

Reviews

Synthesis of Inorganic Solids Using Microwaves

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Use of microwaves in the synthesis of materials is gaining importance. Microwave-assisted synthesis is generally much faster, cleaner, and more economical than the conventional methods. A variety of materials such as carbides, nitrides, complex oxides, silicides, zeolites, apatite, etc. have been synthesized using microwaves. Many of these are of industrial and technological importance. An understanding of the microwave interaction with materials has been based on concepts of dielectric heating and of the resonance absorption due to rotational excitation. This review presents a summary of recent reports of microwave synthesis of inorganic materials. Various observations regarding microwave interaction with materials are also briefly discussed.

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Introduction

Development of new routes for the synthesis of solids is an integral aspect of materials chemistry.¹ Some of the important reasons for this are the continuing need for fast and energy-efficient techniques, necessity to avoid competing reactions in known processes, and the challenge implied in the synthesis of metastable phases bypassing thermodynamically reversible routes. In recent times, development of techniques such as sol-gel and other soft-chemical methods have led to the preparation of engineered materials.^{2–5} The microwave-assisted route is yet another novel method of synthesis^{6–10} and is a very rapidly developing area of research. Clark and Sutton have reviewed various aspects microwave applications reported in the literature.¹¹ In recent times, several reports have appeared where conventional preparative techniques have been substituted by microwave methods. Microwaves have been in use for accelerating organic reactions for a quite awhile.^{7,9,12,13} Microwave synthesis is generally quite faster, simpler, and very energy efficient. The exact nature of microwave interaction with reactants during the synthesis of materials is somewhat unclear and speculative. How-

ever, energy transfer from microwaves to the material is believed to occur either through resonance or relaxation, which results in rapid heating. This knowledge is widely used as the basis in the discussion of reaction mechanisms.

Microwaves are electromagnetic radiation, whose wavelengths lie in the range of 1 mm to 1 m (frequency range of 0.3 to 300 GHz). A large part of the microwave spectrum is used for communication purposes and only narrow frequency windows centered at 900 MHz and 2.45 GHz are allowed for microwave heating purposes. Very few microwave applications involving heating have been reported where frequencies of 28, 30, 60, and 83 GHz have been used.^{14–17} As is well-known, microwaves are produced by magnetrons, which are principally thermionic diodes with heated cathodes acting as sources of electrons. From the magnetrons the microwaves are generally directed toward a target (placed in so-called microwave cavities) with the use of microwaveguides. These guides are usually made of sheet metal, and the intensity distribution within the waveguides is homogenized by the use of mode stirrers.¹⁶

Many microwave preparations reported in the literature have been made on the laboratory scale of only a few grams. These preparations have all been made with the use of domestic microwave ovens operating at 2.45 GHz and with a maximum output power of 1 kW. However, use of higher power levels for specialized applications have also been reported.^{15,17–21}

Recent reports of the syntheses of several inorganic solids have been reviewed in this article, and the new insights gained in some of them have been highlighted and discussed. Many of the illustrative reactions have been chosen from the work of the authors. Processing of ceramics using microwaves^{22–35} and (theoretical) modeling of microwave interaction with ceramic

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Table 1. Microwave-Active Elements, Natural Minerals, and Compounds

element/mineral/compound	time (min) of microwave exposure	T, K	element/mineral/compound	time (min) of microwave exposure	T, K
Al	6	850	NiO	6.25	1578
C (amorphous, <1 μm)	1	1556	V ₂ O ₅	11	987
C (graphite, 200 mesh)	6	1053	WO ₃	6	1543
C (graphite, <1 μm)	1.75	1346	Ag ₂ S	5.25	925
Co	3	970	Cu ₂ S (chalcocite)	7	1019
Fe	7	1041	CuFeS ₂ (chalcopyrite)	1	1193
Mo	4	933	Fe _{1-x} S (pyrrhotite)	1.75	1159
V	1	830	FeS ₂ (pyrite)	6.75	1292
W	6.25	963	MoS ₂	7	1379
Zn	3	854	PbS	1.25	1297
TiB ₂	7	1116	PbS (galena)	7	956
Co ₂ O ₃	3	1563	CuBr	11	995
CuO	6.25	1285	CuCl	13	892
Fe ₃ O ₄ (magnetite)	2.75	1531	ZnBr ₂	7	847
MnO ₂	6	1560	ZnCl ₂	7	882

materials^{36–38} have also been reported extensively in the literature; however, these aspects are not discussed in this review. The present understanding of the nature of microwave interaction with materials is summarized in the following section, which provides the necessary background for the various case studies discussed in the subsequent section. The final section is a brief critique of the state of microwave synthesis.

Interaction of Materials with Microwaves and Dielectric Heating

In general, materials fall into three categories, with respect to their interaction with microwaves; (i) microwave reflectors, typified by bulk metals and alloys, such as brass, which are therefore used in making microwaveguides; (ii) microwave transmitters which are transparent to microwaves, typified by fused quartz, zircon, several glasses, and ceramics (not containing any transition element), Teflon etc.; they are therefore employed for making cookware and containers for carrying out chemical reactions in microwaves; and (iii) microwave absorbers which constitute the most important class of materials for microwave synthesis; they take up the energy from the microwave field and get heated up very rapidly.

Many inorganic materials are known to couple strongly to microwaves at ordinary temperatures. Table 1 lists a number of such minerals and inorganic compounds.^{39,40} The temperatures attained by these materials and the corresponding exposure times when irradiated by microwaves in ordinary domestic microwave ovens (DMO) are also listed in the table. Several chalcogenides, not included in Table 1, such as cinnabar (HgS), molybdenite (MoS₂), orpiment (As₂S₃), sphalerite (ZnS), etc. also interact with microwaves but are not heated so rapidly as those listed in the table. It may be noted from Table 1 that a number of transition metal containing oxides, halides, etc. also get heated up very fast in microwaves. Most forms of carbon interact with microwaves in their powder form. Amorphous carbon powder, in particular, absorbs microwaves (2.45 GHz frequency) most rapidly with its temperature rising to 1550 K in just 1 min in a DMO operating at 1 kW (Table 1).

It is well-known that the interaction of dielectric materials with microwaves leads to what is generally described as dielectric heating.⁴¹ Electric dipoles present in such materials respond to the applied electric field

of microwaves. The reorientation dynamics of the dipoles in the applied alternating field is significant for microwave heating. When the dipolar reorientation is unable to respond to the frequency of the alternating electric field of the microwaves, there results a phase lag in the reorientation and this gives rise to a polarization current which is *in phase* with the applied field. If the phase lag, field strength, and current are δ , E , and I respectively, then the component of the *in phase* current is $I \sin \delta$, (since E and I are 90° *out of phase* in an ideal dielectric). As a consequence, resistive heating occurs in the medium. A convenient measure of the heating effect which occurs in an applied field is therefore, $\sin \delta \approx \tan \delta = \epsilon''/\epsilon'$, which is the energy dissipation factor or loss tangent. In materials where the dipoles rotate freely, such as in liquids, the rotational frequency of the dipole determines the dissipation of energy from the applied field. In general, the dipolar species in any medium possesses a characteristic relaxation time, τ , and the dielectric constant is, therefore, frequency-dependent. This is expressed by representing the dielectric constant as a complex quantity, $\epsilon^* = \epsilon' + i\epsilon''$, where ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant. If the dipolar relaxation is characterized by a single relaxation time τ and ω is the frequency of the applied field (such as of the microwaves), then the relation between dielectric quantities and the frequency are represented well by the Debye equations:

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2}$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)}{1 + \omega^2 \tau^2}$$

ϵ_s and ϵ_∞ are the zero frequency and infinite frequency dielectric constants, respectively. Thus, ϵ'' varies with frequency giving rise to characteristic peak at $\omega\tau = 1$ or $\omega = 1/\tau$. For water at 20 °C, the value of the relaxation peak frequency is about 18 GHz and ϵ'' is quite significant at 2.45 GHz, which is why in commercial ovens, operating at 2.45 GHz, there is rapid dissipation of energy and hence heating of water.

In ionic materials, where ions can drift in the applied field, joule heating can occur because of the ionic current itself. Thus in such situations, the dipolar reorientation

current σ_d and ion drift current, σ_i can be combined so that effectively $\epsilon'' = (\sigma_d + \sigma_i)/\omega\epsilon_0$, where ϵ_0 is dielectric constant of free space. In semiconducting and semi-metallic materials, the conduction loss is dominated by the electronic transport. Hence $\sigma_{\text{electronic}}$, which increases with both increasing temperature and decreasing band gap, leads to high degree of microwave absorption.

The microwave power dissipation per unit volume in a material, P , is dependent upon the total current σ and the square of the electric field E in the sample:

$$P = \sigma|E|^2 = (\omega\epsilon_0\epsilon'')|E|^2$$

or, in terms of ϵ' :

$$P = (\omega\epsilon_0\epsilon' \tan \delta)|E|^2$$

In conjunction with the Debye relations given above

$$P = \frac{\epsilon_0(\epsilon_s - \epsilon_\infty)\omega^2\tau}{1 + \omega^2\tau^2}|E|^2$$

When the heat lost by the system during microwave interaction is negligible, one can estimate the rate of heating as approximately equal to $\Delta T/t = \sigma|E|^2/\rho C$, where ρ is the density and C is the specific heat capacity of the material.

The microwave heating process has been treated more elaborately by using known material properties and Maxwell's equations. For the case of a microwave applicator with single-mode resonant cavity, which simplifies the method of calculation, the heating rate dT/dt is formulated as⁴²

$$\frac{dT}{dt} = \frac{4}{\tan \delta} \frac{1}{\rho C} \frac{\epsilon''}{\sqrt{\epsilon'}} \frac{1}{V_c} P_0 \frac{\xi S(\text{area})}{\rho C(\text{volume})}_{\text{sample}} (273 + T)^4$$

where ρ is the mass density of the sample, V_c is the cavity volume, and P_0 is the microwave power inside the cavity, S is the Stefan-Boltzmann constant, and ξ is the surface emissivity of the sample. The experimental temperature versus power plot obtained for the case of a few ceramics under single mode irradiation conditions is shown in Figure 1, along with the model prediction using the above expression.

It is therefore evident that coupling to microwaves of 2.45 GHz frequency in microwave reactors such as a DMO is possible only if the material has dipolar absorption in the region of the reactor frequency (2.45 GHz). However, dipole relaxation times are affected by temperature and the microwave absorption of the material can therefore be optimally increased by matching the relaxation frequency of the material with the frequency of the reactor (DMO). This is achieved by either varying the temperature or the reactor frequency itself. Also, in a material in which the dielectric loss peak frequency is higher than the microwave reactor frequency, the initial microwave heating shifts the absorption peak further away from the reactor frequency as a result of which microwave coupling decreases and further heating stops. Choice of microwave container materials for safe handling are based on these considerations.

The temperature profile within the material exposed to microwaves depends on several geometrical factors

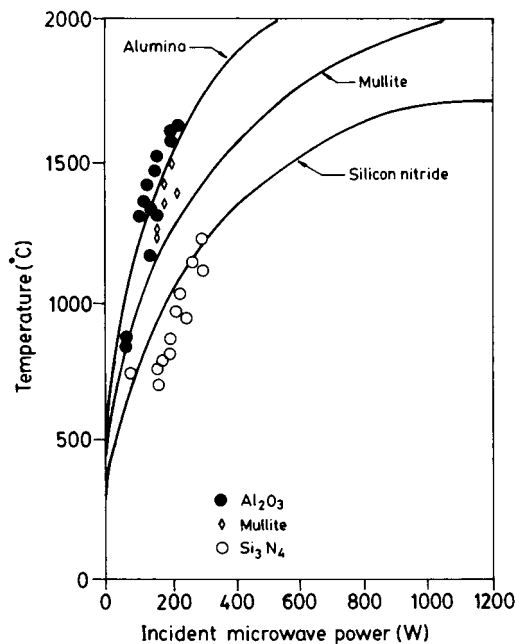


Figure 1. Steady-state temperature vs power plots for three different ceramics under single mode irradiation conditions. Solid lines were calculated from equations for heating rate in a single-mode resonant cavity (see text) (data from ref 42).

related to design of the microwave cavity. However, when microwaves are incident perpendicularly on the surface of the material, its intensity decreases progressively inside the material in the direction of incidence as the microwave energy gets progressively dissipated. This is expressed through the parameter known as penetration depth, D , which is the distance in the direction of penetration at which the incident power is reduced to half its initial value:

$$D = \frac{3\lambda_0}{8.686\pi \tan \delta(\epsilon')^{1/2}}$$

where λ_0 is the wavelength of the microwaves. The equation suggests that there is a slight advantage in working at lower frequencies when large samples are involved, but it is associated with a payoff in terms of power absorbed per unit volume. In bulk metals and alloys which generally reflect the microwaves, the microwave penetration is rather low and it is common practice to describe the microwave penetration in metals through a quantity known as skin depth, δ . This is given by

$$\delta = 1/\sqrt{\pi\nu\mu\sigma}$$

where ν is the microwave frequency ($\omega = 2\pi\nu$), μ is the permeability of free space, and σ is the electrical conductivity.⁴³

Dielectric properties are dependent on both the chemical composition and on the physical state of the material. For example, impurities, aliovalent substitution, and the chemical nature of the material (whether it is a transition metal compound or a chalcogenide, etc.) can give rise to high dielectric constants and losses and result in strong microwave coupling. Similarly, powders which consist of surface defects, surface charge, and polarization can also enhance the dielectric parameters

which are desirable for microwave coupling. Crystal structures which support permanent polarization can similarly be expected to give rise to good microwave susceptibility. In turn it is to be anticipated that materials containing highly polarizable elements (e.g., PbS) should be good microwave susceptors. Powders of inorganic materials which are piezoelectric can give rise to resonance absorption because the thickness vibrational modes in micrometer-sized particles which lie in the microwave regime.⁴³ In highly ionic materials (fast ion conductors), both polarization effects associated with site to site jumps of ions and the ionic current enable them to couple well with microwaves.

Microwave interaction of two other types can also lead to dissipation of energy very rapidly. One of them is the excitation of weak bonds such as secondary bonds in chalcogenides or interlayer bonds in graphite (and similar materials). We may note that microwave frequencies correspond to rotational excitation energies in materials. Thus the incident microwaves may excite rotational modes in a material. They are state-to-state excitations and therefore the energy absorption occurs by resonance. The absorbed energy may be completely dissipated as heat during deexcitation via internal mode coupling. The excitation of weak bonds may fall into the same general category of state-to-state excitations.

The behavior of large metal pieces and corresponding metal powders under microwave irradiation are startlingly different. As noted earlier, skin depths in bulk metals are very low and vary as $1/\sqrt{\sigma}$, and hence, there is little penetration of microwaves. In large metal samples and also in metal films, large electric field gradients occur in the microwave cavity, which gives rise to electric discharges. On the other hand, in metal powders, no such discharge takes place and due to eddy currents and localized plasma effects, very rapid heating takes place which may be as high as 100 K/s.⁴⁴ Eddy current phenomena arises from the alternating magnetic field associated with microwaves. Other manifestations of the microwave coupling via magnetic field effects include hysteresis loss, dimensional resonances in magnetic fields, and magnetic resonance from precession of magnetic moments of unpaired electrons, etc.⁴³

Dielectric heating in microwaves has thus several origins. In a broad sense, they can occur either via resonance modes of absorption, or via relaxational mechanisms as a result of phase lag between alternating microwave field and the motion of the polar species in the material. The dielectric properties themselves being temperature-dependent, both microwave coupling and the resulting temperature profiles of the sample can be very different for different materials. In Figure 2, the behavior of three oxide samples is shown which illustrates this point.⁸ Silica (SiO_2), whose dielectric constant and dielectric loss do not show much dispersion, does not get heated up much when exposed to microwaves even after a long duration. But the temperatures of the two oxides, NiO and Cr_2O_3 , escalate after some initial exposure times. In the case of NiO, the high dielectric loss results in almost a parabolic increase in temperature, while increased dielectric loss at the high temperature is responsible for the fairly abrupt rise in temperature in Cr_2O_3 . The regions of high slopes in the temperature-time plots are referred to as

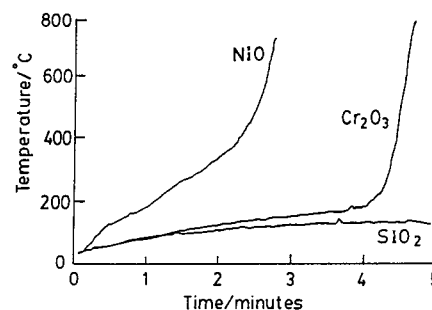


Figure 2. Microwave heating of silica, chromium (III) oxide, and nickel (II) oxide. Note that SiO_2 with low dielectric loss does not heat, whereas NiO and Cr_2O_3 couple well with microwaves and get heated up rapidly. Cr_2O_3 exhibits "thermal runaway" due to increased dielectric loss at higher temperatures (data from ref 8).

"thermal runaways". However, it may be noted that the temperature time profiles are dependent on the microwave power levels as well. The temperature corresponding to the beginning of thermal runaways is designated as T_{critical} .

The expression for the microwave penetration depth suggests that for most materials, D is significantly high and, therefore, microwave power dissipation is fairly uniform throughout the material as long as the sample sizes are not large. This leads to an important feature of microwave heating, namely, volumetric heating, which results in a temperature profile exhibiting a decreasing slope toward the geometrical borders of the sample in a manner opposite to that found in conventional heating.

Case Studies

In this section, we consider examples of the synthesis of the materials achieved through the use of microwaves. These are illustrated under various categories, viz., (i) direct reactions, including those involving the use of simple compounds; (ii) preparation of solids which involve decompositions and combinations giving rise to solids of complex composition; (iii) nitridation reactions; (iv) reactions brought about in liquid media; (v) preparation of glasses; (vi) selective deoxidation reactions; and (vii) plasma-assisted reactions.

(i) Direct Reactions. Simplest, very illustrative, and technologically important microwave preparation starting from the elements is that of $\beta\text{-SiC}$.⁴⁵ SiC is a large volume ceramic used in many industrial applications such as for grinding wheels, etc. It has been prepared very simply by exposing Si and C (charcoal) in their powder form to microwaves. Slight excess of carbon powder is used in the reaction mixture, which is kept in a silica crucible and irradiated with microwaves for 4–10 min in an ordinary domestic microwave oven (DMO) at a maximum power of 1 kW and operating frequency of 2.45 GHz. The temperature attained by the mixture at various power settings is shown in Figure 3a as temperature-time plots. It may be seen that the highest temperature attained is dependent on the power setting and the temperature rises to a maximum within the first 2 min of exposure. The X-ray diffraction pattern of the product obtained is shown in Figure 3b. It was found that an inert ambient was essential for purity of the product. In air, up to 15% SiO_2 was formed in such

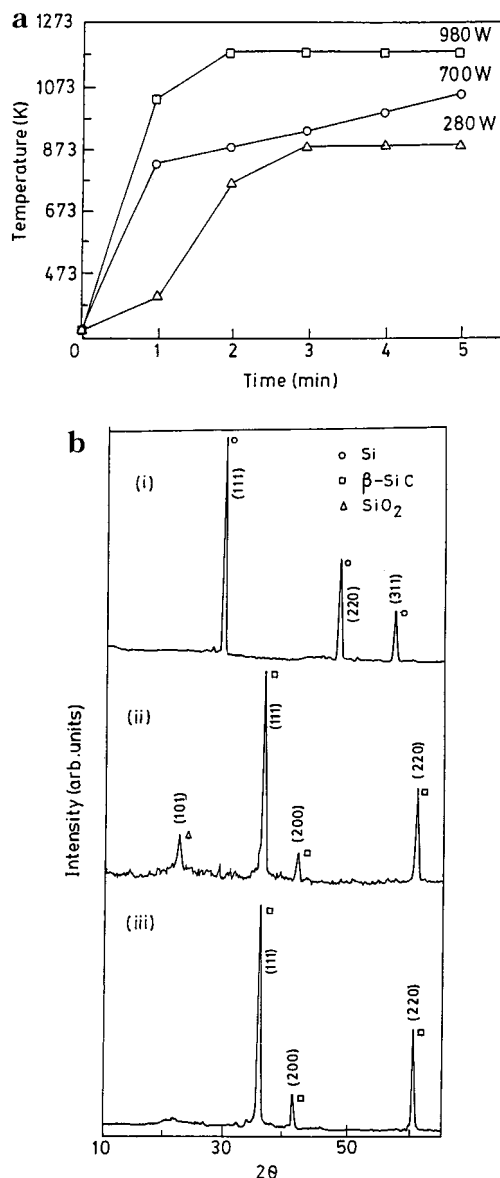


Figure 3. (a) Time-temperature graph for Si-C reaction. The maximum temperature attained during the reaction is dependent on the microwave power. Even at the maximum power used, the temperature attained is only about 1200 K, which is less than the temperature required for conventional preparation of SiC (data from ref 45). (b) XRD patterns for (i) silicon-carbon initial reaction mixture, (ii) reaction products formed in air after 10 min, and (iii) reaction product formed in iodine atmosphere after 10 min. When the reaction was carried out in air, SiO₂ impurities are observed, whereas when the reaction is carried out in iodine atmosphere, pure β -SiC is obtained (data from ref 45).

a reaction while only monophasic β -SiC was formed when surrounded by a shroud of iodine vapor. The shroud of iodine vapors was produced in situ in the microwave oven by a separate but simultaneous reaction (see later). The entire reaction was completed in less than 10 min. Temperatures were measured by interrupting the microwave irradiation and inserting a thermocouple into the reaction mixture.

It was interesting to note that in this microwave preparation, the Si + C reaction occurred at temperatures less than 1250 K, unlike in a conventional heating process, which requires much higher temperature (1673 K).⁴⁶ Therefore, Si does not melt during the reaction.

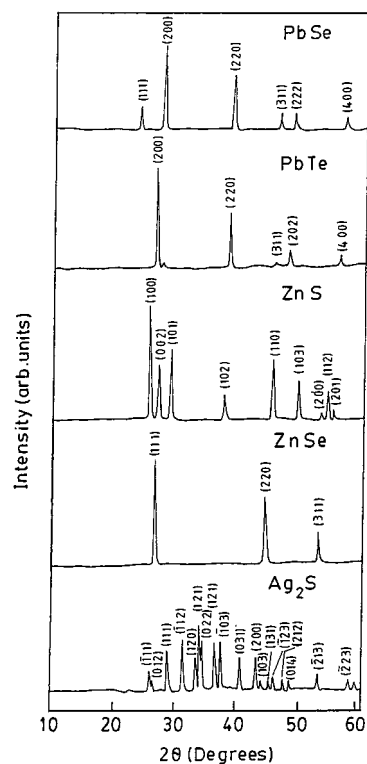


Figure 4. XRD patterns of the metal chalcogenides prepared using microwaves. The reaction was carried out in evacuated, sealed quartz tubes under microwave irradiation for less than 10 min (data from ref 47).

Also, it was found that Si is not a susceptor to microwaves at ordinary temperatures, whereas charcoal is. Therefore high temperatures are initially achieved by the heating of carbon which is attributed to the excitation of weak graphitic bonds by the microwaves. Since the reaction $\text{Si} + \text{C} \rightarrow \text{SiC}$ is exothermic ($\Delta G_{298\text{ K}}^{\circ} = -16 \text{ kcal/mol}$), the rate of reaction increases very rapidly once it is initiated. It was also found that the product was free from any hot spot formation and excess carbon could be simply burned out even at 700 °C. It was even possible to float out any excess carbon powder. The product was remarkably clean, monophasic β -SiC.

Several important chalcogenides have been prepared using microwave irradiation. They include PbSe, PbTe, ZnS, ZnSe, Ag₂S,⁴⁷ and ZnTe.⁴⁸ Stoichiometric quantities of fine powders of the respective metals and chalcogens of high purity were sealed in evacuated quartz ampules (about 10 g of mixture). The sealed ampules were irradiated with microwaves for 5–10 min in a DMO with a power setting of 800–950 W. Reactants were found to melt, and the reaction was often associated with emission of splashes of light. The ampules were then allowed to cool by turning off the microwave oven and then broken to recover the products of good phase purity and crystallinity (see XRD in Figure 4). Whittaker and Mingos prepared several chromium chalcogenides, α -MnS, Fe₇S₉, TaS₂, and SnS₂ by irradiation of the elemental mixtures for times less than 10 min (however, it was found necessary to anneal the products for several hours).⁴⁴

Ternary chalcogenides, CuInS₂ and CuInSe₂, which have high potential for application in solar cells (as they are semiconductors with direct band gaps of 1.53 and 1.04 eV), have been synthesized by microwave irradiation.

tion of elemental mixtures.⁴⁹ The synthesis was accomplished by microwave irradiation of elemental mixtures taken in quartz tubes and sealed under vacuum. Blue flashes were initially observed which has been attributed to the formation of sulfur plasma. Several experiments were performed to identify the reaction mechanism, and it was concluded that Cu first reacts with the chalcogen to form copper chalcogenide and the heat released by the reaction quickly melts the indium. Further reaction takes place in the indium solution of copper chalcogenide and the chalcogen. Copper indium chalcogenide crystallizes from the liquid melt. Scanning electron microscopic studies have been used to provide evidence for the involvement of molten phases.

It may be noted that the conventional preparation of the chalcogenides⁵⁰ involves heating in rotary furnaces up to 48 h. It appears that the rapidity of the reaction in microwave method is a consequence of simultaneous heating of the metal powders through induction of eddy currents and of the chalcogens through activation of the secondary bonds. The release of reaction enthalpies leads to rapid escalation of the reaction rates.

The direct reaction of elemental reactants has been used for the microwave preparation of carbides such as TiC and Mo₂C.⁵¹ The microwave susceptibility of graphitic carbon has been exploited since Mo powder itself is not a very good susceptor. Formation of the carbides is also assisted by the reaction enthalpy. The metals have a strong tendency to form oxides when the irradiation of elemental mixture is performed in the ambience of air. However, use of an iodine shroud as in the case of SiC enables formation of products with high phase purity. However, Kozuka and Mackenzie achieved preparation of SiC, TiC, NbC, and TaC using microwave method where carbidation was preceded by a carbothermal reduction of the required oxides. The temperatures of the reaction were of the order of 1773 K and the product morphologies were found to be dependent on the nature of both the form of carbon used and the physical nature of the oxide.⁵²

Several industrially important silicides have been prepared by direct microwave reactions.⁵³ Notable is the preparation of MoSi₂.⁵⁴ When a stoichiometric mixture of only Mo and Si is irradiated, no reaction seems to occur. When graphitic carbon is mixed with the reactants and irradiated, a pronounced tendency of Si to combine with C is noticed. Mo–Si reaction is nevertheless initiated when the mixture is heated along with amorphous C powder, but small amounts of SiC are formed in the course of reaction. However, when Mo and Si powders are mixed well (by repeated grinding), pelletized, covered with amorphous carbon, and then microwave irradiated in a DMO, Mo and Si react completely, and the product MoSi₂ is found to form as a well-sintered button. The surface of the button was scraped and either dusted or washed. The reaction, Mo + 2Si → MoSi₂, seems to be initiated only at very high temperatures (>1200 K). As noted earlier, microwave coupling of various forms of carbon is very different from one another. Shown in Figure 5 is the time–temperature behavior of two well-known forms of carbon. It may be seen that amorphous carbon attains temperature of approximately 1500 K in less than 2 min while temperatures attained by graphitic carbon is only 1200 K

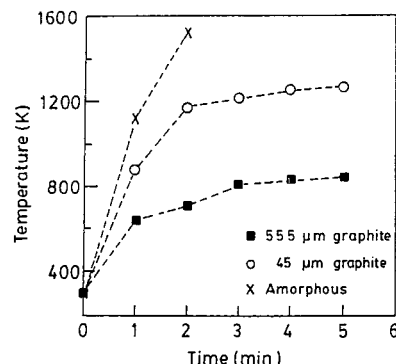


Figure 5. Time–temperature profiles of the graphitic and amorphous forms of carbon under microwave irradiation (lines are drawn as a guide to the eye). Maximum temperature attained is dependent on the particle size. Amorphous carbon gets heated to a higher temperature than graphite (data from ref 51).

Table 2. Microwave-Assisted Preparation of Some Mixed Oxides

compound	starting materials	time of exposure	power used (W)	ref
BaWO ₄	BaO, WO ₃	30 min	50–500	55
CuFe ₂ O ₄	CuO, Fe ₂ O ₃	30 min	50–500	56
La ₂ CuO ₄	La ₂ O ₃ , CuO	≈10 min, (30 min anneal)	130–500	56

which does not increase further. Therefore MoSi₂ formation is initiated only by amorphous carbon and the reaction drives itself to completion due to the liberation of reaction enthalpy. In the case of TiSi₂ (and also CoSi₂) however, the temperature attained by graphitic carbon is sufficient to initiate the reaction. Formation of WSi₂ follows the pattern of MoSi₂, requiring high temperatures for initiation and hence the use of amorphous carbon. The phase purities of these silicides are found to be excellent. The microwave coupling of the metal powders were found to be in the order Ti > Co > W > Mo. It may be noted that the high melting point, oxidation resistance, carbidation resistance, and metallic conductivity of MoSi₂ makes it an important industrial silicide used in making heating elements and high temperature engine parts. The conventional preparation of these silicides, particularly MoSi₂ involves tedious, cumbersome, and expensive procedures such as high-temperature vacuum fusion and laser pulse treatments.

Microwave-induced direct reactions between simple compounds is exemplified by the formation of bismuth and lead vanadates,⁴⁷ BaWO₄ and CuFe₂O₄,⁵⁵ and La₂CuO₄ and YBa₂Cu₃O_{7-x}.⁵⁶ In all these preparations, stoichiometric mixtures of the corresponding oxides have been irradiated by microwaves for times up to 30 min, sometimes followed by longer durations of annealing. The reaction times are much lower than in the conventional procedures. For example, while preparation of Pb– and Bi–vanadates by conventional procedures requires up to 10 h of heating at high temperatures, the microwave-induced reactions are completed in under 15 min in a DMO operating at 900 W. The annealed Bi₄V₂O₁₁ sample is found to exhibit α → β transition at ~725 K, while the unannealed sample shows only a weak transition. This suggests that unannealed product is in metastable state, which is considered to be structurally disordered, the disorder being random orientation of bismuth–oxygen and vanadium–

Table 3. Preparative Conditions for the Microwave Synthesis of Niobates and Titanates^a

compound	initial reactants	power and duration of microwave exposure	conventional method	
			conditions	ref
LiNbO ₃	Li ₂ CO ₃ + Nb ₂ O ₅	15 min (600 W for 10 min + 800 W for 5 min)	needs more than 12 h at 770 K	61
NaNbO ₃	Na ₂ CO ₃ + Nb ₂ O ₅	17 min (600 W for 10 min + 800 W for 5 min + 980 W for 2 min)	several hours of heating at 1523 K with intermittent grinding	62
KNbO ₃	K ₂ CO ₃ + Nb ₂ O ₅	12 min (600 W for 7 min + 800 W for 5 min)	needs 30 h of heating at 1273 K	63
BaTiO ₃	BaCO ₃ + TiO ₂	25 min (600 W for 5 min + 800 W for 10 min + 980 W for 10 min)	several hours of heating of the ball-milled powders at 1673 K	64
PbTiO ₃	PbNO ₃ + TiO ₂	9 min (600 W for 9 min)	more than 8 h heating at 633 K	65
PbZr _{0.52} Ti _{0.48} O ₃	PbNO ₃ + <i>m</i> -ZrO ₂ + TiO ₂	10 min (600 W for 5 min + 800 W for 5 min)	more than 6 h of heating at different temperatures	66

^a Comparison with conventional route is made.

oxygen polyhedra. It is suggested that the random orientation leads to anomalies in XRD intensities. Relevant reaction details are summarized in Table 2.

Recently, a convenient microwave irradiation method has been developed⁵⁷ for preparing YBa₂Cu₃O_{7-x} in which pellets of the reactant oxide powders are embedded in the same mixture of powders and the heat loss from the reaction mixture is prevented by surrounding it with glass wool. Reaction was carried out in a DMO at a power level of 200 W and was found to be completed in just 25 min.

Direct reaction in microwaves has been used in a novel way to prepare composites by Clark et al.⁵⁸ Al₂O₃-TiC composites have been prepared by microwave irradiation of titania along with aluminum and carbon powders. TiC, TiB, and Al₂O₃-TiB composites have also been prepared similarly by the microwave ignition method. Products of relatively high density were obtained in the process. The initial microwave absorption has been both by metal powders and graphite and powerful industrial multimode oven having a maximum power output of 6.4 kW was used.

Microwave-initiated reactions between metal powders and gases have been reported by Whittaker and Mingos.⁵⁹ A number of transition metal halides, oxyhalides and nitrides as also indium and tellurium halides have been prepared by this method. Fluidized beds were used to carry out the reactions.

(ii) Complex Solids. Conventional methods of preparation of industrially important niobates and titanates, such as BaTiO₃, LiNbO₃, and lead zirconate titanate (PZT), require several hours of high-temperature reactions. Use of microwave methods appears not feasible as a first thought since several of the oxides used for these preparations are not microwave susceptors. It is not convenient to make these preparations by using suitable carbonates or nitrates as starting materials because such carbonates and nitrates are also not good microwave susceptors. Microwave methods can be modified for the preparation of this class of materials by including a secondary susceptor in the reaction mixture. The important requirement is that the secondary susceptor only assists the initial heating but does not react with other reactants. For the preparation of titanates, niobates, etc., the transition metal oxide and the nitrate or carbonate of the other metal in the compound are ground together, pelletized under moderate pressures, embedded in graphite powder in a silica or alumina container, and then irradiated with microwaves in a DMO.⁶⁰ Due to its high microwave susceptibility, carbon

(graphite) catches fire and heats the pellets thereby initiating the decomposition of the nitrates or carbonates. The resulting hot oxide mixture of the pellet appears to couple much better with microwave at those temperatures and an extremely fast reaction ensues, giving rise to the desired products. Several of these reactions are summarized in Table 3. The products have been found to possess both good crystallinity and phase purity.

In an illuminating experiment directed toward understanding the effect of microwaves, the reaction rates and activation energies have been evaluated for the BaCO₃ + TiO₂ → BaTiO₃ + CO₂ reaction by making measurements at three different temperatures (achieved by adjusting the power level).⁶⁷ It was found that the reaction was characterized by an activation barrier of 58 kJ/mol, compared to much higher values in a conventional diffusion-controlled reaction.⁶⁸

When one of the reactants is a microwave susceptor, such as in a mixture of K₂CO₃ and V₂O₅ (V₂O₅ is susceptor), decomposition of the carbonate and combination of V₂O₅ and K₂O does not require the presence of graphite. As noted earlier, the role of graphite in these preparations is as a secondary heater and this property of graphite can be fully exploited in any other similar situation provided the oxides are not reduced carbothermally by graphite. BaTiO₃ has also been prepared by the microwave irradiation of stoichiometric mixtures of respective metal-organics (Ba(OCOCH₃)₂ and Ti(OC₃H₇)₄).⁶⁹

Polycrystalline Y₃Fe₅O₁₂⁷⁰ has been synthesized by starting from Y₂O₃ and Fe₃O₄ mixtures and using a monomode microwave source and the reaction temperature has been found to be below 900 K. Microwave irradiation enabled preparation of YFe₂O₄ also in a similar manner.

A wide range of complex oxides are used as cathodes in lithium batteries.⁷¹ LiMn₂O₄ is a cubic spinel and is considered as an important cathode material. LiMn₂O₄ has been prepared using microwave irradiation of a mixture of LiI and MnO₂ in a DMO for just 6 min.⁷² The product is found to be high-purity monophasic cubic spinel. Iodine, which is liberated in the reaction, acts as an antioxidation shroud. However when Li₂CO₃ and MnO₂ are used as reactants, only a defect spinel phase is found to result after microwave irradiation.

Similarly, a stoichiometric mixture of CuO and Bi₂O₃, irradiated with microwaves for just 5 min, has been found to yield monophasic, tetragonal CuBi₂O₄. This compound is reported to have been tested as cathode in

Table 4. Microwave Susceptibility of Different Phosphates

compound	microwave exposure time	observations and inference	temperature reached in 5 min (K)
NaH ₂ PO ₄ ·2H ₂ O	7 min	the two coordinated water molecules get completely removed after 50 s; the third water fully leaves after 125 s and the material is melted within 150 s; the weight loss observed corresponds to three H ₂ O molecules	951
Na ₂ HPO ₄ ·2H ₂ O	9 min	no weight loss, no red hotness and no melting observed; not a good microwave susceptor	328
Na ₃ PO ₄ ·12H ₂ O	7 min	weight loss observed; found dehydrated, but no further microwave absorption noticed after 2 min; no melting or red hotness seen	365
KH ₂ PO ₄	9 min	no microwave absorption; no weight loss and no melting	316
(NH ₄) ₂ HPO ₄	8 min	no weight loss and no melting; not a good microwave susceptor	323

Li batteries using glassy electrolytes.⁷³ The conventional preparation of CuBi₂O₄ requires different stages of heat treatment and the total heating time of about 18 h with three intermittent grindings.

Microwave preparation of LiCoO₂ using metal–organics has been reported by Yan et al.⁷⁴ The synthesis involves an initial calcination at 673 K, and from the XRD pattern, it appears that the compound is formed even at this stage and microwave irradiation helps in further crystallization of the product.

The reaction between LiI and V₂O₅ has been used to produce an iodine shroud (referred earlier in preparation of SiC). This simple microwave reaction between V₂O₅ and alkali iodides was found to lead readily to the intercalation of alkali ion into the layered V₂O₅ resulting in the formation of alkali vanadium bronzes and liberation of iodine.⁷⁵ However, these bronzes appear to be characterized by significant cation disorder leading to intensity disparities of the XRD peaks compared to those prepared by conventional methods and need further annealing.

Preparation of phosphates and phosphatic materials generally involves long reaction times and high temperatures in conventional methods. But phosphates are not susceptible to microwaves and therefore it is difficult to use microwaves for the preparation of phosphates except when one of the other reactants is a susceptor. However, recently it has been found that crystalline NaH₂PO₄·2H₂O is a good microwave susceptor.⁷⁶ When NaH₂PO₄·2H₂O is irradiated by microwaves, heating occurs initially due to the presence of water of crystallization. This type of microwave susceptibility is common to most crystalline hydrates. But in the case of NaH₂(PO₄)·2H₂O the elimination of 2H₂O is followed by continued microwave heating, resulting in the loss of the remaining chemically bound (structural) water molecule. At this point the product, metaphosphate NaPO₃, attains a temperature of ~700 K, with a reasonably high microwave susceptibility of its own. NaPO₃ gets heated further to its melting temperature. Finally NaPO₃ melt attains a temperature of about 1000 K. These decomposition stages while heating have been identified by thermal analysis.

Initial microwave absorption in hydrated phosphates is likely to be due to rotational excitation of the H₂O molecules. Phosphates such as KH₂PO₄ and (NH₄)₂HPO₄ in which water of crystallization is absent do not couple to microwaves at all. The vibrational–rotational energy spectrum of water of crystallization appears to influence the microwave activity. Thus, for example, in Na₂HPO₄·2H₂O, where a proton has been substituted

by Na⁺ ion (in a chemical sense), the microwave susceptibility of the water of crystallization is reduced enormously and Na₂HPO₄·2H₂O does not dehydrate like NaH₂(PO₄)·2H₂O does under microwave irradiation. The behavior of some of the related alkali phosphates is summarized in Table 4. Na₂HPO₄·2H₂O is therefore unique in its microwave susceptibility and the nature of its heating in microwaves can be likened to a step-ladder in which the first stage of heating with the loss of two molecules of water of crystallization takes it to a temperature of ~500 K and the next stage of loss of water takes it to ~800 K due to increased tan δ. In the following stage, temperature rise occurs for the same reason (increased tan δ) and takes the phosphate to the molten state around 1000 K.

Phosphates of the general formula A_xB_y(PO₄)₃ where A is an alkali element and B is a transition element or Si or Ge are generally designated as NASICONs, which is an acronym for sodium superionic conductors and the archetypes, NaZr₂(PO₄)₃ and NaSiGe(PO₄)₃, have been good Na⁺ ion conductors.^{77,78} This class of crystalline phosphates possesses unique open structure and properties, like high ionic conductivity, low thermal expansivity, etc. They have also been considered as possible hosts for nuclear waste disposal. The conventional method of preparation of NASICONs involves several hours of controlled heating. It has now been found possible to prepare NaZr₂(PO₄)₃ and Na₃Fe₂(PO₄)₃ in less than 8 min of microwave irradiation in a DMO from mixtures containing Na₂HPO₄·2H₂O and the other oxides (ZrO₂ and Fe₂O₃) in proper stoichiometry. The XRD of the microwave-prepared products are shown in Figure 6.

(iii) Nitridation Reactions. There has been a revival of interest in nitrides because of the versatility of these materials. While Si₃N₄ and SiAlONs represent superior structural ceramics,^{79,80} GaN is a blue laser material⁸¹ and AlN is a superior material for substrates;⁸² GaN together with AlN and InN span wide semiconductor band gaps of 1.9–6.2 eV. They form complete (wurtzitic) solid solutions and, therefore, provide versatile semiconductors with tunable band gaps. TiN is similarly a well-known diffusion barrier material⁸³ in the form of coatings and is also used as gold-colored hard coating on a variety of consumer products. VN is used as a catalyst.⁸⁴ Nitrides in general, however, are relatively unstable compared to oxides at high temperatures, which accounts for their virtual absence in earth's crust. The unreactivity of N₂ is the main reason for the great difficulty encountered in the preparation of nitrides.

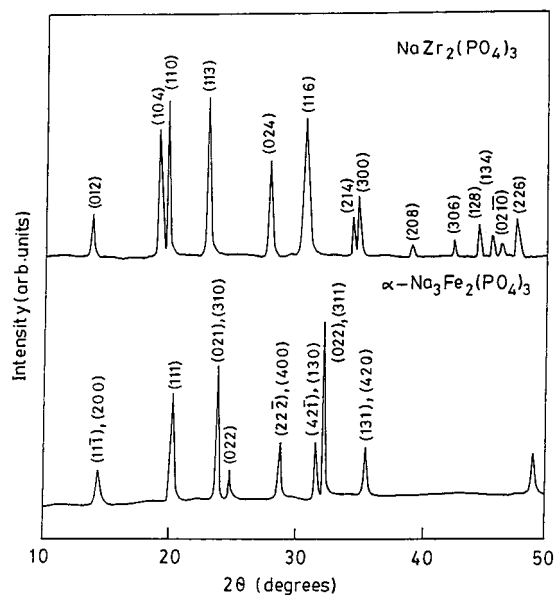


Figure 6. XRD patterns of microwave-prepared crystalline NASICONs. $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ couples well with the microwave raising the temperature and assists the reaction resulting in the formation of NASICONs (data from ref 76).

The rotational modes of N_2 may be expected to be excited in microwaves and help nitridation. NH_3 is also often used to introduce N into chemical compounds particularly when replacing O by N. NH_3 can also be expected to be microwave-active because of its rotational modes. It should therefore be anticipated that nitridation by the use of N_2 or NH_3 is assisted by microwaves. This approach has been used effectively for the preparation of nitrides of the third group elements and some of the industrially important nitrides of transition metals.

AlN has been prepared by a microwave method via direct nitridation of Al powder.⁸⁵ Al and charcoal powder mixtures taken in an all-quartz container with an attached inlet and outlet arrangement was microwave irradiated in a DMO in the ambience 99.999% purity N_2 . It was found that nitridation proceeded to about 40% in 15 min but no further. The partially nitrided mixture was taken out, ground well, and again subjected to nitridation in the same manner. It required six repeated grinding and nitriding operations for achieving complete conversion of Al into AlN. The X-ray diffractograms of the nitrided powders at various stages of nitridation were recorded. In Figure 7, the percentage of conversion and the actual time for nitridation are shown along with the X-ray diffractograms before and after the completion of the reaction. The repeated grinding and microwave irradiation leads to the formation of extremely fine powders, as noted from electron micrographs of the powders. The nanosized AlN particles appear as aggregates in the final product. The temperature of the reaction was not found to exceed 1173 K at any stage. This temperature is significantly lower than temperatures employed in conventional processes. The temperature of the charge was found to increase rapidly initially due to both the susceptibility of carbon and formation of eddy currents in Al particles. The nitridation, which occurred at the surface of each Al particle, resulted in the formation of a N_2 -impervious coating of AlN which therefore required grinding to expose unreacted Al to N_2 in subsequent stage of microwave

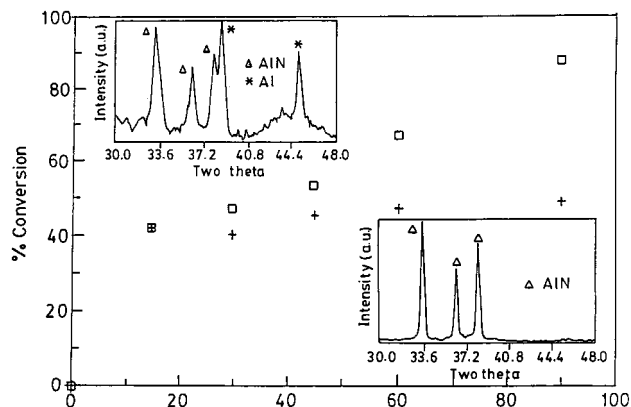


Figure 7. Amount of AlN formation with microwave exposure time. The reactants were subjected to periodic grinding by interrupting the reaction every 15 min. Top inset: XRD pattern of the product mixture after 15 min of microwave exposure (no grinding). Bottom inset: XRD patterns of the product mixture after 120 min of microwave exposure (eight grindings) (□, with intermediate grinding; +, without intermediate grinding). Single phase AlN is obtained only with intermittent grinding and reexposure to microwaves (data from ref 85).

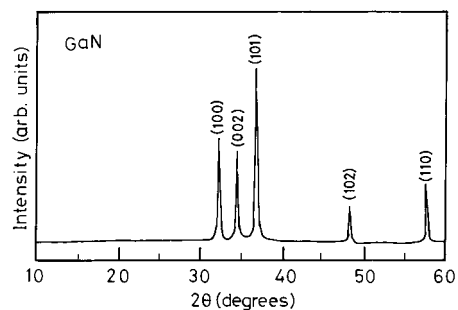


Figure 8. XRD pattern of the microwave-prepared GaN. The nitridation was complete only when NH_3 was used. Also, the reduction was possible only with amorphous carbon (data from ref 86).

irradiation. Since there was no evidence of melting and aggregation of Al, particularly since $2\text{Al} + \text{N}_2 \rightarrow 2\text{AlN}$ is a highly exothermic reaction, it appears that the high thermal conductivity of AlN coating could have quickly dissipated the heat to the surroundings. The nitridation occurring at metal surface may involve excitation of the $\text{N}\equiv\text{N}$ bonds but the mechanism of nitridation is still not clearly established.

Yet another approach to the preparation of nitrides with the use of a microwave is exemplified by the carbothermal reduction and nitridation using high-purity NH_3 .⁸⁶ In the case of GaN, for example, high-purity gallia (Ga_2O_3) was ground with an excess of high-purity amorphous carbon black and kept in a fused quartz container that was exposed to microwaves in a DMO, which allowed continuous flow of high purity NH_3 over the irradiated mixture. Due to the high microwave susceptibility of amorphous carbon, the mixture attained a high temperature within a short time. Gallia was completely converted to GaN (Figure 8). However, when N_2 was used in place of NH_3 , complete nitridation did not occur even after 35 min of exposure. As noted earlier, amorphous carbon attains much higher temperatures on microwave exposure than other forms of carbon and is a particularly powerful reducing agent. However, in addition to reduction (removal of oxygen),

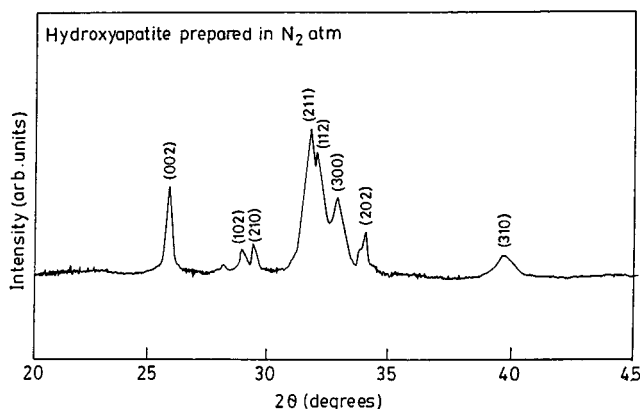


Figure 9. XRD pattern of microwave-prepared hydroxyapatite. The reaction was carried out with optimum microwave power and was over in less than 25 min (data from ref 87).

nitridation requires attachment of nitrogen to the gallium ions at the same time as reduction occurs. It is suggested that a plasma is created around the reaction mixture, through the coupling of NH_3 with microwaves, which may consist of species like NH_2^- and NH^{2-} . This increases electron density on nitrogen and creates a more favorable condition for the attachment of nitrogen to Ga^{3+} ions. Eventually other hydrogen atoms are eliminated and GaN is formed. However, no confirmation of the presence of amide (NH_2^-) or imide (NH^{2-}) has been made.

(iv) Reactions in Liquid Media. Reactions in aqueous media where microwaves play an important role is exemplified by the preparation of hydroxyapatite (HAp).⁸⁷ HAp is the inorganic material which composes the skeletal structure in living beings. It is also naturally available as an inorganic mineral. Stoichiometric apatite is a hydroxy phosphate of calcium with the formula $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ and is very useful for prosthetic applications.⁸⁸ The conventional preparation of HAp is an elaborate process in which solutions of $\text{Ca}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{HPO}_4$, and NH_4OH are reacted at high and critical values of pH for long times when HAp is precipitated.⁸⁹ The hydrothermal process of preparation of HAp is even more tedious.⁹⁰ This important bioceramic material is, however, prepared very easily by the microwave method. An aqueous suspension of a stoichiometric amount of $\text{Ca}(\text{OH})_2$ and a solution of $(\text{NH}_4)_2\text{HPO}_4$ are mixed together in a glass container and irradiated in a DMO. The power level is adjusted so as not to allow the solution to spill over while boiling off water. In less than 25 min, a fine, dry powder of HAp is formed. The X-ray diffraction pattern of the product compares extremely well with that of standard commercial samples (Figure 9); the IR spectrum clearly reveals the presence of a triplet band in the region of $550\text{--}650\text{ cm}^{-1}$, which is very characteristic of HAp (Figure 10). The fast reaction is attributed to the microwave coupling of water bound to Ca^{2+} ions in an aquation sheath. The rotational excitation of the water molecules by microwaves disengages them from Ca^{2+} ions. This has the effect of denuding the Ca^{2+} ions and enabling them to interact with the phosphate and hydroxyl ions much more readily than when they (Ca^{2+} ions) have to get out of the aquation sheaths by themselves. It almost mimics a soft chemical route in that the entire process occurs in an aqueous solution

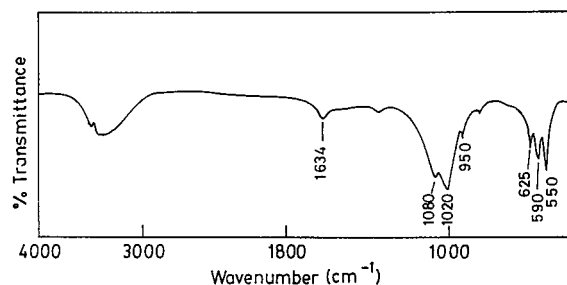


Figure 10. Infrared spectrum of microwave-prepared hydroxyapatite. The spectrum reveals the triplet band around $550\text{--}650\text{ cm}^{-1}$, which is characteristic of HAp (data from ref 87).

although microwave power has the effect of tearing away the water molecules from the calcium ions. Precipitation of nanosized hydroxyapatite using microwave irradiation from citrate–phosphate solutions (whose chemistry controls the growth kinetics of apatites) has been reported recently.⁹¹

An important application of the microwaves in the synthesis of materials from aqueous media is that of large pore zeolites and aluminum phosphates (AlPOs).^{92–95} Synthesis of zeolites is achieved through crystallization of aluminosilicate gels under hydrothermal conditions over long times. This stage of crystallization from the gel is found to be accelerated to a high degree by exposure of gels to microwaves. Synthesis of cloverite which is a large pore zeolite with ring openings of the size of $\sim 13.2\text{ \AA}$ and cavity diameters of up to 30 \AA has been achieved by exposure of appropriate gels to microwaves.⁹² It has been emphasized in this work that the initial step in microwave synthesis of zeolites is not just a simple replacement of thermal heating by microwave heating but it involves gel preparation with additional optimizations. The time required for crystallization of gels has been found to decrease from 1–2 days to 20 min with the use of microwaves. It has also been found possible to achieve isomorphous substitution (e.g., by Ti, Co, or Ni) or metal atom attachments inside the pores. The synthetic scheme used for the preparation of cloverite⁹² is reproduced in Figure 11.

Microwaves have also been used for the isomorphous substitution in AlPOs to introduce Brønsted acid sites at a very fast rate and with high efficiency. Indeed, large single crystals of AlPO-5 and cloverite have been synthesized by the use of microwaves. It has been shown recently that with the use of microwaves, Al-rich zeolites can be prepared within minutes.⁹² The absorption of microwaves has been attributed to increased dipolar nature in AlPOs, GaPOs (gallium phosphates), and Al-rich silicates, but the energy transfer from microwaves in Si-rich preparations is considered to be mainly through interaction with water. Several zeolites have been synthesized by combining pressure with microwave irradiation using Parr autoclaves. Microwave power levels were maintained at just 600 W, and less than 3 min of microwave exposure was found sufficient. Zeolites so prepared include sodium zeolite A, faujasite, and hydroxy sodalite.⁹²

Microwave treatment of gels made from potassium permanganate and maleic acid yielded cryptomelane at a lower temperature (593 K) than in conventional synthesis and in a much shorter time.¹⁸ It was also

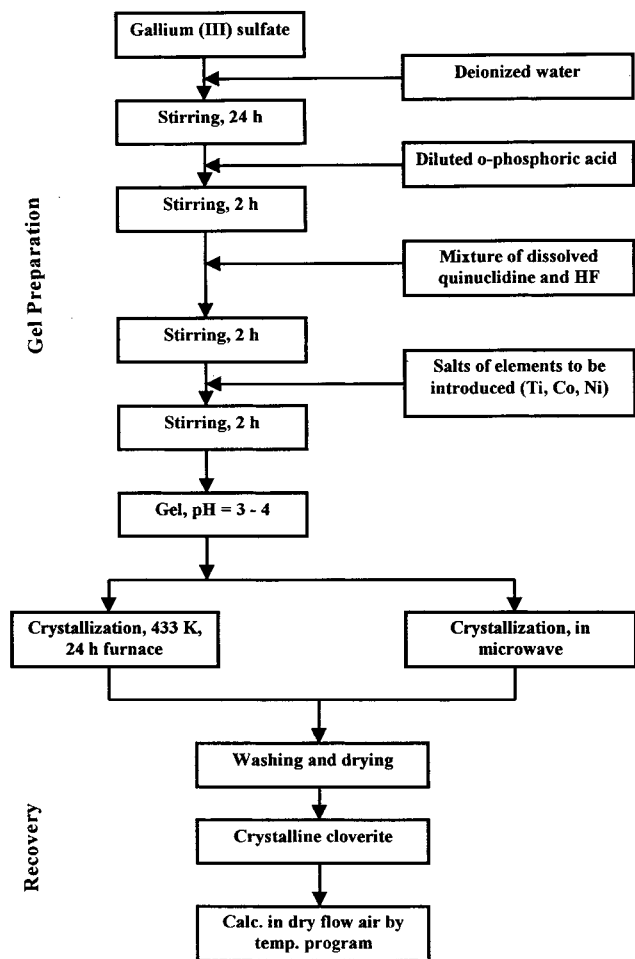


Figure 11. Microwave synthesis scheme of cloverite. The crystallization of gels takes approximately 20 min in microwaves. Also it is possible to achieve isomorphous substitution of metal atoms such as Ti, Co, or Ni. (data from ref 92).

found that the same gels yield bixbyite at a similarly lower temperature, compared to conventional methods. The rates of formation of cryptomelane and bixbyite is attributed to the presence of Mn^{4+} (MnO_2) which has a much higher microwave susceptibility and therefore helps in microwave-assisted crystallization.

The microwave heating method has also been used successfully for the preparation of layer and open structure compounds such as synthetic hollandite ($\text{K}_2\text{Mn}_8\text{O}_{16} \cdot n\text{H}_2\text{O}$) and synthetic todorokite (typically $\text{MgMn}^{2+}_2\text{Mn}^{4+}_{4.5}\text{O}_{12} \cdot 4.5\text{H}_2\text{O}$).⁹⁶ These are powerful catalysts, used for oligomerization of hydrocarbons such as methane, and are prepared in ~16 h of microwave heating compared to 4–7 days required by conventional methods. Microwave-prepared samples are found to be generally free of impurities such as bixbyite (Mn_2O_3).

Microwave irradiation in aqueous media has been used effectively in intercalation of pillared clays.⁹⁷ Recently, Al-intercalated montmorillonite has been prepared by irradiating montmorillonite clays suspended in water to which aluminum chlorohydrate was added and held in sealed tubes. A low microwave power level of 90 W was used for various times up to 15 min. Good quality, Al intercalated product, with greater surface area than the samples obtained by conventional methods, have been obtained.

Mingos and co-workers⁹⁸ found that $\alpha\text{-VOPO}_4 \cdot 2\text{H}_2\text{O}$ can be intercalated with pyridine, and its derivatives

at extremely fast rates in microwaves (2 orders of magnitude faster than in the absence of microwave irradiation). Intercalation reactions were carried out in Teflon containers and the maximum temperature employed was about 473 K. The microwave products were also far more crystalline than the products obtained by conventional methods. The rapidness of the reaction was attributed to an autocatalytic effect which operates as a consequence of better microwave coupling of intercalated products.

Intercalation of Li in transition metal sulfides has been achieved by using microwaves.⁹⁹ In these reactions, Li is introduced as butyllithium. Suspensions of the host transition metal sulfides (MoS_2 and TiS_2) along with butyllithium solutions in *n*-hexane and benzene were irradiated by microwaves at low power (350 W), and the temperature was maintained at about 333 K. The intercalation reaction was found to occur in 5–6 min in the case of MoS_2 , compared to more than 24 h in conventional method. Such a 100-fold increase in the rate of intercalation under microwave irradiation has also been noticed in intercalation of pyridine and substituted pyridines into layered $\alpha\text{-VOPO}_4 \cdot 2\text{H}_2\text{O}$; the intercalation was carried out at 473 K and a high pressure of about 50 atm.⁹⁸

(v) Preparation of Glasses. Glasses are prepared by quenching the corresponding melts. But the process of melting and homogenizing in conventional methods involves undesirable decomposition, oxidation/reduction of component oxides, loss of materials by evaporation, etc. Therefore the rapid heating attainable by microwave exposure can be expected to assist in glass preparation. The only requirement is that at least one component of the charge used for making glass is microwave-active. Many ionic materials are quite microwave-active because of the ionic current which cause coupling to microwaves. Therefore, rapid heating occurs with the use of microwaves when highly ionic compounds are present in any multicomponent glass composition. Once the components are melted which occurs very rapidly, within about 5 min in a DMO, the melts appear to couple to microwaves to a lesser extent (the dipolar relaxation times become much too short compared to 2.45 GHz frequency) and thus melts exhibit a temperature plateau which is insensitive to the power setting of the DMO. These temperature plateaus appear to be determined dominantly by the composition. The melts are then quenched in the usual way. Hence microwave heating has been particularly useful in preparing a variety of glasses. Microwave-prepared glasses reported in the literature include silver iodide containing fast ion conducting glasses as well as several plumbovanadate glasses, containing ZnO , MoO_3 , CuO , WO_3 , and Bi_2O_3 .^{100–102} Glasses with compositions corresponding to crystalline NASICONs have also been prepared by this method.⁷⁶ The microwave heating route being very fast helps avoid undesirable decomposition of the components, particularly when silver and copper salts are involved. The interesting feature of the microwave preparation is the temperature plateau that the glass-forming melts attain which acts as an automatic temperature control for the melt.

Solid electrolytes based on bismuth vanadate composition have been prepared recently with substitution of

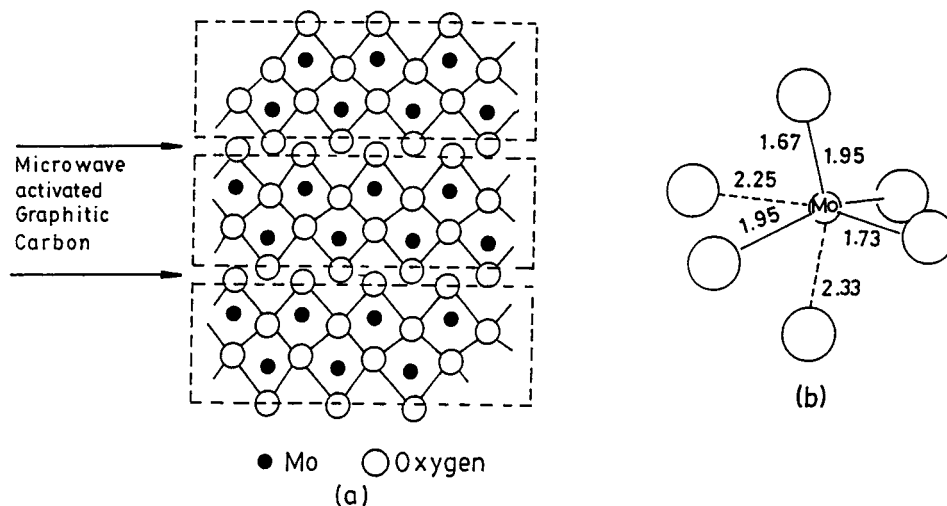


Figure 12. A schematic representation of the mechanism of microwave-assisted deoxidation; (a) Layered MoO_3 structure. Two layer blocks are shown. Oxygen atom between the layers is reacted away by carbon as marked. (b) The coordination of Mo atoms in MoO_3 . The longest bond has a Mo–O distance of 2.33 Å (data from ref 104).

vanadium sites by several lower valent ions, like Ag^+ , Mn^{4+} , Ga^{3+} , Y^{3+} , and Ce^{4+} . The resulting materials exhibit very high oxygen ion conductivities. The preparation involves exposure of the pellets made from mixtures of oxides taken in appropriate proportions to microwaves in a DMO for about 15 min.¹⁰³ The products referred to as BIMEVOXs were all found to have been stabilized in their high-temperature γ phases.

(vi) Selective Deoxidation Reactions. A very interesting application of microwaves is in bringing about highly structurally selective reduction reactions. It is observed that by microwave irradiation of mixtures of graphitic carbon and layered oxide materials the interlayer oxygens are rapidly and completely removed in very short irradiation times.¹⁰⁴ The resulting reduced oxides generally possess nonlayered structures and the reaction stops at the end of this stage of reduction. Thus MoO_3 (to MoO_2), CrO_3 (to Cr_2O_3), V_2O_5 (to VO_2), $\alpha\text{-VOPO}_4 \cdot 2\text{H}_2\text{O}$ (to VPO_4), and $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ (to $\text{Ag} + \text{MoO}_2$) were all found to reduce readily in microwaves in less than 5 min and at temperatures lower than 1000 K. Nonlayered oxides such as WO_3 , etc. are unaffected under identical conditions. This reduction is, in fact, a selective deoxidation which can be used as a very general strategy in microwave preparation of materials. The mechanism appears to be that carbon atom layers first emerge after the excitation of interlayer weak bonds in graphite and the sheet of carbon atoms themselves slip into the interlayer regions of the oxides, leading to reaction between the reactive sp^2 carbons and the weakly bound oxygens in the interlayer regions of the host as depicted in Figure 12.

(vii) Plasma-Assisted Reactions. Several microwave plasma-assisted reactions have been described in the literature and the subject cannot be adequately reviewed here. Only a few plasma-based synthesis reported in the literature are considered here. A number of nitrides such as TiN , AlN , and GaN have been prepared recently with the use of a plasma reaction starting from oxides by exposing them to a plasma of N_2/H_2 .¹⁰⁵

Microwave-assisted synthesis of binary (TiN , AlN , and VN) and ternary (Li_3FeN_2 , Li_3TiN_2 , Li_3AlN_2) ni-

trides have been reported where a direct reaction between metal powder and nitrogen was established by first striking a N_2 plasma for which a low power microwave source was used.¹⁰⁶ Ternary nitrides were produced by direct reaction of either the component nitrides or a mixture of Li_3N and metal powder again reacted in nitrogen plasma. However, it was also noted that sustaining a plasma in the domestic microwave oven is unfeasible. Microwave-generated N_2 plasma reactions have been used to demonstrate formation of Si_3N_4 and BN as well.

A rapid synthesis of alkali metal fullerenes has been reported by Douthwaite et al.¹⁰⁷ by using microwave-induced argon plasma. Reaction times appear to be reduced to only a few seconds while the conventional preparation takes a very long time. The microwave plasma was generated in argon held at a pressure of 10^{-5} mbar in evacuated quartz tubes. Fullerenes and alkali metals are kept physically separated, and the tube was so positioned that the microwave amplitude was highest at the position where alkali metal was kept. The alkali metal quickly heated and vaporized, and the C_{60} reacted with condensed K under the Ar plasma. Under these conditions, K intercalated easily. It was also confirmed that uncondensed K in the plasma did not intercalate. It has been shown by alteration of reaction conditions that there is a thermal action of the plasma which is responsible for the rapid synthesis.

Another interesting microwave plasma enhanced CVD process is the formation of films of carbon nitride compounds over Si wafers using an intermediate layer of Si_3N_4 . The plasma was first struck in a mixture of methane and nitrogen, and a negative dc bias was used to obtain a covering layer of carbon nitride.¹⁰⁸

Microwave applications for dispersing cobalt clusters in sodium zeolites using low-power microwave plasma of cobalt carbonyl vapors diluted with argon is well known.¹⁰⁹ Several possible mechanisms were suggested to be operative in these reactions which together lead to deposition of cobalt atoms in zeolite matrixes. Several of these mechanisms which operate in microwave plasma reactions were discussed by Sharp.¹¹⁰

Epilogue

In the preceding sections, a summary of recent reports on microwave-assisted preparation of inorganic solids has been presented. The microwave-synthesized materials encompass a wide variety of solids and most of them are of industrial and technological importance. The motivation for use of microwaves obviously has been to design cleaner, faster, and economically viable methods of synthesis. While the preparation of intended materials has been achieved, an understanding of the reaction mechanism in microwave field is still not satisfactory. Since it is a relatively new field of activity in materials chemistry, there is a growing volume of empirical knowledge about microwave-material interaction.

One of the most important issues in microwave applications for syntheses of materials is whether there is a genuine nonthermal effect of microwaves which Sutton¹¹ has most appropriately referred to as "microwave effect". It is observed almost universally that reactions occur faster under microwave irradiation than in conventional methods. Rate increases have been seen even in mineral leaching such as leaching of complex copper sulfide concentrates using FeCl₃ under microwave irradiation.¹¹¹ Several references were made earlier to the occurrence of microwave reactions at temperatures lower than in conventional methods. There have been careful studies to measure activation barriers in microwave-assisted reactions such as in sintering of Y₃Fe₅O₁₂ garnets. It was noted by Lin et al.¹¹² that very high densities (97.3%) were achieved at 1573 K within 20 min, while the conventional process required a temperature of 1693 K and a reaction time of 8 h. The activation energy in microwave sintering was found to be almost half (83.3 kcal/mol) of that observed in conventional sintering (163.2 kcal/mol), and this value is even lower than the barrier for grain boundary migration (94.8 kcal/mol). As a consequence, not only was the sintering process very rapid and very effective, but it also leads to extremely fine grains, a feature noted in ZrO₂-CeO₂ sintered products.¹¹³ Reduction in barrier heights appears to be a genuine microwave effect. But in liquid media, increased reaction rates under microwave irradiation has been carefully analyzed and attributed to a purely thermal effect since organic solvents such as ethanol have been found to be capable of being superheated under microwave irradiation by up to 26 °C.¹¹⁴ Although the temperatures of the reactions and the activation barriers are found to be lowered, exceptions have also been noted in the literature. For example, the transition temperature of BaCO₃ (at 811 °C) was found to be unaffected by microwave irradiation.¹¹⁵

A very thoughtful experiment was performed by Freeman et al.¹¹⁶ who examined the effect of microwave irradiation on ionic diffusion currents in single crystal NaCl, which were measured using varying external bias voltages. Diffusion current was found to increase when irradiated by microwaves. This increase was attributed to a rectified potential arising from the rectifying effect of uneven distribution of surface charge and the associated space charge polarization. The rectified potential is coupled to the microwave field. This indeed is a genuine microwave effect, since it produces a variation in transport coefficient under microwave irradiation.

This effect can manifest quite generally in a variety of microwave-induced reactions and processes such as microwave reaction of BaCO₃ + TiO₂, leading to formation of BaTiO₃ as noted by Zhang et al.⁶⁷ It is possible that when a plurality of pathways and activation barriers characterize a process, microwaves may abet that path which has the lowest activation barrier.

While analyzing the effect of microwave irradiation, it is tempting to draw parallels between the action of lasers and microwaves since they are just two regions of electromagnetic spectrum. In suitably designed microwave processes, it should be possible to exploit fully the aspect of coherence of microwave beams. Since the regime of rotational-vibrational excitations is central for chemical reactions, the role of microwave irradiation in chemical reactions can be readily appreciated. The very fact that the energy can be supplied where it is needed (a microwave coupling material can be introduced into the system by design) has opened up a veritable treasure trove for synthetic chemists. The observation that the temperatures of reaction in microwaves are almost always lower than in conventional processes, and correspondingly the activation energies are also significantly lower, are features of significance in developing synthetic strategies.

However, the reported literature suggests that no material has been prepared using microwaves which has not been prepared earlier by conventional methods. This aspect itself provides new opportunities and challenges in the field of microwave synthesis. Similarly, the use of pressure, coupled with microwave heating has been reported in only few cases (see earlier sections) since it requires development of nonmetallic pressure vessels that can stand both reasonably high temperatures and pressures. Such developments are bound to occur and enhance the advantages associated with microwave synthesis.

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