

Microwave-induced plasma-promoted materials synthesis

Richard E. Douthwaite

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The discovery of new materials requires the development of a diversity of synthetic techniques. Microwave methods offer the opportunity to synthesise and modify the composition, structure and morphology of materials, particularly composites *via* differential heating. Microwave-induced plasmas (MIPs) allow any solid mixture to be heated, and can promote direct microwave heating at elevated temperature, greatly expanding the use of microwaves for reactions between solids and gas–solid mixtures.

Synthetic methods for the preparation of materials are extremely varied reflecting the importance not only of composition and structure, but also morphology, defects, and particle size distribution. For the vast majority of reactions to proceed at an appreciable rate, energy input is required and the development of different synthetic techniques is one approach to preparing a diversity of materials. Most often energy is applied as heat, and commonly utilised procedures include resistive ‘furnace’ heating, hydrothermal synthesis, and gas phase deposition.

Synthetic molecular chemistry has also benefited from advances in methodology and perhaps the most widespread innovation of recent years has been the application of microwave technology. Rapid preparation of libraries of molecules using commercial apparatus, usually operating at 2.45 GHz, is now routine. In

comparison, synthetic solid state microwave chemistry is relatively underdeveloped. Although commercial apparatus are in operation for processing (curing, drying, ceramic sintering) and microwave plasma surface etching and cleaning, synthetic work has been limited to select examples of mainly ceramic oxides, semiconductors, and intermetallics.¹

Microwave heating occurs principally *via* coupling between the electric component of microwave electromagnetic radiation and the reactants or reaction medium. In solution chemistry, polar solvents and many organic precursors couple sufficiently with microwaves at 2.45 GHz to give rapid volumetric heating. However, interactions in the solid state are more complex being dependent on a number of factors including the presence of dipoles, ion and electron mobility, and particle size. Heating of solids primarily occurs *via* dipolar or conduction losses but it should be noted that terminology can be ambiguous when identifying the physical phenomena responsible for microwave heating. Measurements can elucidate the contribution of dipolar, conduction, or other loss mechanisms to overall heating but these require specialist equipment and are rarely performed. In this article, only the overall loss will be considered and the terms *microwave heating* or *dielectric loss heating* will refer to the total heating from direct interaction between microwaves and a material irrespective of their physical origin.

A significant limitation of solid state microwave synthesis is that many technologically important classes of solids do not couple significantly with microwaves and are essentially microwave transparent. Due to legal and magnetron production constraints the vast majority of reactions are conducted at 2.45 GHz and therefore the opportunity to heat using alternative frequencies is rarely available. Nevertheless, heat can be transferred to microwave transparent reaction precursors using a ‘susceptor’ that exhibits dielectric loss heating at room temperature thus mediating energy transfer between the microwaves and the solid precursors.² However, obvious disadvantages of using a susceptor are that it may require removal, or participate in unwanted side reactions.

An alternative method of generating heat using microwaves is *via* a plasma. A microwave-induced plasma (MIP) is essentially a partially ionised gas at non-equilibrium where the electron temperature is significantly higher than that of the ions.³ It is important to distinguish between ion and electron temperatures and the heat available for chemistry. In this article, temperature refers to that

Department of Chemistry, University of York, York, Heslington, York, UK YO10 5DD. E-mail: red4@york.ac.uk

Richard Douthwaite obtained a PhD under the supervision of Prof. Malcolm Green FRS, at the University of Oxford and post-doctoral work was performed at Cornell University with Prof. Peter. T. Wolczanski. In 2002, Richard acquired a lectureship at the University of York. Research interests are primarily synthetic, encompassing molecular compounds and complexes for application to homogeneous catalysis, and the development of microwave-induced plasmas for materials synthesis.



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achieved by the solid reactant(s) in the absence of other heating mechanisms (*vide infra*) and is considered an indirect measure of the equilibrium plasma temperature. By plasma standards MIP are generally considered 'cold' but can contain enough heat to cause exposed objects to reach temperatures in excess of 1000 °C *via* ion bombardment. MIPs have been studied for decades and are used extensively in industry for welding, etching and thin film formation *via* deposition techniques, particularly for diamond.⁴

At the user level the apparatus required to generate and apply MIPs is not complex essentially comprising a microwave cavity and a gas manifold. Microwave applicators can be constructed from commercial apparatus or a modified domestic microwave oven (DMO). The most significant difference is the power and control of field intensity in the vicinity of the sample. Commercial apparatus allow single mode operation where a standing wave can be tuned to have maximum intensity at the sample and applicator powers on the order >2 kW are routinely available. In comparison DMOs operate in multimode exhibiting variable positional and temporal field intensity and powers of 1 kW maximum are typical.

The most common experimental configuration for application of MIP to materials modification is to place a material downstream of the microwave source. Here the material is exposed to an MIP that contains little heat (though the material may be heated by conventional means) and is not exposed to a significant intensity of microwaves. A variant is to pass gases, aerosols, or powders through an MIP zone, and to subsequently accumulate MIP exposed product downstream, as for example in microwave plasma chemical vapour deposition. Alternatively, a solid or mixture of solids can be immersed in an MIP that contains significant heat and simultaneously be exposed to a significant microwave field. In our research, we have used the latter configuration and a schematic of the apparatus constructed from a DMO is shown in Fig. 1.⁵ MIP can be derived easily from a range of gases and we have routinely used Ar, N₂, H₂, NH₃, O₂, Cl₂ and H₂S allowing access to a range of inert and reactive plasma gas mixtures (Fig. 2).

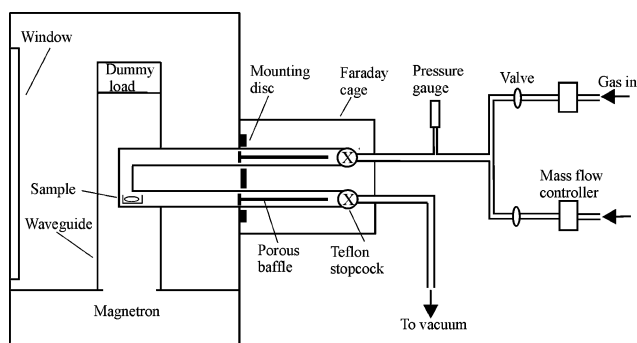


Fig. 1 Microwave-induced plasma reactor. From ref. 5.

Examples of using MIP for materials modification include powders of superconducting compositions La_{2-x}Sr_xCuO_{4-y} and YBa₂Cu₃O_{7-x} that have been exposed to O and F containing plasmas, respectively, downstream of the microwave source with the aim of tuning properties by anion doping.⁶ Hot MIPs of N₂ and N₂/H₂ have also been used to prepare nitrides from metal and metal oxide powders and surface plasma modification of metallic tool parts has been shown to give materials with superior mechanical properties.⁷

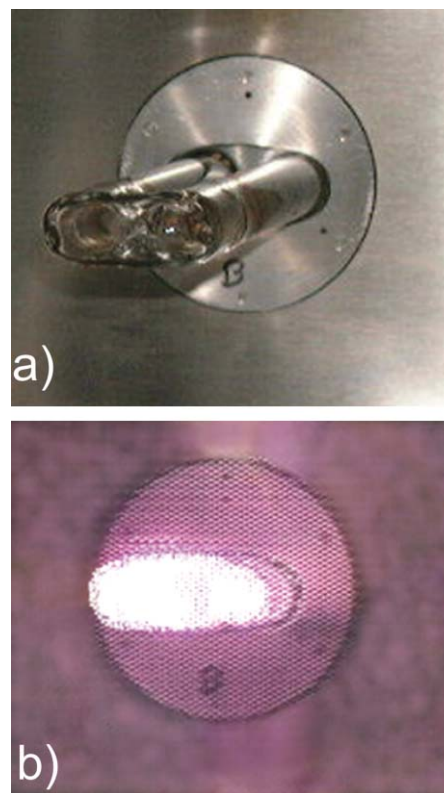


Fig. 2 Internal view of microwave cavity: (a) before reaction; and (b) during reaction using an NH₃ MIP.

More generally, any material immersed in a plasma will heat driving ion diffusion and therefore circumvent the sample limitations of direct microwave heating. Control experiments have shown that many technologically useful precursors including metal oxides and carbonates do not exhibit direct microwave heating and therefore the reaction does not proceed. However, examples have now been described where MIP can be used to drive reactions rapidly using oxide or carbonate precursors for perovskite and spinel phases.⁸ The rapid preparation of oxide materials can be beneficial with respect to processing and potential reduction in energy requirements, however, from a chemist's perspective the synthesis of new morphologies, structures or composites is perhaps inherently of more interest.

Plasma prepared compounds generally give products of different morphology and microstructure to those prepared using more traditional thermal techniques. Perhaps this is not surprising given that plasma heating is very rapid and surface interactions between a fluid far from equilibrium are likely to differ significantly from resistive heating methods using gases at thermal equilibrium. For example tungsten and zirconium sulfide nanostructures have been prepared from reaction between bulk WO₃ and H₂S/Ar MIP, and from dehydrosulfurisation of ZrS₃ using NH₃ MIP, respectively.⁹ Inorganic fullerene spheres of WS₂ and nanotubes of ZrS₂ are produced and electron microscopy shows that a greater proportion of defects are present in comparison to structures prepared using resistive heating methods (Fig. 3). Inorganic nanostructures of this type have been proposed as candidates for gas storage materials. Sorption characteristics are clearly dependent on the

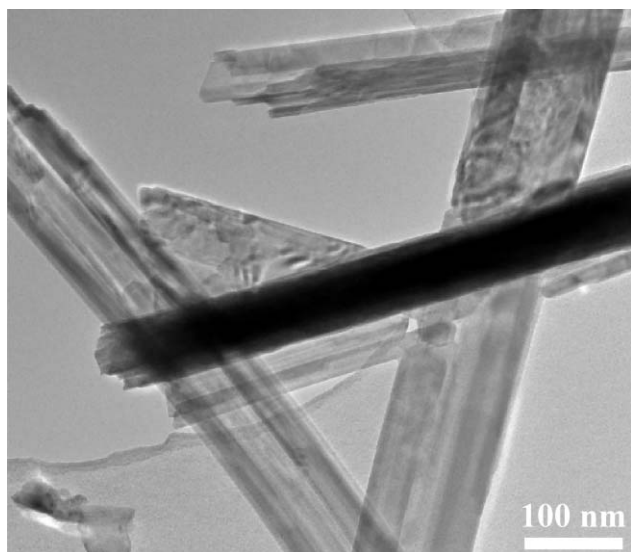


Fig. 3 TEM image of MIP prepared ZrS_2 nanotubes.

microstructure of the host material and MIP treatment offers the opportunity to potentially modify storage properties.

Perhaps of more interest are observations with respect to direct microwave heating in the presence of MIP. An example of dual plasma and microwave heating is provided in a series of reactions investigating the synthesis of various spinel phases.⁸ Calibration of MIPs using melting point standards that are known not to exhibit significant temperature dependent microwave heating showed that in our apparatus MIP contain sufficient heat to melt standards to a maximum of 1100 °C.⁵ Control experiments comparing the rate of reaction for MIP and resistively heated samples showed that in some cases (e.g. MAl_2O_4 (where M = Mg, Zn and Ni)) MIP products had experienced temperatures well in excess of 1100 °C. Although many solids do not directly heat in a microwave at room temperature, dielectric heating is temperature dependent and therefore at elevated temperatures direct heating can be promoted to give local sample temperatures in excess of the heat content of the MIP. In the spinel examples the precursor Al_2O_3 is one of the few compounds where the temperature dependence of the dielectric permittivity has been determined and is known to exhibit a phenomenon called thermal runaway where microwave heating increases with increasing temperature. For Al_2O_3 sample temperatures in excess of 1600 °C are common and such high temperature microwave heating has been used for microwave sintering of some ceramics.^{4a,f}

A more direct demonstration of MIP promoted dielectric heating is given by the synthesis of BaTiO_3 that exhibits a number of polymorphs. Reaction between BaCO_3 and TiO_2 using an O_2 MIP for 10 min gives single phase tetragonal BaTiO_3 as would be expected for conventional reaction occurring at approximately 1100 °C. However, analysis of reaction products on MIP exposure for 5 min shows an approximate 1 : 1 mixture of tetragonal and hexagonal phases of BaTiO_3 .^{8b} Several studies have analysed the mechanism and distribution of intermediates from several precursor mixtures to tetragonal BaTiO_3 and the hexagonal phase is not observed.¹⁰ Typically, the synthesis of stoichiometric and oxygen deficient hexagonal BaTiO_3 is performed at temperatures well above 1400 °C.¹¹ For MIP prepared material the implication

is that the local temperature of the sample is in excess of the MIP and additional direct microwave heating of an *intermediate* is occurring to give a temperature in excess of 1400 °C. After 5 min, quenching the MIP gives sufficiently rapid cooling that allows stabilisation of the hexagonal phase at room temperature. However, product BaTiO_3 does not exhibit significant microwave heating because BaTiO_3 possess a non-polar cubic structure above 120 °C. Therefore, further heating anneals product BaTiO_3 at the MIP temperature of ca. 1100 °C giving the single tetragonal phase.

The above information has been presented from the perspective that reaction (ion diffusion) proceeds *via* thermal (*i.e.* equilibrium) phenomena. In solution based chemistry the virtue of microwaves is the rapid preparation of compounds arising from volumetric (super)heating. There is no convincing evidence to suggest any effect other than thermal. So called microwave effects are dogged by the difficulties associated with accurate temperature measurement.

However, in the solid state, recent experiments have convincingly demonstrated that the electric field can influence the rate at which ion diffusion occurs.¹² Polarised microwaves were applied to concentric samples of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ / $\text{YbBa}_2\text{Cu}_3\text{O}_{6+\delta}$ and Ag^+/Na^+ β'' -alumina, and the ion diffusion distance measured as a function of angle to the polarisation. In these elegant experiments only the relative rate of diffusion is important rather than an absolute rate and therefore precise temperature measurement is not required. It was found that non-isotropic ion diffusion occurs and diffusion is more rapid parallel to the field.¹² The effect is also time dependent and as reaction and sintering proceed, diffusion tends towards isotropic on extended microwave heating. Potential explanation for dependence on electric field orientation and time has been provided based on interactions at grain boundaries, and a ponderomotive force,¹³ but whatever the exact mechanism it is clear that the electric field of microwaves directly influences ion diffusion and is more significant at the early stages of reaction.

One of the major barriers to using microwave techniques in materials synthesis is the paucity of data enumerating the dielectric permittivity of solids as a function of temperature. Therefore identifying which solids will exhibit microwave heating, at what temperature, and to what extent, is currently a matter of trial and error. Measurements of this type would clearly aid in selection of precursors where microwave heating is, or is not, desirable.

One area where information on the temperature dependence of dielectric permittivity could be directly applied is for the synthesis of composite materials. By definition composite materials contain a mixture of compounds that will exhibit different temperature dependent dielectric properties. Therefore *differential* heating is potentially possible allowing selective reaction at a particular surface or modification e.g. chemically using reactive MIP. Differential heating has been demonstrated for comminution of rocks for mineral extraction¹⁴ and in heterogeneous catalytic applications of ceramic supported metal particles.¹⁵ However, the rate of heat transfer between hot and cold particles will restrict the temperature gradient that can be maintained over the reaction time. Clearly thermal conductivity is also material dependent and therefore understanding of interface interactions relevant to heat transfer and consequently ion diffusion is also required.

MIP heating and MIP promoted dielectric heating greatly expand the potential application of microwave techniques to materials synthesis. Given the observations of MIP promoted heating of BaTiO_3 and the time dependent influence of the electric

field on ion diffusion the future search for new single phase products, and particularly composite materials, should perhaps focus on minimising reaction times or using pulsed microwave methods to maximise temperature gradients.

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References

- (a) D. R. Baghurst, A. M. Chippindale and D. M. P. Mingos, *Nature*, 1988, **332**, 311; (b) C. C. Landry and A. R. Barron, *Science*, 1993, **260**, 1653; (c) A. G. Whittaker and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1995, 2073; (d) D. Vollath and K. E. Sickafus, *J. Mater. Res.*, 1993, **8**, 2978; (e) K. J. Rao, B. Vaidyanathan, M. Ganguli and P. A. Ramakrishnan, *Chem. Mater.*, 1999, **11**, 882; (f) M. P. Selvam and K. J. Rao, *Adv. Mater.*, 2000, **12**, 1621; (g) R. Roy, D. Agrawal, J. Cheng and S. Gedevarishvili, *Nature*, 1999, **399**, 668.
- (a) M. Gasgnier and A. Petit, *J. Alloys Compd.*, 2003, **358**, 302; (b) M. Panneerselvam and K. J. Rao, *J. Mater. Chem.*, 2003, **13**, 596; (c) B. G. Ravi, P. D. Ramesh, N. Gupta and R. J. Rao, *J. Mater. Chem.*, 1997, **7**, 2043.
- R. J. Goldston and P. H. Rutherford, *Introduction to Plasma Physics*, Institute of Physics Publishing, Bristol, 1995.
- (a) D. K. Agrawal, *Curr. Opin. Solid State Mater. Sci.*, 1998, **3**, 480; (b) G. Hancock, L. Lanyi, J. P. Sucksmith and B. K. Woodcock, *Pure Appl. Chem.*, 1994, **66**, 1207; (c) K. Suzuki, K. Ninomiya and S. Nishimatsu, *Vacuum*, 1984, **34**, 953; (d) S. Veprek, *Pure Appl. Chem.*, 1982, **54**, 1197; (e) D. Vollath and K. E. Sickafus, *J. Mater. Sci.*, 1993, **28**, 5943; (f) C. E. G. Bennett, N. A. McKinnon and L. S. Williams, *Nature*, 1968, **217**, 1287.
- D. J. Brooks and R. E. Douthwaite, *Rev. Sci. Instrum.*, 2004, **75**, 5277.
- (a) B. G. Bagley, L. H. Greene, J. M. Tarascon and G. W. Hull, *Appl. Phys. Lett.*, 1987, **51**, 622; (b) C. Magro, A. Tressaud, L. Lozano, N. Hudakova, C. Cardinaud and G. Turban, *J. Mater. Sci.*, 1994, **29**, 4225.
- (a) A. G. Whittaker and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1993, 2541; (b) J. D. Houmes and H. C. zur Loye, *Chem. Mater.*, 1996, **8**, 2551; (c) H. T. Cong, H. B. Ma and X. C. Sun, *Physica B*, 2002, **323**, 354; (d) M. Belmonte, V. A. Silva, A. J. Fernandes, F. Costa and R. Silva, *J. Am. Ceram. Soc.*, 2003, **86**, 749.
- (a) D. J. Brooks, R. E. Douthwaite and L. J. Gillie, *Chem. Commun.*, 2005, 4857; (b) D. J. Brooks, B. R. and R. E. Douthwaite, *Adv. Mater.*, 2005, **17**, 2474.
- D. J. Brooks, R. E. Douthwaite, R. Brydson, C. Calvert, M. Measures and A. Watson, *Nanotechnology*, 2006, **17**, 1245.
- (a) L. K. Templeton and J. A. Pask, *J. Am. Ceram. Soc.*, 1959, **42**, 212; (b) S. Tsutai, T. Hayashi, S. Hayashi and Z. Nakagawa, *J. Ceram. Soc. Jpn.*, 2001, **109**, 1028.
- (a) K. W. Kirby and B. A. Wechsler, *J. Am. Ceram. Soc.*, 1991, **74**, 1841; (b) D. C. Sinclair, J. M. S. Skakle, F. D. Morrison, R. I. Smith and T. P. Beales, *J. Mater. Chem.*, 1999, **9**, 1327.
- A. G. Whittaker, *Chem. Mater.*, 2005, **17**, 3426.
- S. A. Freeman, J. H. Booske and R. F. Cooper, *Phys. Rev. Lett.*, 1995, **74**, 2042.
- S. W. Kingman, *Int. Mater. Rev.*, 2006, **51**, 1.
- X. L. Zhang, D. O. Hayward and D. M. P. Mingos, *Catal. Lett.*, 2003, **88**, 33.