_2O_4, M = Mg, Zn, Mn) using an O_2 microwave-induced plasma (MIP) and conventional (tube furnace) methods indicate that a MIP promotes microwave dielectric heating at elevated temperatures.

The use of microwave techniques for the synthesis of solid state compounds from bulk solid precursors has been shown to be very effective for a diverse range of compounds including ceramic oxides,[1–3] semiconductors,[4] and intermetallics.[5] However, solid state microwave synthesis is largely underdeveloped primarily because many materials do not couple effectively at room temperature with the most commonly available frequency of 2.45 GHz.[6,7] If coupling between the electric field of the microwaves and the material is weak, heating will be minimal and consequently a reaction will be prohibitively slow. Unfortunately many technologically useful metal oxides fall into this class of material, being essentially transparent to microwave radiation at room temperature. Furthermore, many materials, which have been reported as exhibiting dielectric heating do not do so reproducibly, because of sensitivity to sample and particle size, non-stoichiometry, and water content; only after an ill-defined induction period, if at all, does significant heating occur.

To circumvent these problems an alternative procedure that has been developed over recent years is the use of a secondary susceptor that reproducibly exhibits significant dielectric heating and mediates energy transfer between microwaves and the reactants.[8–10] For example, and relevant to the work described here, the spinel phases $NiAl_2O_4$[11] and $MgAl_2O_4$[12] have been prepared from precursor oxides using the susceptors SiC and amorphous carbon, respectively. This method is very effective for many solid state reactions, however, if the susceptor is mixed intimately with the precursors, separation becomes an issue and in some cases the susceptor may be liable to participate in unwanted side reactions, *e.g.* reduction using amorphous carbon.

In an effort to generalise the application of microwave techniques to bulk solid state synthesis we have recently been interested in developing the use of microwave-induced plasmas (MIPs).[13] MIPs can be initiated and sustained easily in a range of gases at pressures <50 mbar and may serve as a source of heat, or reactants, for any solid state reaction. Uses in solid state science include etching, thin film formation, powder processing, and bulk modification using reactive gas plasmas.[2,14–21]

Here we describe, using an O_2 MIP, the synthesis of several spinel phases from mixtures of oxide precursors that do not exhibit significant microwave heating at 25 °C. Importantly, comparison of the rates of MIP synthesis with conventional synthesis, and their relative phase purity, indicate that a MIP promotes additional dielectric heating at elevated temperatures.

All reactions were performed in a microwave reactor which has been described in detail elsewhere.[13] A feature of the apparatus is that the sample is contained in a silica 'U'-tube (Fig. 1) that can be inserted into a microwave cavity and which is also of appropriate dimensions to fit into the working tube (55 mm diameter) of a furnace. This allows comparison between microwave and conductive heating experiments under identical gas flow conditions and minimises as far as possible differences in thermal properties of an apparatus.

In a typical experiment, approximately 3 g of precursors are ground and formed into two identical 13 mm pellets under 5 tonnes pressure. One pellet is exposed to an O_2 MIP (900 W, 2.45 GHz) and the other heated for the same period of time using a conventional tube furnace. In a previous study using melting point standards we found the equilibrium temperature of an O_2 MIP to be between 1069 (K_2SO_4) and 1127 °C ($MgSO_4$)[13] and in this study furnace reactions were conducted at 1150 °C. To obtain similar heating profiles between MIP and furnace heated samples, the furnace is preheated to reaction temperature and the 'U'-tube inserted, and subsequently removed at the reaction temperature, and allowed to cool in air. MIP and furnace synthesised materials were then compared using powder X-ray diffraction (XRD (Stoe STADI P)) and scanning electron microscopy (SEM (Sirion 200)).

It was our initial intention to explore the use of MIPs as a heat source to drive solid state reactions and compare the synthesis with

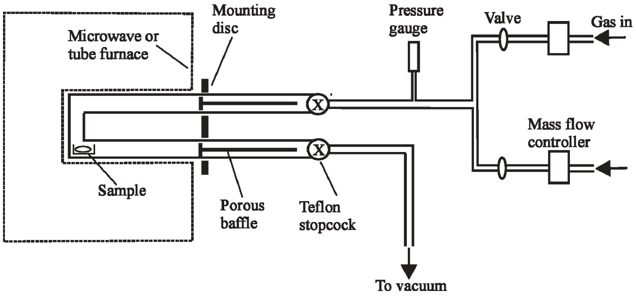

Fig. 1 Apparatus used to control gas flow and pressure. The porous steel baffle and mounting disc are used to confine a plasma and prevent leakage of microwave radiation.

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[a] *Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: red4@york.ac.uk; Fax: +44(0)1904 432516; Tel: +44(0)1904 434186*
[b] *Department of Engineering materials, University of Sheffield, Mappin Street, Sheffield, UK S1 3JD*

conventional methods. We assumed that reported synthesis times using conventional methods are unoptimised and therefore it was necessary to perform control experiments using the apparatus in Fig. 1 so that relative rates could be more accurately compared. It should also be noted that any thermal lag that may occur in the heating stage of the conventional and MIP synthesis has been neglected. This is based on comparison between the experiment heating times ($\geqslant$120 min except for entry 2 of Table 1) and the time required to melt K_2SO_4 under the experimental conditions (<5 min in both cases). In addition, pelletised precursors were also exposed to microwave radiation without inducing a plasma, using a higher O_2 pressure (500 mbar), and in all cases significant heating, and therefore reaction, did not occur.

Table 1 shows the spinel phases investigated and the main results comparing MIP and furnace synthesised materials. It can be seen that for many of the reactions MIP syntheses exhibit a greater rate of reaction and the lattice parameters of both MIP and furnace synthesised materials are very similar to the average values available from the JCPDS-International Centre for Diffraction Data.

The first class of compounds investigated were three spinels MAl_2O_4 (where M = Mg, Zn, Ni) (Table 1, entries 1–3) prepared from stoichiometric quantities of Al_2O_3 and MO. Comparison of XRD patterns of the MIP and furnace prepared samples after 90 min showed significant differences in the relative proportions of product and precursor phases. For example, $MgAl_2O_4$ that is typically prepared from reaction between MgO and Al_2O_3 at >1500 °C, is as expected very sluggish at 1150 °C, as shown in Fig. 2a. Continued heating for an additional 65 h still showed a significant quantity of precursors remained. In contrast the equivalent reaction conducted using an MIP shows a far higher proportion of product after 90 min (Fig. 2b) that on further exposure for a further 300 min contains $MgAl_2O_4$ with a high level of phase purity. However, continued MIP treatment did not improve phase purity. For MAl_2O_4 (M = Zn and Ni) very similar results were obtained where the rate of MIP synthesis is significantly greater and a small quantity of precursors remained in each case.

Although enhanced diffusion rates have been proposed in microwave fields,[22] temperature measurement is notoriously difficult[23] and the clear implication from our experiments is that the actual reaction temperature using MIP synthesis is much greater that that of the conventional synthesis. The furnace temperature (1150 °C) was chosen to be at the upper limit of the range (1069–1127 °C) determined for the MIP and therefore an additional heating contribution must be present.

Dielectric properties are temperature dependent and many materials that do not exhibit dielectric loss heating at room temperature will do so at higher temperature.[24] Indeed microwave dielectric heating at high temperatures has been used frequently in the densification of ceramics.[12] We therefore attribute the relative increase in rate of MIP *vs.* conventional synthesis to a higher temperature for the MIP reaction resulting from additional microwave dielectric heating.

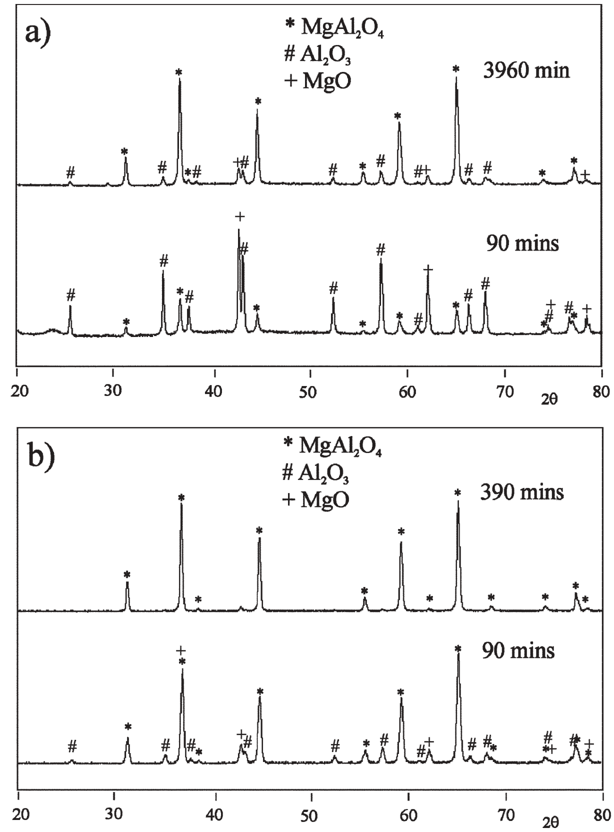

Fig. 2 PXRD patterns from reaction between MgO and Al_2O_3 using (a) tube furnace at 1130 °C and (b) O_2 MIP.

The source of the additional heating in entries 1–3 could arise from microwave dielectric loss heating of precursor(s), product, or intermediates. Given the reactions are not driven to phase purity it is unlikely that the product exhibits significant dielectric loss. Unfortunately there are very few studies detailing the temperature dependence of dielectric loss factors of solids. However, Al_2O_3 is known to exhibit significant microwave heating at temperatures >1000 °C[24] and with respect to entry 3, NiO has also been reported to exhibit significant microwave heating above 400 °C.[11] Al_2O_3 is common to all the reactions and therefore we suggest that the increase in rate is a consequence of dielectric heating of Al_2O_3 (and NiO for entry 3) promoted by the MIP. Furthermore as the reaction proceeds and the concentration of the precursors

Table 1 Comparison of MIP and furnace synthesised phases

Entry	Spinel	Precursors	MIP/min	Furnace/min	a_{MIP}/Å	a_{Furnace}/Å	$a_{\text{ave JCPDS}}$ /Å
1	$MgAl_2O_4$	MgO + Al_2O_3	390	>3960	8.0858(1)	8.0803(3)	8.084
2	$ZnAl_2O_4$	ZnO + Al_2O_3	150	840	8.0881(1)	8.0865(1)	8.086
3	$NiAl_2O_4$	NiO + Al_2O_3	540	1440	8.0410(1)	8.0473(1)	8.050
4	$MgFe_2O_4$	MgO + Fe_2O_3	10	120	8.3635(4)	8.3666(3)	8.368
5	$ZnFe_2O_4$	ZnO + Fe_2O_3	2	2	8.4388(3)	8.4246(4)	8.426
6	$MnFe_2O_4$	MnO + Fe_2O_3	10	120	8.4925(4)	8.4973(9)	8.510

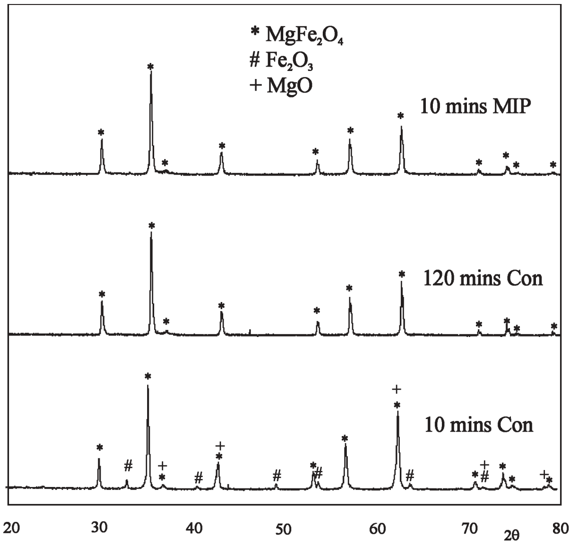

Fig. 3 XRD patterns from reactions between MgO and Fe_2O_3 using an MIP and conventional (Con) methods.

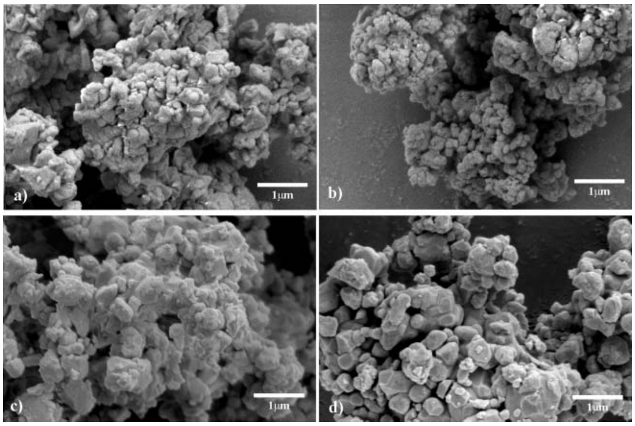

Fig. 4 SEM of (a) $MgAl_2O_4$ (MIP), (b) $MgAl_2O_4$ (Con), (c) $MgFe_2O_4$ (MIP), and (d) $MgFe_2O_4$ (Con).

decreases, a reduction in dielectric heating and hence reaction rate will result, ultimately leading to the observed incomplete reaction.

Intrigued by these observations we investigated the synthesis of MFe_2O_4 (M = Mg, Zn, Mn) derived from Fe_2O_3 (Table 1, entries 4–6). In common with Al_2O_3, the compound Fe_2O_3 does not exhibit significant dielectric heating at 2.45 GHz.[24] However, we found that the rate of formation of the spinel phases derived from Fe_2O_3 was much more rapid than those derived from Al_2O_3 and in all cases single phase materials were obtained. Example XRD data are given in Fig. 3 for $MgFe_2O_4$ comparing MIP and conventional methods. It can be seen that after 10 min a single phase is obtained as judged by XRD in comparison to 120 min using conventional methods. A similar rate enhancement is observed for $MnFe_2O_4$ whereas $ZnFe_2O_4$ is formed in 2 min or less using either an MIP or conventional methods.

SEM of MIP and conventionally prepared materials for $MgAl_2O_4$ and $MgFe_2O_4$, which are representative of all the product phases, are shown in Fig. 4. The differences between the MIP and conventional materials are not considered striking but it does appear, particularly for the Fe_2O_3 derived compounds, that there is a greater degree of agglomeration, again indicative of a higher temperature synthesis.

We have shown that a MIP is very effective for driving reactions between solid oxide precursors that do not exhibit microwave dielectric heating at room temperature, thus widening the potential application of microwave techniques to solid state synthesis. Of perhaps greater interest, comparison of the rate of MIP and conventionally synthesised materials indicates that the MIP promotes an additional local heating mechanism that we attribute to dielectric heating. Further work is in progress to determine if MIP promoted dielectric heating can be used to selectively access new solid state compounds.

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