Russian Chemical Reviews **76** (5) 397 – 413 (2007) © 2007 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2007v076n05ABEH003650

Microwave-assisted synthesis of individual and multicomponent oxides

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Abstract. Data on the synthesis of individual and multicomponent oxides from salts with microwave initiation published over the last 15 years are analysed. The advantages and drawbacks of using microwave heating in the synthesis of oxide materials are noted. Criteria for the selection of chemical systems for microwave heating are proposed. The bibliography includes 162 references.

I. Introduction

The development of new synthetic methods that would allow decreasing the energy expenditure and increasing the rate of formation of the final multicomponent products is an important problem of modern inorganic chemistry and materials science. The rate of solid-phase reactions can be often increased by using the starting compounds in the active state (salt or hydroxide co-precipitation, cryochemical crystallisation, spray drying, hydrothermal treatment, *etc.*).[1] Another way for accelerating the reaction is additional treatment (apart from heating, *e.g.*, mechanochemical or ultrasonic treatment) of reaction mixtures, which intensifies diffusion processes *in situ*.[2,3] It is noteworthy that the physicochemical characteristics of the compounds synthesised using these approaches are not inferior to the characteristics of substances prepared by conventional procedures and, moreover, often surpass them.

Microwave heating of reaction mixtures is a promising method of increasing the rate of solid-phase reactions.[4–6] Microwave radiation is a non-ionising electromagnetic radiation with a frequency of 300 MHz to 30 GHz. Microwave heating is used to carry out important physicochemical processes such as dehydration, decomposition of salts and hydroxides, synthesis of multicomponent compounds and ceramics sintering. The time and energy expenditures in such processes are much lower than those in conventional processes. Moreover, in some cases, microwave treatment provides results that cannot be achieved by other methods.[7,8]

Microwave treatment has a number of advantages over the usual methods of heating of condensed media (solids and liquids), in particular, high speed and low inertia of heating, the absence of contact between the heated body and the heater, the uniformity of heating throughout the whole material bulk, the possibility of selective heating of mixture components and high oven efficiency (50% for the ovens with radiation frequency of 2.45 GHz and 85% for the ovens with radiation frequency of 915 MHz).[4–7]

The first studies dealing with microwave heating of materials were performed in 1967. Ford[9] carried out systematic research of the behaviour of oxides and sulfides under microwave heating at a 2.45 GHz frequency. Subsequently, the effect of microwave heating on many oxides[10] and natural minerals[11] has been studied.

During the last 10 – 15 years, the number of publications devoted to the use of microwave heating in various fields of chemistry has increased severalfold. In particular, the synthesis of individual and multicomponent oxides using microwave radiation were documented. Nevertheless, despite the considerable interest in this method, no attempts to generalise the accumulated experience in using microwave heating for the synthesis of oxide materials or to formulate the criteria for evaluating the efficiency of microwave heating for inducing various chemical processes have been undertaken as yet. This review is aimed to fill this gap at least partially.

II. Foundations of the theory of interaction of microwave radiation with the matter

In the electromagnetic radiation scale, the microwave radiation is situated between the IR radiation and radiowaves and corresponds to the wavelengths (λ) from $\sim$1 m to 1 cm.[12] The waves with frequencies of 1 to 30 GHz are actively used in radars and the rest frequency range is employed in telecommunication. On the basis of international agreement, frequencies of 2.45 GHz ($\lambda \approx 12.2$ cm) and 915 MHz ($\lambda \approx 32.7$ cm) were allocated for laboratory and domestic microwave ovens (Fig. 1).

Currently, the microwave heating theory has been fairly well developed.[6–9,12] In this review, we will restrict ourselves to a brief description of the principal mechanisms of absorption of microwave radiation by condensed matter, related to heat

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Received 1 June 2006
Uspekhi Khimii **76** (5) 435 – 453 (2007); translated by Z P Bobkova

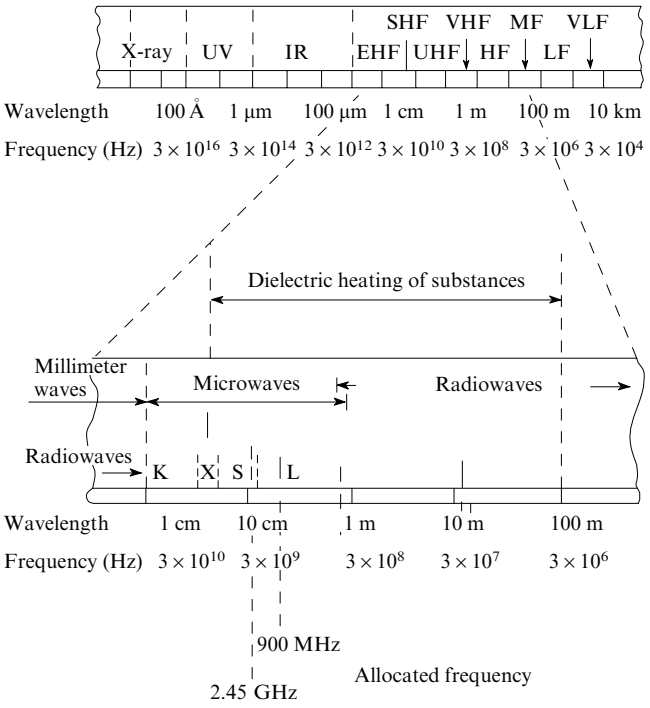


Figure 1. Electromagnetic scale.[12]
EHF are extremely high frequencies, SHF are super high frequencies, UHF are ultra high frequencies, VHF are very high frequencies, HF are high frequencies, MF are medium frequencies, LF are low frequencies, VLF are very low frequencies.

evolution due to dielectric loss on polarisation and to induced currents flowing in the material.

A set of microscopic processes of interaction of electromagnetic waves with charged particles of the matter can correctly be described only by means of quantum mechanical models. Nevertheless, for description of microwave heating, it is often sufficient to take into account the macroscopic properties of the absorbing matter, which are described in terms of classical physics.[11, 13–17]

Electromagnetic field affects the electric charges in the matter, which are usually classified into free and bound. Free charges can be carried by electrons, vacancies or ions able to move by macroscopic distances. Under the action of an external electric field, conduction currents appear in the matter due to free charge migration

$$\vec{J}_c = \sigma_c \vec{E}, \tag{1}$$

where $\vec{J}_c$ is the conduction current density vector, σ_c is the electrical conductivity of the matter, and $\vec{E}$ is the electrical field vector.

The migration of bound charges is confined to the microscopic size of an atom, a molecule or a crystal cell. Under the action of an external field, the bound charges are merely displaced from their equilibrium states giving rise to macroscopic polarisation. If no free charge carriers are present, the substance is a dielectric and its capacity for polarisation is determined by the relative dielectric permittivity (ε_b)

$$\vec{P}_b = (\varepsilon_b - 1)\varepsilon_0 \vec{E}, \tag{2}$$

where $\vec{P}_b$ is the polarisation vector resulting from bound charges (electrical dipole moment of the unit volume of the substance), $\varepsilon_0 = 10^{-9}/36\pi$ (F m^{-1}) is the dielectric permittivity of vacuum.

In the case of an alternating field, the displacement of the bound charges from the equilibrium states is time-dependent; this implies effective movement of charges and, hence, an alternating electric current

$$\vec{J}_b = \frac{\partial \vec{P}_b}{\partial t}, \tag{3}$$

where $\vec{J}_b$ is the polarisation current density.

Thus, in an alternating field, the separation of effects related to the migration of free and bound charges is rather arbitrary.

Currents of any nature in the matter give rise to heat evolution. In the case of high-frequency fields, it is convenient to use field period-averaged characteristics. Therefore, the expression for the power of heat source per unit volume (q) can be written as follows:

$$q = \langle \vec{J}\,\vec{E} \rangle, \tag{4}$$

where $\vec{J} = \vec{J}_c + \vec{J}_b$ is the total electric field density vector in the matter.

In general due to the inertia of free and bound charge carriers the conduction current and the polarisation vector lag behind the electric field in phase. These effects are often formally described using the so-called complex amplitude method in which all oscillating values are given by

$$\vec{E} = \mathrm{Re}\left[\vec{E}_\omega \exp(\mathrm{i}\omega t)\right], \tag{5}$$
$$\vec{J} = \mathrm{Re}\left[\vec{J}_\omega \exp(\mathrm{i}\omega t)\right],$$

etc., where ω is the field circular frequency, t is time, i is the imaginary unit, the values with the subscript ω designate the corresponding complex amplitudes. In the complex form, Eqns (1) and (2) are represented as follows:

$$\vec{J}_{c\omega} = \sigma_c(\omega)\vec{E}_\omega, \tag{6}$$
$$\vec{P}_{b\omega} = [\varepsilon_b(\omega) - 1]\varepsilon_0 \vec{E}_\omega,$$

where $\sigma_c(\omega) = \sigma_c'(\omega) - \mathrm{i}\sigma_c''(\omega)$ and $\varepsilon_b(\omega) = \varepsilon_b'(\omega) - \mathrm{i}\varepsilon_b''(\omega)$ are the complex values describing the above-mentioned phase lag of the conduction current and the polarisation vector behind the electric field strength. In the microwave range, the dependence $\sigma_c(\omega)$ and its imaginary part can be neglected for the vast majority of materials, taking that $\sigma_c(\omega) \cong \sigma_c$. The dependence $\varepsilon_b(\omega)$ and its imaginary part are determined by the type and properties of the bound charges in the dielectric and can be substantially different for different substances.

Within the complex amplitude formalism, Eqn (4) can be written in the form

$$q = \frac{1}{2}\omega\varepsilon_0\varepsilon''|\vec{E}_\omega|^2 = \frac{1}{2}\omega\varepsilon_0\varepsilon_b'\tan\delta|\vec{E}_\omega|^2, \tag{7}$$

where $\varepsilon'' = \varepsilon_b'' + \sigma_c/\omega\varepsilon_0$ is the imaginary part of the equivalent dielectric permittivity of a substance, ε' is its real part, $\tan\delta \equiv \varepsilon''/\varepsilon_b'$ is the dielectric loss tangent.

If the substance has pronounced magnetic properties, a term corresponding to the specific power of heat evolution caused by dissipative processes upon magnetisation should be introduced into Eqn (7)

$$q = \frac{1}{2}\omega\varepsilon_0\varepsilon_b'\tan\delta|\vec{E}_\omega|^2 + \frac{1}{2}\omega\mu_0\mu''|\vec{H}_\omega|^2, \tag{8}$$

where μ_0 is the magnetic permittivity of vacuum, μ'' is the imaginary part of the magnetic permittivity of the substance, $\vec{H}_\omega$ is the magnetic field strength complex amplitude.

It can be seen from Eqn (8) that the intensity of heat evolution in a sample being treated depends on many factors, in particular, on electrophysical properties of the material, the frequency and the intensity of the applied field. Note that this equation implies circumstantially the dependence of the heating efficiency on various parameters including the geometric size of the treated sample and the resonator cavity. As characteristics of the microwave treatment system largely depend the field amplitude in the sample, they also affect the heat evolution in its body. For irradiation of a sample with a flat electromagnetic wave with all parameters except ε'' being fixed, the highest heating power is observed at some ε'' value specific for the given substance. Below this value, the wave would pass through the sample without being significantly absorbed, while above this value, the wave would be largely reflected from the sample.

When selecting the conditions for microwave heating, it is important to take into account the depth of penetration of the electromagnetic wave into the substance under treatment. This factor greatly affects the distribution of the field amplitude in the sample and, hence, uniformity of heat distribution.[18–21]

If the depth of field penetration into the matter (δ_E) is defined as the distance at which the field strength decreases e-fold (e is the Napierian base), then

$$\delta_E = \frac{\lambda}{\pi\sqrt{2\varepsilon'(\sqrt{1+\tan^2\delta}-1)}}. \quad (9)$$

If $\tan\delta \ll 1$, then

$$\delta_E = \frac{\lambda}{\pi\sqrt{\varepsilon'}\tan\delta}. \quad (10)$$

Thus, an increase in frequency entails an increase in not only the heating power but, unfortunately, also in the heating non-uniformity; this may imply overheating of the outer layers of the sample. The penetration depth of the microwave field into material can vary over broad ranges, from several microns to several metres. For example, at 25 °C, the penetration depths of the radiation with 2.45 GHz frequency into copper and graphite are 2.6 and 38 μm, while those into epoxide resin and alumina are 0.73 and 187 m, respectively. If the geometric size of the sample is much larger than the penetration depth of the microwave radiation, heating of the sample will be non-uniform.

It is noteworthy that the δ_E value characterises the heat treatment depth only to a first approximation, because the field penetrates to a greater depth, and its energy may be sufficient for the required heating effect. The dielectric parameters of the matter, and, hence, the penetration depth depends on temperature and can change during heating. Thus, the depth of heat treatment during given technological process can be determined exactly by solving the problem of temperature field in the volume of sample. It is important not only to choose the optimal frequency and amplitude of the electromagnetic field, but also to select the resonator geometry.

In standard domestic microwave ovens with a rectangular resonator (these ovens are still used in most experiments), materials with medium conductivities, *i.e.*, semiconductors, oxides with mixed metal oxidation states, and some powdered metals, are heated more efficiently than good conductors (some metals) or dielectrics (oxides and halides) (Table 1).

This effect may be due to the fact that dielectric losses at room temperature are low for insulators; therefore, no effective heating takes place, although the microwave field penetrates to a high depth. In the case of metals, the microwave radiation is considerably reflected.[9] Thus, effective heating of substances with low or, conversely, high ε'' values requires selection of optimal geometric parameters of the resonator. It is often a complicated engineering problem.

Table 1. Efficiency of microwave heating of substances with different types of conduction (radiation frequency 2.45 GHz, power 800 W).[9,10]

Substance	Resistivity /Ω m	T/°C	Heating duration /min
Metal powders			
Al	10^{-8}–10^{-6}	577	6
Co	10^{-8}–10^{-6}	697	3
Cu	10^{-8}–10^{-6}	228	7
Fe	10^{-8}–10^{-6}	768	7
Mg	10^{-8}–10^{-6}	120	7
Mo	10^{-8}–10^{-6}	660	4
Semiconductors			
FeS_2	10^{-5}–10^{-3}	1019	7
PbS	10^{-5}–10^{-3}	956	7
$CuFeS_2$	10^{-5}–10^{-3}	920	1
Oxides with mixed oxidation states			
Fe_3O_4	10^{-4}–10^{-2}	1258	3
Co_3O_4	10^{-4}–10^{-2}	1290	4
NiO_x	10^{-4}–10^{-2}	1305	6
Graphite	~10	1300	4
Alkali metal halides			
KCl	10^4–10^5	31	3
KBr	10^4–10^5	46	1
NaCl	10^4–10^5	83	7
NaBr	10^4–10^5	40	4
LiCl	10^4–10^5	35	1
Oxides			
SiO_2	10^4–10^{14}	79	7
Al_2O_3	10^4–10^{14}	78	4
Salts			
$KAlSi_3O_8$	10^4–10^{14}	67	7
$CaCO_3$	10^4–10^{14}	74	4

In heterogeneous systems containing phases with different dielectric properties, an external electromagnetic field may produce charges at interfaces (the Maxwell–Wagner effect). It has been shown[22] that the simplest and most correct description for this type of polarisation is provided by the model of spherical particles of a highly conducting phase distributed uniformly in a dielectric. The reactive component of the dielectric permittivity of such a system can be described by the equation

$$\varepsilon_i'' = \frac{(9V\varepsilon\omega_{\max})\omega\tau}{1.8\times10^{10}\sigma(1+\omega 2\tau^2)}, \quad (11)$$

where V is the volume fraction of the dispersed phase; $\omega_{\max}$ is the circular frequency of the electromagnetic field corresponding to the maximum loss for the dielectric phase; τ is the relaxation time of the dielectric (the time span during which the system returns to the equilibrium state after removal of the electromagnetic field); σ is the conductivity of the dispersed phase. This model was verified experimentally using paraffin with dispersed isotropic particles of copper phthalocyanine as a semiconductor.[23] A good correspondence between the theoretical and experimental results was noted (Fig. 2).

Unfortunately, the contribution of the Maxwell–Wagner effect to the solid- and liquid-phase transformations occurring under microwave irradiation has not been quantitatively

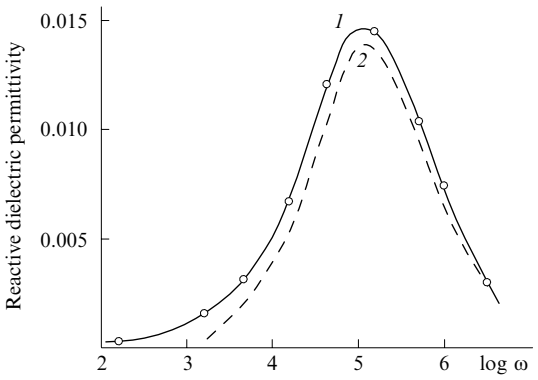


Figure 2. Frequency dependences of the reactive component of the dielectric permittivity of the copper phthalocyanine – paraffin system.[23] (*1*) Experimental data, (*2*) calculation by the Maxwell – Wagner model.

estimated as yet. Nevertheless, in some studies (see, for example, Ref. 12), it was suggested that surface polarisation is responsible for the so-called 'non-thermal' effects of microwave treatment resulting in acceleration of processes in a microwave field.

Apart from the above-described features of the propagation of microwave radiation and its interaction with the matter, an important role in microwave heating is played by thermophysical properties of the sample, because the efficiency and uniformity of microwave heating depend on not only the dielectric properties of the material, but also its ability to dissipate the evolved heat throughout the bulk. Thus a main cause of non-uniform heating is the sharp increase in the dielectric loss factor with temperature. The rate of heat dissipation in the sample bulk is insufficient, and areas with higher temperature characterised by more intense absorption of microwave radiation appear in the sample (the so-called 'hot spots'). Thus, despite the widely accepted view that microwave heating produces uniform dissipation of heat throughout the sample bulk (see above), one should thoroughly select the experimental conditions to avoid sharp temperature differences within the sample.[24–26]

When performing any experiments on microwave heating, it is necessary to take into account the following properties of the sample material.

1. Electronic and ionic conduction. There exists an optimal range of electronic conduction that ensures the most efficient interaction of the matter with the microwave field: good insulators are transparent for the microwave field, while substances with high electronic conductivity (metals) reflect microwave radiation. Analysis of published data on microwave heating of substances with high ionic conductivity demonstrated that these substances possess rather high absorption capacity. The absence of substances reflecting microwave field due to high ionic conductivity is attributable to the too low concentration of free ionic charge carriers and their relatively low mobility even in the best ionic conductors.

2. Dielectric permittivity and dielectric loss factor. There exists an optimal range for the dielectric loss factor, which determines the absorption capacity of a substance; an increase in this factor entails a decrease in the depth of penetration of the microwave field into the sample. Thus, the more efficiently the substance absorbs, the smaller is the sample that can be heated in a microwave field without formation of temperature gradients within the sample bulk. It should be borne in mind that at low temperatures the contribution of dielectric losses to microwave heating is quite insignificant for most of substances.

3. Heat conductivity. Heating of substances with low heat conductivity usually produces local overheating giving rise to above-mentioned 'hot spots', because the evolved heat has no time to dissipate uniformly throughout the bulk. Uniform microwave heating requires a relatively high heat conductivity of the sample. The more efficiently the substance absorbs and the more pronounced is the temperature dependence of the absorption capacity, the higher heat conductivity is expected for this substance.

Thus, one can define the main criteria for the selection of chemical systems for microwave heating and the range of problems that can be solved using this way of heat supply to condensed matter.

1. Non-uniform temperature distribution within the sample bulk can be avoided if the microwave-treated substance has rather high heat conductivity. In each particular case, it is necessary to determine experimentally the maximum dimensions of the sample of a given substance (or a mixture of substances) that can be heated uniformly throughout the whole bulk without formation of pronounced temperature gradients.

2. The substances that can be heated by microwave radiation should possess either a high dielectric loss factor (*i.e.*, they should contain mobile dipoles with a relatively high dipole moment) or a high electronic, hole or ionic conductivity at the experimental temperature. It is noteworthy that for specific conductivity of less than $\sim 10^{-5}\ \Omega$ m, the sample starts to reflect the microwave radiation. The dielectric properties depend on temperature and, hence, the absorption mechanism can change during heating not only upon chemical transformations in the sample, but also due to a change in the parameters of microwave radiation absorption by the sample.

It is evident that dipole fragments with zero effective charge have the highest mobility in the crystal structure. Among inorganic compounds, water meets best of all the above requirements (high mobility of molecules and high dipole moment). The Rehbinder classification, which is based on the work of isothermally reversible detachment of one mole of water from the material framework, distinguishes three main types of binding of water in solid systems: physicomechanical (for example, capillary water), physicochemical (for example, adsorption water) and chemical binding (water of crystallisation, hydroxy groups). Chemically bound water is most interesting for solving synthetic problems, because this is characterised by the highest energy of detachment from the crystal lattice (from 20 to 80 kJ per mole of H_2O approximately depending on the number of water molecules removed from the crystal structure), and the supply of this amount of energy often results in decomposition of the dehydrated substance. Thus, salt crystal hydrates and hydroxides appear promising precursors for the microwave synthesis of oxide compounds.

Analysis of published data on the use of microwave heating for the synthesis of inorganic compounds has shown that, despite the large number of publications, no information that allows predicting the efficiency of the use of microwave radiation for heat treatment of chemical systems is available. Most papers discuss experimental data; the choice of starting reactants for the synthesis is not substantiated, and the discussion of the results concerns the microstructure and the structure-sensitive properties of the products but does not include any fundamental conclusions about their dependence on the physicochemical properties of the starting compounds, the way of organisation of the reaction area, or on the mechanism of interaction of microwave radiation with the sample.

Therefore, of particular interest are papers dealing with the theoretical substantiation of the microwave action on a substance. In most studies of this type, augmentation of mass transfer upon microwave treatment is attributed both to uniform heating of the whole sample bulk and creation of the reversed temperature gradient and to specific 'non-thermal' mechanisms of microwave field action on diffusion processes.

A theoretical substantiation [27–29] of the 'non-thermal' activation of mass transfer under the microwave treatment has been proposed.† Consider one-dimensional diffusion of a substance in an alternating electromagnetic field. In this case, mass transfer equation has the form

$$\frac{\partial c}{\partial t} = D\frac{\partial}{\partial x}\left[\frac{\partial c}{\partial x} - U(t)\frac{\partial c}{\partial x}\right]. \quad (12)$$

The additional term $U(t)$ depends on external field parameters $U(t) = qE\cos(\omega t/kT)$, where q is the ion or vacancy charge, ω is the circular field frequency, k is the Boltzmann constant, T is temperature.

No analytical equation relating the rate of mass transfer to the electromagnetic field strength and frequency can be derived for the case of three-dimensional diffusion. However, approximate solution provides the conclusion that the most pronounced influence of the microwave field should be expected at an early stage of the solid-phase process and at short diffusion distances. As the time of action of microwave radiation increases, the process gradually becomes steady-state, and according to Bokhan,[27] the contribution of the electromagnetic field to the driving force of diffusion rapidly decreases. In conformity with this model, the diffusion fluxes in the matter are directed from regions with high electric field strength to regions with low electric field strength. The diffusion processes are fairly intense, resulting in redistribution of the electromagnetic field strength and, hence, in a change in the direction of diffusion fluxes. As a consequence, the rate of solid-phase processes increases and the temperature of the process onset decreases.

Unfortunately, this approach is too simplified for the mathematical modelling of processes taking place under microwave heating of solid systems, and the experimental verification of the assumptions made by Bokhan [27] is today impossible.

Another approach to the theoretical substantiation of the 'non-thermal' effects of microwave heating has been reported.[30–32] It was assumed that a high-frequency electromagnetic field should create fluxes of charged species (ions or vacancies) in the matter, their intensity being changed in parallel with the strength of the external electromagnetic field. Within the sample bulk, these fluxes counterbalance one another and the overall concentration of charged species remains spatially uniform; however, near the surfaces, discontinuity of the medium gives rise to harmonic oscillations of the charged species concentrations the frequency of which coincides with (or is close to) the electromagnetic field frequency (Fig. 3).

It has been asserted [30] that oscillations of this type produce uncompensated fluxes of charged species along any extended crystallite imperfections (free surfaces, phase interfaces or grain boundaries). In the opinion of the researchers cited, this is responsible for the fact that microwave treatment does not increase the rate of charged species migration, but creates an additional driving force for diffusion (F), which is defined by the following expression:

$$F = \frac{c_i}{c_i^0} q_i E, \quad (13)$$

where c_i is the concentration of the ith sort of charged species at the crystallite boundary under the action of an external electromagnetic field, c_i^0 is the concentration of the ith sort of charged species at the crystallite boundary in the absence of an external electromagnetic field, q_i is the charge of the ith sort of charged species.

† The information was partially gained from a Yu I Bokhan's private communication.

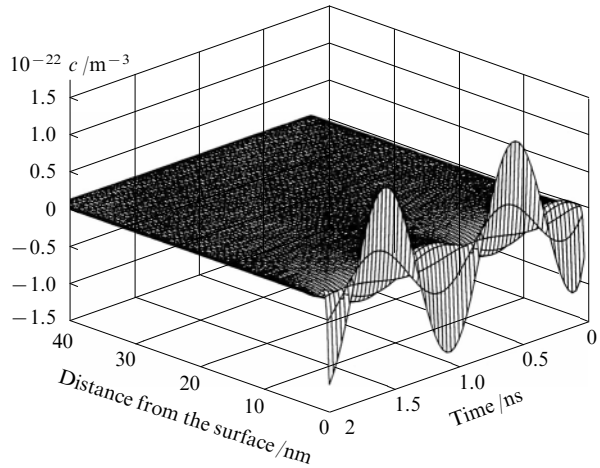


Figure 3. Time dependence of the variation of the concentration of charged species (c) near the surface and in the sample bulk upon the action of high-frequency electromagnetic field (calculated).[32]

According to this theory, the more dispersed the system under treatment, the stronger the 'non-thermal' microwave effects. The effect of an external electromagnetic field on the ionic current in the NaCl crystal was studied in order to confirm this hypothesis (Fig. 4).[32] It was stated that the experimentally detected change in the ionic current density in the NaCl crystal located in an external electromagnetic field is equal to the calculated gain in the ionic current induced by the microwave field.

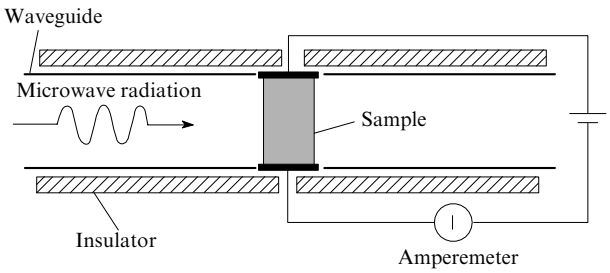


Figure 4. Setup for measurement of the ionic current in a NaCl crystal.[32]

It is clear that the proposed model of the 'non-thermal' microwave effects on the diffusion processes can hardly be practically verified. Indeed, it is not clear whether the experiment mentioned above (see Fig. 4) allows one to draw unambiguous conclusions about the change in the mass transfer mechanism during the solid-phase reaction under microwave heating. In any case, verification of this model requires additional experiments.

III. Design and key principles of operation of microwave heating systems

Almost all microwave heating facilities are designed according to a chart shown in Fig. 5. The microwave energy comes out of the source through transmission line and is directed to the working chamber into which the sample is supplied through a loading system. The fraction of energy absorbed by the sample depends on the sample size and electrophysical characteristics briefly considered above. The microwave treatment parame-

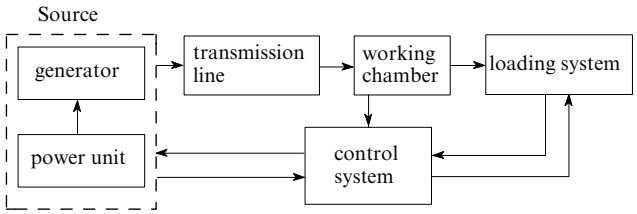


Figure 5. Microwave heating unit.[11]

ters are controlled by the control system. Some devices envisage a 'feedback', which allows the change in the supplied power during heating following a change in the sample temperature (or pressure in the case of treatment in an autoclave).‡

Currently there is no generally accepted classification of microwave heating facilities. Arkhangelskii [11] proposed a classification (Fig. 6) in which the power, the design, the mode of operation and the technological purpose of the setup were taken as the determining features. Detailed consideration of the operation principles and the possible designs of microwave heating devices is beyond the scope of this review; therefore, we will present only a brief analysis. More detailed information on this topic can be found elsewhere.[7, 11, 12, 19, 20] The designs and the main operation principles of magnetron systems will be considered in somewhat more detail, because most studies have been performed using domestic microwave ovens or devices based on them. An important part of the microwave heating device is the working chamber in which the sample is treated. When designing or choosing the working chamber, it is reasonable to consider its dimensions, the pattern of field distribution and type of transmission line as the principal parameters (Fig. 7).

Magnetron is used most often as the microwave radiation source for the synthesis and sintering of oxide materials. Among other sources, mention should be made of gyrotron

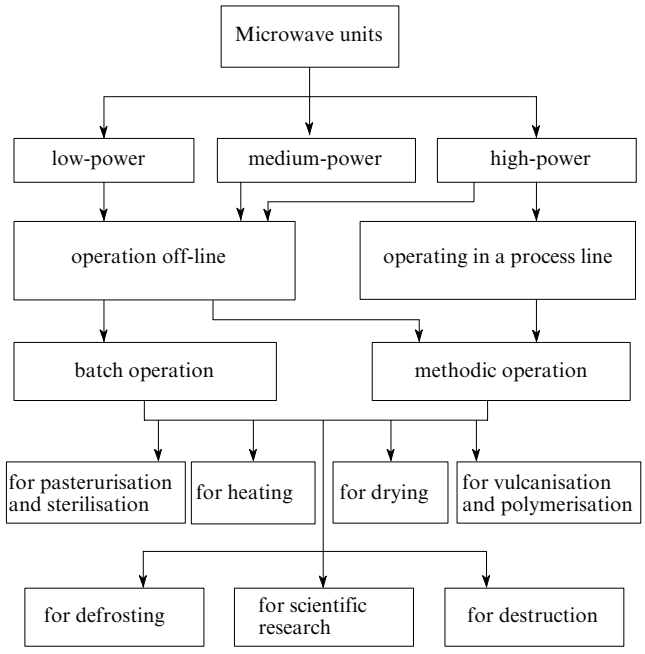


Figure 6. Classification of microwave heating units.[11]

‡ Unfortunately, commonly used domestic microwave ovens lack this feedback.

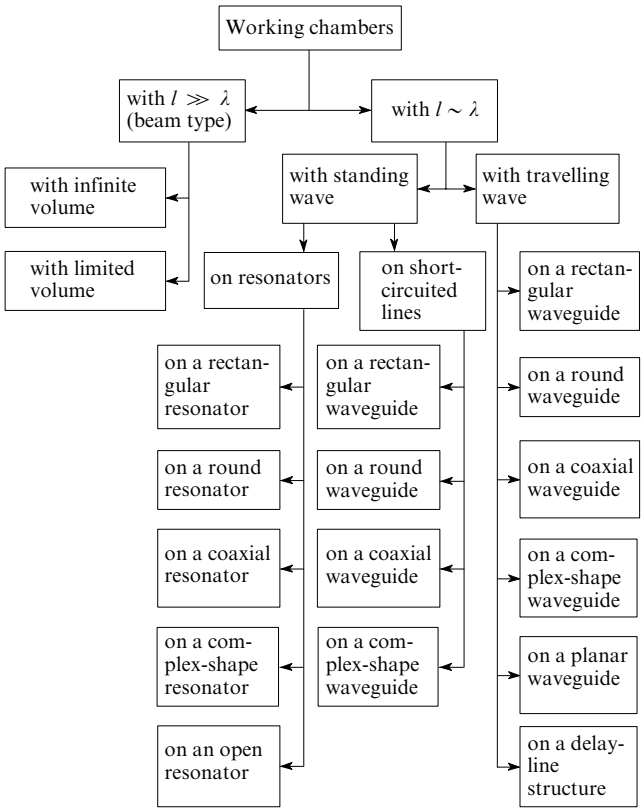


Figure 7. Classification of the working chambers of microwave heating units.[11]

systems with a radiation frequency of ~30 GHz designed at the Institute of Applied Physics of the RAS, klystron tubes and microwave triodes.[20] Due to the high radiation frequency, treatment in gyrotron systems is more efficient and less sensitive to the electrophysical characteristics of the material. The gyrotron microwave heating systems are fairly promising for syntheses and especially for sintering. Unfortunately, the complexity of the design and high cost of gyrotron systems hamper their extensive use in scientific practice.

On the one hand, devices based on domestic microwave ovens are used most widely, but on the other hand, they are least adapted for experiments under definitely specified and reproducible conditions. Therefore, it is expedient to consider the operation principle of domestic microwave ovens and the key parameters affecting the operation, in order to find whether it is possible to carry out experiments under controlled conditions in these ovens and what should be done to achieve this goal.

The magnetron used in domestic microwave ovens is a cylindrical diode onto which a magnetic field directed along the cathode is applied. The potential between the cathode and the anode representing a ring of linked cavity resonators reaches several thousand volt. In the non-adjustable magnetron, the oscillators are designed in such a way that they emit energy with a particular frequency. Most domestic microwave devices make use of non-adjustable magnetrons with an output frequency of 2450 ± 13 MHz. This magnetron consumes ~1200 W from the supply line; this is converted into a 600 W electromagnetic power output. The rest is converted into heat, which is dissipated by air cooling. The designs of magnetrons and other microwave emitters are described in detail in specialised literature (see, for example, Refs 7, 19 and 20).

In estimation of the power of domestic microwave systems, the averaged rather than the full output power of magnetron is

used. The magnetron duty factor, *i.e.*, the ratio of the time the magnetron is switched on (t_1) to the sweep time (t_s), is used for this purpose. Thus if $t_1 = 5$ s and $t_s = 10$ s, the duty factor is 0.5. Hence, in order to obtain the average radiation power of 300 W (half of the output power), the magnetron of domestic microwave oven should be switched on during some time t_1 and switched off during time t_2. Domestic microwave ovens usually have the sweep time equal to

$$t_s = t_1 + t_2 = 10 \text{ s}.$$

This long sweep time is undesirable for microwave heating of substances and materials, because with magnetron being switched off for a long period (5 s for a duty factor of 0.5), the loss of heat can be rather high. Most of laboratory microwave heating equipment have shorter sweep times, which is much more convenient for experiments, especially for heating of solids. Many modern facilities provide for the fine power adjustment without switching-off the magnetron.

The full output power of the magnetrons of domestic microwave ovens is usually about 600–700 W. A simple method for its determination is to measure the temperature of a fixed mass of water able to absorb almost all energy supplied to the resonator. Usually, the apparent output power is determined by measuring the temperature of 1 litre of water heated during 2 min at the full magnetron power.

Equation for the calculation of the apparent output power (P/W) has the form [4]

$$P = Kc_p \frac{\Delta T m}{t}, \tag{14}$$

where K is the conversion factor of the thermodynamic units cal min^{-1} into Watts; c_p is the specific heat capacity/cal deg^{-1}; $\Delta T = T_{\text{ф}} - T_{\text{и}}$ (the difference between the final and initial temperatures/°C); m is the sample mass/g; t is time/s. If the heated substance is water, Eqn (14) can be simplified

$$P = 35 \frac{\Delta T m}{t}, \tag{15}$$

where the numerical multiplier includes the conversion factor and water heat capacity. The correctness of power determination depends on the arrangement of sample inside the resonator and on the identity of the containers used. Since energy scattering by a dielectric and energy loss as radiation depend on temperature, the same initial temperature and approximately equal differences ΔT should be used. Power determination is most accurate if the initial temperature of water is equal to 20 ± 2 °C.

The output power of the magnetron is markedly affected by the overheating due to reflection of a part of radiation back to the magnetron. The modes that ensure energy transfer from one medium to another without reflection are called wave coupling match. A mismatch may result in magnetron overheating, loss of output power or even failure of the magnetron.[4] For magnetron protection in case of wave coupling mismatch and for reaching the required output power, devices that eliminate reflection of microwave radiation have been designed. Domestic microwave ovens are usually devoid of such devices, but they are stipulated in industrial microwave systems. The device used most often is the output circulator (ferrite valve or the Faraday isolator), which allows microwave radiation to propagate in the forward direction but directs the reflected radiation to an absorber located outside the resonator, which is a heavy ferrite rod where energy dissipates as heat without damaging the microwave device.[7] The magnetron-generated microwave radiation is transmitted to the working chamber (resonator) by means of a waveguide made of a reflecting material, for example, a metal sheet.

Considering the working chamber classification shown in Fig. 7, one can see that the working chamber of a domestic microwave oven is a rectangular resonator with stationary waves. In such devices, it is often rather difficult to achieve uniform heating of a sample. In most domestic devices, this problem is solved using a rotating sample holder (usually, as a dish). There exist rotating holders that continuously rotate by 360° and cyclic holders rotating in both directions by 180°. Alternating rotation is used when the sample has various detectors attached. Unfortunately, all these methods for equalisation of the field energy density throughout the resonator volume do not ensure uniform heat treatment of the sample.[11]

In conclusion of this Section, we will consider a highly important problem of temperature measurement during microwave heating of the sample. Correct measurement of the process temperature is a very complicated problem. A faulty way of introducing a temperature indicator and perturbations induced by the microwave field on the measuring instrument may give rise to substantial errors in the temperature measurement and, hence, in the evaluation of the efficiency of microwave heating.

The use of conventional bimetallic thermocouples is precluded under microwave heating conditions, because a high-frequency electromagnetic field generates additional currents in the thermocouple and induces disturbance on measuring devices. In addition, the introduction of a metallic item into the resonator changes the distribution of the microwave field power, which may result in local overheating.[4] The only solution to this problem is the use of a screened thermocouple grounded to the resonator wall. It is necessary to determine beforehand the position at which the thermocouple would not disturb the uniform distribution of microwave energy over the resonator volume. Currently, the patterns of electromagnetic field distribution over resonators with different geometries have been determined both experimentally and by calculations.

If the sample is relatively large, the gradients formed upon microwave heating preclude the possibility of accurate characterisation of the sample temperature using only one detector. Accurate temperature measurement requires a good contact between the sample and the measuring detector, which may pose problemss if the sample changes its volume or moves during the experiment. The use of other contact methods of temperature measurement is markedly complicated by such effects as indicator heating, screening and local overhearting at the site of detector contact with the heated body.[5,9] When optical devices are used for temperature measurement, it is necessary to establish an accurate correlation between the radiating power of the sample in the given wavelength range and the sample temperature. Apart from temperature, the radiation intensity depends on the state of the sample surface and on the sample homogeneity. If the optical device for temperature measurement and the heated item are separated by a barrier (for example, in domestic microwave ovens, the working chamber door is usually made of metallic grid), it is necessary to take into account attenuation of the radiation from the heated item, as part of radiation is absorbed by the barrier. It should be borne in mind that the attenuation factor depends appreciably on the radiation wavelength. These difficulties can be overcome by using a pyrometer, which measures the temperature based on the ratio of radiation intensities of the sample at two different wavelengths.

IV. Use of microwave heating for the synthesis of individual and complex oxides

It was noted above that microwave radiation is a promising alternative to usual heating for performing various processes including sintering, dehydration, decomposition of salts and hydroxides for the synthesis of individual and multicomponent

compounds, solid-phase and liquid-phase syntheses.[7] A rather well-developed theory allows one to predict how efficiently a particular substance will absorb microwave radiation. Nevertheless, in practice, it is very difficult to predict the system behaviour in a microwave field. This is mainly due to the fact that electrophysical characteristics that determine the absorption capacity of substances are highly temperature-dependent: as the substance is being heated in a microwave field, its absorption capacity continuously changes. Exact account of this phenomenon is complicated, and data on the temperature dependence of the absorption capacity have been fully accumulated to date only for a limited range of compounds. Apart from the electrophysical characteristics, the heat conductivity and heat capacity of substances and, in many cases, also their micromorphology also change during heating. The change in these parameters affects the absorption of the microwave energy by the substance. Elucidation of the influence of each of the listed parameters on the system behaviour in a microwave field is hardly possible; however, since these characteristics change rather smoothly and monotonically, the heating dynamics can be roughly estimated.

This task becomes much more difficult if chemical processes take place in the system during heating. Upon changes in the chemical and phase composition, electrophysical characteristics of the system change jumpwise and often uncontrollably. As the temperature rises, the sample properties also change. Therefore, it is almost impossible to predict the absorption capacity of the system in which a chemical reaction occurs. This accounts for the lack, in the vast majority of publications, of data on the system behaviour under microwave treatment or attempts at its targeted use for performing processes with allowance for this information.

From the chemical standpoint, sintering is the simplest process; it is not by chance that this application of microwave heating is best studied. Most often, sintering does not change the chemical or phase composition of the sample; the change in the absorption capacity is mainly due to a change in density and grain composition during heating. These characteristics change rather monotonically; therefore, in most cases, one can control sintering to achieve specified results.

Starting with the1970s, a large number of publications have been devoted to the use of microwave heating for sintering of various materials ranging from weakly absorbing compounds (Al_2O_3, TiO_2) to compounds that actively interact with the microwave field even at room temperature (SiC, TiB_2, B_4C).[33–66] The main advantages of microwave-assisted sintering include high rate and uniformity of heating. This gives rise to ceramics with a more homogeneous microstructure compared to ceramics produced by traditional methods.[67, 68]

Thirty years ago the first experiments on sintering of alumina and zirconia in a microwave unit with a radiation frequency of 2.45 GHz were carried out.[33] This demonstrated both the advantages (high rate of sintering, uniform heating of the whole sample bulk) and specific drawbacks (complexity of temperature measurement and risk of local overheating) of microwave heating. Subsequently, microwave sintering of β-alumina has been studied.[34, 35] It was found that microwave treatment leads to substantial (severalfold) decrease in the sintering time required to reach a nearly theoretical density of the material. Nevertheless, no fine-grain ceramics with a narrow grain size distribution have been obtained in these studies.

The temperature and time dependences of the density of yttrium and cerium oxide-doped zirconia samples during sintering in a microwave oven and in an electric resistance furnace have been considered.[36] In the case of low-temperature exposure, samples sintered in a microwave oven had higher density. Nevertheless, nearly theoretical densities are attained in both cases only at temperatures of about 1500 °C. Generally, the change in the time dependences of sample densities indicates that microwave-induced sintering proceeds at an appreciably higher rate. In addition, samples with equal densities are characterised by much smaller crystallites when sintered in a microwave field. Experiments on microwave field-induced sintering of alumina powders have been described.[37, 41, 42] It was shown that densities and microstructures of samples sintered in a microwave oven and in an electric resistance furnace are actually equal. Upon comparison of the results of these studies, one can suggest that the influence of microwave heating on the grain shrinkage and growth during sintering is manifested to a higher extent in substances with ionic conduction than in dielectrics. This probably can be attributed to intensification of diffusion processes caused by microwave field excitation of ionic currents in samples possessing ionic conduction.

Apart from papers devoted to microwave heating of alumina, titania and zirconia, a large number of publications dealing with sintering of oxide powders with complex compositions have appeared in recent years. Microwave radiation has been successfully used[44, 45] for sintering of lead zirconate titanate- and mixed niobium and magnesium zirconate-based powders (PZT and PMNT, respectively) used as piezoelectrics. Note that the use of a microwave system with a magnetron operating at 2.45 GHz[44] did not result in better ceramic properties compared to those obtained by conventional sintering techniques. Meanwhile, ceramics with much more uniform size distribution of crystallites was produced using a gyrotron system with radiation frequencies of 30 and 83 GHz. Microwave heating was also successfully used for sintering of nanocrystalline hydroxylapatite powders.[46] The compacted samples reached a density of 95% of the theoretical after a 5-min treatment and 98% after a 15-min treatment, and the microhardness of the ceramic samples was as high as 5.9 ± 0.8 GPa.[46]

Manganese nickel, nickel zinc and nickel copper zinc ferrite powders were sintered using a high-power (3 kW) microwave radiation with a 2.45 GHz frequency.[47, 48] The microstructure and the magnetic properties of the ceramic samples thus obtained were not inferior to the properties of samples annealed in a conventional furnace. The degradation during annealing is much slower for ceramics with a 'microwave' prehistory. The ceramics thus formed was used for the design of multilayer chips the magnetic properties of which were not inferior to the properties of chips manufactured using standard industrial processes, while the manufacture time was significantly reduced.

It is noteworthy that owing to the relative ease of changing the electrophysical characteristics of a sample during sintering, it is often possible to distinguish and describe the specific effects of microwave treatment. Many researchers noted a considerable decrease in temperature during microwave sintering with respect to control experiments carried out using an electric resistance furnace. The most significant result was attained by Janney and Kimrey,[52, 53] who managed to reduce the sintering temperature of an Al_2O_3 powder by 400 °C using radiation at 28 GHz. The decrease in the sintering temperature of ZrO_2,[54, 55] $ZrO_2-Al_2O_3$ composite ceramics[56] and $LaCrO_3$ (Ref. 57) was also reported. Similar results were obtained for sintering of ceramics based on oxygen-free compounds, for example, B_4N (Ref. 58) and Si_3N_4.[59, 60] Analysis of published data showed that the decrease in the sintering temperature is more pronounced at higher frequencies of electromagnetic radiation.[61, 62] A considerable decrease in the sintering temperature can be achieved for microwave heating of dielectrics or ionic conductors but not for electronic conductors, which suggests the influence of the microwave field on the diffusion processes taking place during sintering of powders.[5, 63, 64] Unfortunately, the validity of such assumptions largely

depends on the correctness of temperature measurement in the microwave field. In most cases, even using screened thermocouples and fibre optic systems for temperature measurement, one cannot state unambiguously that a significant lowering of the sintering temperature was attained during microwave heating. Indeed, a very thorough investigation of the sintering of stabilised ZrO_2 was carried out.[69] The sample shrinkage was monitored by dilatometric measurements *in situ*. It was shown that the microwave effect that cannot be reduced to the thermal component does actually exist; however, its contribution is moderate: under identical conditions, shrinkage in a microwave field to the same density as in the case of heat treatment takes place at a 50–80 °C lower temperature. In addition, the contribution of the 'non-thermal' factor decreases with an increase in the temperature. This was attributed[69] to the decrease in the field strength within the sample with an increase in the temperature. Thus, the results of studies published in Refs 52–57 appear to be not quite reliable, as the temperature measurement during sintering was, most likely, improper.

Many researchers totally deny the fact of lowering of the sintering temperature in a microwave field. For example, Levinson *et al.*,[65] who studied sintering of zinc oxide powders, did not notice any substantial difference between the sintering time in a microwave field and in an electric resistance furnace. In a study[39] devoted to the microstructure and the ionic conduction of yttrium oxide-doped ZrO_2 ceramics sintered in a microwave field, no significant differences were noted between the microstructures and properties of samples obtained by microwave treatment and in an electric resistance furnace, except for some decrease in the sintering time. In another publication,[40] it was concluded that the difference between the properties of ceramics obtained by microwave and conventional sintering is insignificant.

In view of these different opinions, one can suggest that the effect of microwave treatment on the sintering processes depends appreciably on the chemical nature of the sample, in particular, the type of conduction. On the one hand, microwave and thermal sintering of dielectrics and substances with considerable electronic conduction almost do not differ, but on the other hand, the rate of compaction of clear-cut ionic or hole conductors is much higher in a microwave field.

On passing to more complex processes, namely, to the synthesis of individual oxides by decomposition of salts or hydroxides, it is much more difficult to control the absorption properties of the sample and to identify the effect of microwave radiation on the processes. During the synthesis of individual oxides, microwave radiation is mainly used in order to obtain more uniform grain-size composition of the resulting powders and a smaller average particle size. A few papers are devoted to the synthesis of oxide particles with a controlled habit. For example, star-like Cu_2O particles were prepared by microwave-assisted treatment of a copper sulfate solution with sodium hydroxide in the presence of a complex composition containing a surfactant and ascorbic acid as the reducing agent.[70] Well crystallised copper oxide was prepared by hydrolysis at 95 °C. On the basis of these results, it was concluded that the particle size distribution and habit depend appreciably on the method of heating and on the concentration of a copper sulfate solution. Conventional heating gives rise to cubic copper(I) oxide crystallites with a rather broad size distribution. The use of microwave heating results in practically monosized star-like crystallites. An increase in the concentration of the starting solution of copper sulfate in both cases resulted in particles with a nearly spherical habit. This was attributed to enhancement of the homogeneous nucleation in the case of microwave heating, which suppresses secondary nucleation and promotes fast uniform growth of the nuclei.

The synthesis of zirconia powders by hydrolysis of aqueous ethanolic solutions of zirconyl chloride under microwave treatment has been described.[71, 72] The uniform heating of the whole bulk of the solution in the microwave field afforded ZrO_2 powders with spherical particles having a monomodal size distribution. It is of interest that, as in the study of Fetter *et al.*,[73] microwave heating resulted only in the tetragonal ZrO_2 modification. However, in another study,[74] the monoclinic modification formed under similar conditions.

Nanocrystalline tin(IV) oxide[75] and $SnCl_2$–graphite composites[76] were synthesised by hydrolysis of a saturated solution of tin(IV) chloride. The authors emphasised that tin oxide prepared by these procedures is formed in the nanocrystalline state only when microwave heating is used. In their opinion, this is due to acceleration of the olation–oxolation processes in amorphous precipitates under microwave treatment and also to the fact that owing to the uniform heat supply, nucleation predominates over the growth of nuclei.

The synthesis of NiO, ZrO_2 and CeO_2 powders by microwave-assisted hydrolysis of aqueous solutions of the corresponding metal salts in the presence of urea has been described.[77] It was shown that uniform heat supply to the heated solution produces oxide powders with spherical particles with a narrower size distribution compared to powders obtained by hydrolysis with conventional heating (Fig. 8).

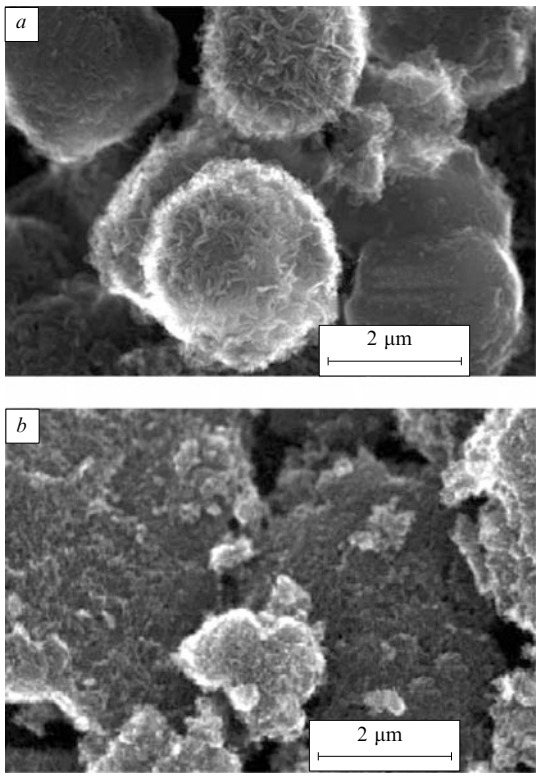


Figure 8. Microphotographs of ZrO_2 powders synthesised by hydrolysis of an aqueous ethanolic solution of zirconyl chloride in a microwave oven (*a*) and in a conventional furnace (*b*).[77]

Spatz *et al.*[78] prepared titanium dioxide nanoparticles from solutions of various titanium alkoxides in reverse micelles of polymeric molecules (Fig. 9 *a*). It was shown that the sharp decrease in the duration of the synthesis and selective heating of a microquantity of a titanium alkoxide solution inside the micelle allows one to avoid evaporation of HCl, which stabilises micelles, and thus prevent aggregation of TiO_2 nanoparticles in a polymeric matrix (Fig. 9 *b*).

In recent years, publications dealing with the synthesis of various nanodispersed materials by 'soft chemistry' techniques

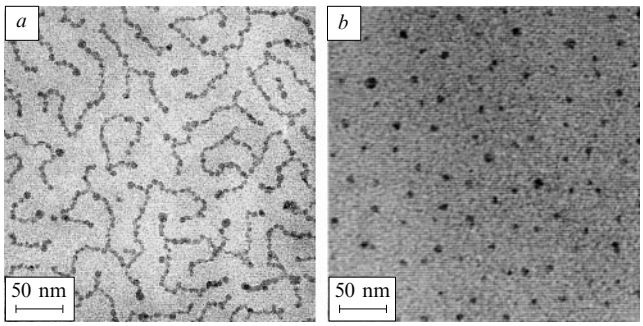


Figure 9. Microphotograph of titanium nanoparticle images in a polymer matrix synthesised in a conventional furnace (*a*) and a microwave oven (*b*).[78]

using microwave treatment have appeared more and more often. Many of these publications are devoted to the synthesis of various sulfides and nitrides,[79–85] but some works deal with the synthesis of nanosized oxides. For example, copper(II)-oxide-based nanostructures have been synthesised.[86, 87] The micromorphology of the obtained powders was shown to be substantially affected by the chemical nature of the initial compounds and the surfactant concentration. For example, hydrolysis of copper acetate in the presence of poly(ethylene glycol) affords virtually isotropic highly aggregated CuO particles, while hydrolysis of an aqueous solution of $CuCl_2$ in the presence of 1-n-butyl-3-methylimidazole tetrafluoroborate yields slightly aggregated nanowhiskers and nanoplates with a narrow size distribution. Note that by using microwave radiation, it is possible to increase substantially the rate of synthesis and increase the degree of crystallinity of the products.

High-temperature hydrolysis of an aqueous iron chloride solution in the presence of poly(ethylene glycol) and urea as the precipitating agent gave an Fe_2O_3 powder with a particle size of 3–5 nm.[88] However, despite the presence of a surfactant in the solution, powder particles were highly aggregated as shown by transmission electron microscopy. The results of magnetic measurements showed that, as expected, iron oxide nanoparticles occurred in the superparamagnetic state. During annealing at 400 °C, the oxide was crystallised to give α-Fe_2O_3; this was accompanied by an increase in the particle size to 30–40 nm. The researchers discussed the possible mechanism of formation of iron oxide upon high-temperature hydrolysis. According to calorimetric data, the following reaction takes place as an intermediate stage of the process

$$Fe(H_2O)_x(OH)_y^{(3-y)+} + H_2O \longrightarrow Fe_2O_3 \cdot n\,H_2O + H_3O^+.$$

More uniform heating of the solution exposed to microwave radiation favours the formation of a large number of hydrated oxide nuclei.

The synthesis of nanocrystalline SnO has been reported.[89] Hydrolysis of an aqueous solution of tin(II) chloride in the presence of ammonia as a precipitating agent afforded tin oxide powders with an average particle size of 30 nm and a specific surface area of ~ 40 m^2 g^{-1}. It is of interest that unlike usual heating, microwave heating almost does not induce the oxidation of Sn^{2+} ions to Sn^{4+}. This was attributed to the fact that, as shown by additional experiments, tin(II) oxide absorbs microwave radiation much more intensively than tin(IV) oxide. The researchers also noted that it was impossible to establish the exact mechanism of the specific 'non-thermal' microwave radiation effect in this experiment. The study cited [89] is a rare example of successful use of the above-discussed change in the absorption capacity of the system upon the change in its phase or component composition.

The synthesis of nanocrystalline SnO_2 by hydrolysis of an aqueous solution of tin(IV) chloride in the presence of urea has been described.[90] Highly aggregated powders with a crystallite size of ~ 3 nm were obtained. During the subsequent annealing of these powders, regular particle coarsening and coalescence take place up to micron-size aggregates. The advantage of using microwave radiation is reduced in this case to an increase in the hydrolysis rate.

The synthesis of $Mg(OH)_2$ nanofibres by hydrolysis of a solution of magnesium hydroxide with a highly dilute aqueous solution of sodium hydroxide supplied through a semipermeable membrane has been reported.[91] Microwave radiation with a relatively low power (20 W) was used and hydrolysis took place at room temperature over a period of 5 days. Owing to these mild conditions, well crystallised magnesium hydroxide powder with 100–150 nm-long and 20–40 nm-thick nanofibre-shaped particles was obtained. The control experiments carried out under similar conditions without microwave heating gave virtually isotropic crystallites with a broad size distribution. Unfortunately, the authors [91] did not discuss the possible mechanism of action of microwave radiation on the crystallisation and the growth of crystallites in this system.

Analysis of the effect of the crystal structure of reactants and the phase composition of the reaction mixture on the intensity of absorption of microwave radiation has been reported.[92] The author was able to establish the relationship between the crystal structure and absorption capacity of various modifications of Al_2O_3. In particular, it was shown that, owing to the presence of structure-bound water molecules in the mullite-like modification of alumina formed upon hydrolysis of aluminium salts in the presence of alkali metal ions, this compound absorbs microwave radiation much better than α-Al_2O_3 (this oxide is almost transparent for microwave radiation; therefore, it is used for heat insulation of samples during microwave heating). Using this effect, it was possible to perform one-stage synthesis and sintering of β-Al_2O_3-based ceramics without additives that absorb microwave radiation, which are usually added for microwave sintering of alumina-based ceramics.

Microwave heating is also successfully used for sol–gel processes. Thus microwave-induced crystallisation of the SiO_2-TiO_2 xerogel gave [93] the phase TS-1 used as a molecular sieve. Crystallisation was shown to proceed at a much higher rate than crystallisation induced by conventional heating (Fig. 10) and the microstructure and the catalytic properties of the product were not inferior to the properties of samples synthesised with conventional heating.

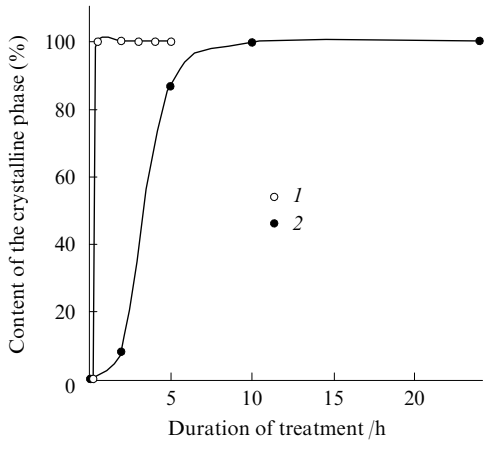


Figure 10. Crystallinity of the TS-1 sample *vs.* residence time in a microwave oven (*1*) and a conventional furnace (*2*).[93]

The sol–gel synthesis of zirconia-based catalyst powders with copper oxide dispersed over the surface has been reported.[73] The effect of pH and the duration of microwave heating on the micromorphology and the catalytic activity of the synthesised powders was established. Upon conventional heating during the sol–gel process, particles of tetragonal ZrO_2 are formed only in the pH range from 3–4 to 13–14, while in the case of microwave heating, these particles are formed irrespective of the pH of hydrolysis of the zirconium n-butoxide solution. Unfortunately, the authors offered no interpretation for this finding. Note that the above result [73] is at variance with the generally accepted view stating that diffusion processes are intensified in the microwave field, because this field eliminates the kinetic and diffusion hindrance to the metastable modification–stable modification transition. It was also shown that the use of microwave heating results in a more even distribution of copper oxide over the ZrO_2 surface, which in turn results in an increase in the catalyst acidity.

Several papers [94–96] devoted to the synthesis of highly dispersed cerium dioxide-based catalyst powders using microwave heating have been published. The first of the cited publications represents an attempt to use microwave and ultrasonic treatment for the targeted formation of the micromorphology of cerium dioxide powders prepared by hydrolysis of aqueous solutions of $(NH_4)_2Ce(NO_3)_6$ in the presence of surfactants. As in the studies cited above,[89–91] microwave-induced high-temperature hydrolysis yielded spherical oxide particles with a rather narrow size distribution. The average particle size was 2–3 nm. Analysis of electron diffraction data showed that the powders were composed of well-crystallised cubic CeO_2 phase. The specific surface area measured by the low-temperature nitrogen adsorption technique was equal to 200–250 $m^2\ g^{-1}$. Powders with approximately the same micromorphology were synthesised using ultrasonic treatment with conventional heating. The width of the band gap in the resulting nanopowders was 5.5 and 4.1 eV for samples synthesised with ultrasonic and microwave radiation, respectively; that of coarsely crystalline cerium dioxide is 3.19 eV. It is worth noting that the widths of the band gap in the samples with approximately equal average particle sizes obtained by different methods are essentially different. This was attributed [94] to activation of the surface of particles formed under the action of ultrasound caused by the collapse of cavitation bubbles and formation of microstreams during the sonochemical treatment. The key drawback of this procedure is inevitable contamination of the surface of oxide particles by the surfactant, which would obviously have an adverse influence on the catalytic activity of cerium dioxide.

Solid solutions based on cerium dioxide with partial substitution of zirconium and samarium atoms for cerium were synthesised by thermal and microwave-assisted decomposition of the corresponding nitrates mixed with urea,[95] glycine, alanine and citric acid.[96] Presumably, the mechanism of this process is similar to the mechanism of SHS synthesis where metal nitrates act as internal oxidants and urea is the reducing agent. As expected, the oxide particles formed had an order of magnitude greater average size than the particles obtained by Wang *et al.*[94] (according to X-ray diffraction data, the average particle size was 10–20 nm and the specific surface area was 40–60 $m^2\ g^{-1}$). An increase in the rate of formation of the oxide phase under microwave radiation was noted.[95,96] In addition, the effect of the chemical nature of the internal reducing agent on the micromorphology of the oxide powders formed was analysed.[96] It was noted that the use of citric acid markedly decreases the average particle size (to 6–8 nm); unfortunately, this result was not interpreted.

Hydrothermal synthesis deserves particular attention as an application of microwave radiation in inorganic chemistry. Microwave heating was used for the hydrothermal process to prepare nanocrystalline strontium, barium and lead titanate, zirconate and niobate powders possessing piezoelectric properties,[97–99] zinc, nickel and manganese ferrites,[100] various ferrates and bismuthates,[101,102] layered double hydroxides,[103] zeolites and molecular sieves [104–106] and metal powders.[107]

As advantages of the microwave-assisted hydrothermal synthesis, most of the cited authors list high rates of phase formation and processes in a microwave field caused by both heat supply features and the possible acceleration of nucleation due to 'non-thermal' effects. Thus an order of magnitude higher rate of formation of $LiMnO_2$ under microwave heating of hydrothermal solutions of lithium hydroxide and Mn(O)OH with respect to conventional hydrothermal synthesis has been noted.[108] It was shown [109] that by varying the duration of microwave action, one can control the morphology of the resulting powders. In addition, some hydrothermal processes carried out with microwave heating gave new phases that could not be obtained by conventional methods. For example, titanium and tin phosphates were first synthesised in this way.[106]

A promising trend in the use of microwave action is the combination with the sol–gel process. The uniformity and high rate of microwave heating favour fast decomposition of the gel with the formation of powders with narrow particle size distributions. For example, barium molybdate was prepared by precipitation of citrate gels followed by thermal and microwave-induced decomposition.[110]

The effect of parameters of microwave radiation on the synthesis of layered double hydroxides with hydrotalcite structure by co-precipitation from aqueous solutions of nitrates followed by microwave treatment of the resulting gels has been studied.[111] The authors were able to prepare layered magnesium aluminium double hydroxides with different cation ratios. For this purpose, they varied the duration and power of microwave action. It was found that the use of microwave heating increases the gel crystallisation rate, which is in line with the assumption of intensification of diffusion processes in a microwave field. Interestingly, the variation of the microwave power is accompanied by parallel variation of the cationic composition. As the power of microwave radiation (W) increases, the Mg : Al ratio in the final product approaches the rated one.§

W/W	200	400	600
Mg : Al	5.53	4.54	3.62

This fact was attributed to different diffusion mobility of ions. The researchers also noted [111] that an increase in the power and duration of microwave heating induces the formation of powders with smaller uniform particles.

The synthesis of $LiCoO_2$ and $Li_2Mn_2O_{4+\delta}$ powders (used for the preparation of cathode materials) from mixtures of lithium hydroxide hydrate with cobalt (Co_3O_4) and manganese (MnO_2) oxides has been described.[112,113] It was noted that as regards the particle size and shape, the products of microwave synthesis do not differ much from the powder particles prepared by conventional heating at the same temperature. In both cases, the powder morphology is determined by the morphology of the starting oxides (Fig. 11).

The microwave heating of co-precipitated nickel and aluminium hydroxides was used to prepare nickel aluminate.[114] The microwave-induced decomposition of hydroxides yields a single-phase porous nickel aluminate consisting of finely dispersed particles. The attempt to prepare nickel aluminate from gels obtained by hydrolysis of aluminium alkoxide in the presence of nickel nitrate failed: according to

§ The rated ratio of magnesium to aluminium cations is 3.

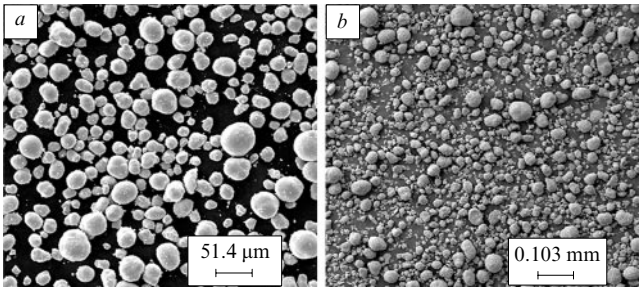


Figure 11. Photomicrographs of initial MnO_2 powder (*a*) and $Li_2Mn_2O_{4+\delta}$ powder synthesised in a microwave oven (*b*).[113]

IR spectroscopic data, the amorphous intermediate formed upon microwave heating of the gel contained a lot of nitrate ions. Unfortunately, no explanation for the difference between the mechanisms of interaction of various initial mixtures with the microwave field is given in the paper.

Nickel aluminate was synthesised by microwave-assisted decomposition of co-precipitated hydroxides.[115] Despite the fairly long microwave treatment of the mixture, the final product was rather poorly crystallised, which is unusual for microwave heating.

The solid-phase reactions between substances that poorly absorb microwave radiation at room temperature are often carried out, like sintering, using the so-called 'hybrid' microwave heating, which implies addition, to the reaction mixture, of a compound that actively absorbs microwave radiation and provides the primary heating of samples. Amorphous carbon or graphite, silicon carbide, copper(I) and copper(II) oxides, MnO_2, $MoSi_2$, *etc.* are normally used as such additives. Two methods are used most often to introduce the additive, namely, mixing of reactant powders with the powdered absorbing substance and placing the sample into a container made of the absorbing material. Both methods have advantages and drawbacks. Mixing of the reactants with the absorbing additive ensures faster and more uniform heating of the sample; however, there is a risk of contamination of the final product. Placing of the sample into an absorbing container, although decreases the probability of formation of by-products, actually levels-off all the advantages of microwave heating, because in this case, as during of conventional heating, heat is mainly supplied to the sample from the container walls.

Despite these drawbacks, the 'hybrid' microwave heating procedure has found wide use and was employed to synthesise numerous oxide compounds. For example, magnesium aluminate with the spinel structure was prepared by solid-phase reaction of aluminium hydroxide and magnesium oxide in the presence of carbon.[116] The optimal amount of the absorbing additive (50 mass %) was found and the micromorphologies and sintering characteristics of powders obtained by microwave and conventional heating were compared. It was shown that the use of microwave heating not only markedly reduces the duration of synthesis but also results in the formation of powders with higher sintering ability. The same method was used to prepare Sr_2CeO_4,[117] $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-x}$ (Ref. 118) and $Li_{0.35}La_{0.55}TiO_3$.[119] In all studies, appreciable acceleration of the solid-phase synthesis upon the use of microwave treatment was noted.

Solid-phase synthesis of a number of niobates and titanates from oxides and salts in the presence of graphite to absorb microwave radiation was carried out.[120] It was noted that the use of microwave heating reduces the duration of synthesis of these compounds by 1–2 orders of magnitude. This pronounced acceleration of a solid-phase reaction can hardly be attributed to high uniformity and rate of microwave heating alone; however, researchers [120] did not make any assumptions on this issue.

If a component of the reaction mixture actively absorbs microwave radiation at room temperature, the reaction can be carried out without an absorbing additive. However, it should be noted that the reactants and products have different absorption capacities, which gives rise to local temperature differentials in the system. This effect was studied in detail [121] in relation to the solid-phase synthesis of barium and yttrium ferrites and nickel aluminate from the corresponding oxides. Each reaction mixture consisted of an oxide efficiently absorbing microwave radiation and a weakly absorbing material (Fe_3O_4 and $BaCO_3$, Fe_3O_4 and Y_2O_3, NiO and Al_2O_3, respectively). In the researchers' opinion,[121] the particles of highly absorbing oxides functioned as heat sources in the microwave field, while weakly absorbing particles were heat receivers. A permanent temperature gradient was established in the reaction area, which, in turn, resulted in redirection of diffusion fluxes during the solid-phase interaction. Control experiments with the Y_2O_3 and Fe_3O_4 diffusion pair have shown, first, that the difference between the reactant temperatures reaches, in the limiting case, 400 °C, and, second, the diffusion flux is inverted with respect to that observed with conventional heating, in particular, iron ions diffuse in yttrium oxide. It is not quite clear what makes the authors confident that in the case of conventional heating, yttrium ions diffuse into the Fe_3O_4 structure. (In a study [122] dealing with the mechanism of ferrite formation under conventional heating, diffusion of iron ions into yttrium oxide is considered to be the predominant process.) Nevertheless, this study is of interest for elucidation of specific effects of microwave heating during solid-phase reactions. The diffusion flux is directed from the higher-temperature region to the 'cold' region. If the reaction product actively absorbs microwave radiation, this additionally intensifies the subsequent interaction. The substantial acceleration of solid-phase reactions under microwave treatment observed by many researchers was attributed to this fact.

It is quite probable that the temperature gradient formed during microwave heating of the reaction mixture between reactants with different absorption capacity has actually a considerable effect on the course of reactions, because most data on the acceleration of solid-phase processes concern systems containing both highly and poorly absorbing components. These processes include the preparation of alkali and alkaline-earth metal and lanthanide ferrites, manganites, cobaltites, vanadates, molybdates and cuprates. Uematsu *et al.*[123] synthesised Eu^{3+}-doped yttrium vanadate from the corresponding oxides. They also studied the dynamics of absorption of microwave radiation by the reaction mixture depending on the dielectric properties and conductivity of the reactants and the products. It was found that yttrium and europium oxides, like yttrium vanadate, poorly absorb microwave radiation, whereas vanadium oxide intensively absorbs microwave radiation even at low temperatures. After completion of the synthesis, temperature sharply drops, apparently, due to the disappearance of highly absorbing vanadium oxide from the reaction mixture. The authors recommended the use of microwave heating for performing solid-phase processes in which the reactants efficiently absorb microwave radiation, while the products, conversely, are transparent for microwaves.

Yet another approach to the investigation of the mechanisms of solid-phase interactions during microwave heating has been developed [124] in relation to the kinetics of the reaction between barium carbonate and titanium dioxide under quasi-polythermal conditions (samples were heated as fast as possible to different temperatures and quenched and then the reaction mixtures were analysed quantitatively by powder X-ray diffraction). Using kinetic data, the activation energy of the solid-

phase interaction was calculated in terms of the diffusion model proposed in another publication.[125] The activation energy of the solid-phase reaction was found to be almost 4 times lower in a microwave field than with conventional heating. The authors noted that this result attests in favour of the intensification of the surface diffusion by the electromagnetic field rather than in favour of the vacancy jump mechanism considered by Katz *et al.*,[66] as in this case, one would rather expect a change in the pre-exponential factor in the Arrhenius equation but not the activation energy for diffusion.

Solid-phase synthesis of lanthanide chromite and sodium cobaltite with partial replacement of cobalt ions by manganese ions from the corresponding oxides was carried out.[126, 127] The researchers used a microwave system operating at 28 GHz, which, as they believed, ensured more uniform distribution of the electromagnetic field strength within the sample bulk. It was found that the synthesis of lanthanum chromite with microwave heating can be carried out at 450 °C, which is much lower than that required with conventional heating (about 1200 °C). Measurement of the sample temperature during the process showed that the temperature increases in the first stage (less than 4 min) and then remains constant throughout the whole synthesis. Note that the change in the microwave power from 0.3 to 1 kW does not affect significantly the 'saturation' temperature. Apparently, this temperature is determined by the absorption capacity of components of the reaction mixture and the intensity of heat removal from the sample surface. The latter conclusion contradicts other data,[121] because the sample composition changes appreciably during microwave heating. It cannot be ruled out that these discrepancies are caused by the higher absorption capacity of lanthanum chromite compared with yttrium vanadate.

It is of interest to compare these data with the results of another work [128] in which lanthanum chromite, cobaltite and nickelate were also synthesised from oxides but in the presence of an absorbing additive (graphite). The temperature substantially increased during the synthesis (to 1100 – 1200 °C) and the duration of synthesis of the single-phase product was markedly reduced (to 5 min). Thus, the introduction of the absorbing additive was justified in this case.

The $SrFeCo_{0.5}O_y$ phase with a mixed conduction type used for the design of solid-state fuel cells was prepared by 'hybrid' microwave heating with SiC as the absorbing additive.[129] A powder with a narrow particle size distribution and high sintering ability was produced using this procedure.

In the synthesis of complex oxide compounds from salts, it is even more difficult to identify the specific microwave effect, as the number of processes influencing the absorption of microwave radiation by the reaction mixture increases. No studies devoted to the effect of the phase composition of such systems on the absorption of microwave radiation have been published. Most of researchers only state the fact of considerable increase in the reaction rates in the microwave field and make no attempts to determine the reaction mechanisms.

A procedure for the synthesis of a broad range of oxide compounds including individual manganese, iron, cobalt and copper oxides, multicomponent ferrites, manganites and cobaltites based on microwave heating of the corresponding nitrates has been developed.[130 – 137] It was shown, that using microwave heating, it is possible not only to shorten the time of synthesis of multicomponent oxide products with various crystal structures, but also, in most cases, to substantially decrease the temperature of synthesis. The latter apparently indicates that microwave heating intensifies the diffusion owing to the appearance of circulating ionic currents on the crystallite surface ('non-thermal' action). The oxide phases synthesised with microwave heating were not inferior in performance properties to the control samples produced by conventional thermal treatment.

The synthesis of phases based on lanthanum chromite from the corresponding nitrates has been described.[138, 139] A considerable decrease in the time of synthesis and more uniform micromorphology of the resulting powders upon the use of microwave treatment were noted; in the authors' opinion, this was a consequence of a high uniformity of heat supply favourable for fast formation and even distribution of the oxide phase nuclei.

A method for the synthesis of a powdered $MnCo_2O_4$-based catalyst by microwave decomposition of the corresponding nitrates has been developed.[140, 141] The introduction of some amorphous carbon to the reaction mixture (5 mass % – 30 mass %) with a high specific surface area resulted in a higher rate of formation of the final product and a higher catalytic activity, probably, due to greater surface area. Analysis of the dependence of the specific surface area of the oxide powder on the carbon content demonstrated that after some limiting value has been reached, further increase in the carbon content in the initial mixture does not affect the specific surface area of the oxide powder. Unfortunately, the authors did not analyse the mechanism of microwave action on the reactions and the micromorphology of the final product.

Quite a few papers are devoted to the synthesis of various lithium-containing oxide compounds used as cathodes in lithium rechargeable batteries. The vast majority of these publications deal with the synthesis of materials based on the $LiMn_2O_4$ phase, which is considered to be most promising for lithium batteries. Nakayama *et al.*[142] compared two procedures of microwave-assisted synthesis of the $LiMn_2O_4$ phase, *viz.*, decomposition of a mixture of the corresponding nitrates and a mixture of Mn_2O_3, $LiOH \cdot H_2O$ and copper oxide as the absorbing additive. The former method was preferred, because a single-phase product was formed over a shorter period of time and no $LiMnO_2$ impurity phase was present. This was attributed to faster attainment of thermal equilibrium in the case of liquid-phase synthesis and to 'non-thermal' effects of microwave heating, which are more pronounced in the absence of an absorbing additive.

Detailed analysis of the effect of the chemical nature of the starting compounds on the course of the reactions in a microwave field has been carried out [143] using the synthesis of lithium nickelate as an example. Lithium carbonate and hydroxide and nickel hydrocarbonate, hydroxide and oxide in various combinations served as the reactants. Note that the use of microwave treatment markedly reduced the temperature of formation of lithium nickelate. However, in all cases, microwave heating was followed by additional annealing of the sample in a conventional furnace in an oxygen stream in order to obtain a single-phase product. In the authors' opinion, a mixture of hydroxides is the best choice for the synthesis of $LiNiO_2$, as in this case slightly aggregated powders with a narrow particle size distribution were produced.

A series of publications [144 – 148] report the efficiency of the synthesis of complex ferrites and manganites by microwave-assisted decomposition of nitrate mixtures in the presence of urea. The large volume of gases evolved upon decomposition of nitrates and urea favours deaggregation of the oxide powders. Despite the abundant factual data, the authors unfortunately did not consider the relationship between the microwave treatment conditions and the composition, on the one hand, and the morphology of final products, on the other hand.

A rational approach to the choice of the starting compounds for the microwave-assisted synthesis has been reported.[149] The $La_{0.7}Ba_{0.3}MnO_3$ phase possessing giant magnetoresistance (Fig. 12) was prepared by microwave-induced decomposition of a mixture of metal nitrates. The authors

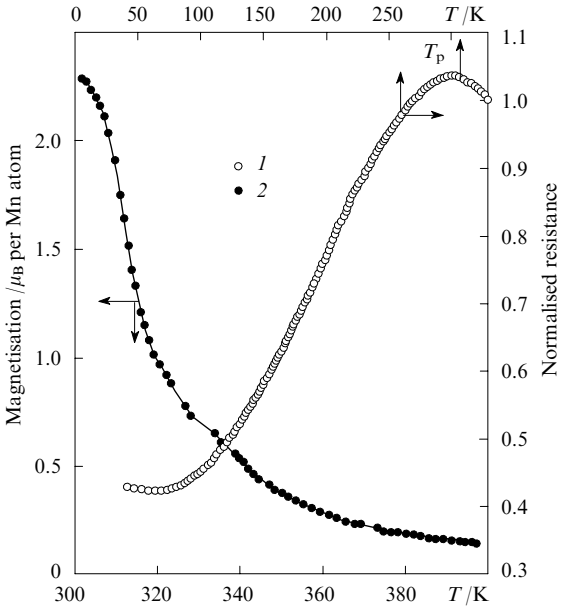


Figure 12. Temperature dependences of the magnetic properties of the ceramics based on the $La_{0.7}Ba_{0.3}MnO_3$ phase synthesised in a microwave field.[149]
(*1*) $T_p = 307$ K; (*2*) $H = 0.5$ *T*, $T_c = 318$ K.

substantiated the choice of nitrates as precursors by a large dipole moment of the nitrate ion, which should actively interact with the microwave field. In addition, nitrates readily melt in their water of crystallisation, and aqueous solutions always absorb efficiently microwave radiation. Additional heat is evolved, in the authors' opinion, upon the oxidation of manganese(II), which takes place during decomposition of manganese nitrate. Heat evolution upon oxidation is the main reason why heating does not stop after removal of water from the solution but continues up to decomposition of the precursors to give the oxide phase. It was also found [149] that apart from the substantial decrease in the time of synthesis, the powders obtained by microwave-assisted decomposition of a nitrate mixture have a better microstructure than the powders synthesised by the ceramic technique. It was shown that the properties of ceramics produced using the obtained powders are not inferior to the properties of samples synthesised by the traditional techniques.

In the publications [147, 150] devoted to the synthesis of ferrites $Ni_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ and $SrFe_{12}O_{24}$ by pyrolysis of a metal nitrate mixture in the presence of urea, a modification of the procedure considered above was proposed. The reaction of metal nitrates and urea at elevated temperatures is accompanied by evolution of a gas mixture (NH_3, HNCO, O_2 and NO), which spontaneously ignites after a particular critical temperature has been reached and heats the mixture of solid reaction products to 1000 °C or higher. This process lasts for 10–15 min and is accompanied by the formation of single-phase powders of the corresponding ferrites. The microstructure of the synthesised powders is characterised by a loose framework composed of 3- to 6-μm aggregates. The formation of such structures is typical of pyrolysis of salts. Despite the high reaction temperature, the primary crystallites are rather small (50–75 nm) (Fig. 13), which is probably due to high rate of the process. The subsequent annealing of the synthesised samples results in a regular enlargement of particles upon recrystallisation. By correct adjustment of the temperature of the subsequent annealing of the powders, it is possible to reach saturation magnetisations and coercive forces that are rather

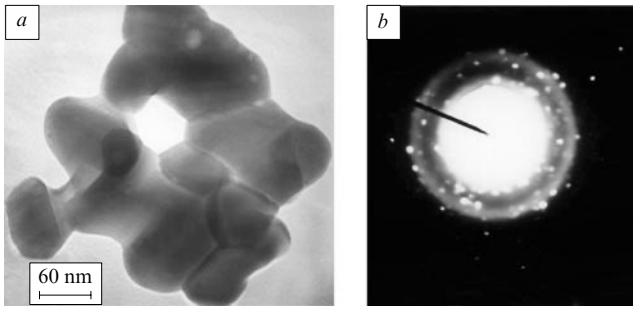


Figure 13. Transmission electron microscopy image (*a*) and electron diffraction pattern (*b*) for the particles of the $Ni_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ sample prepared in a microwave field.[150]

high for this type of ferrite systems (Fig. 14). Unfortunately, the authors did not compare the properties of samples prepared by microwave-assisted decomposition of a salt mixture with those treated in a conventional furnace; therefore, it is difficult to make conclusions about the advantages of microwave heating. In addition, analysis of the publication [149] casts doubt on the necessity of addition of urea for decomposition of a nitrate mixture in a microwave field.

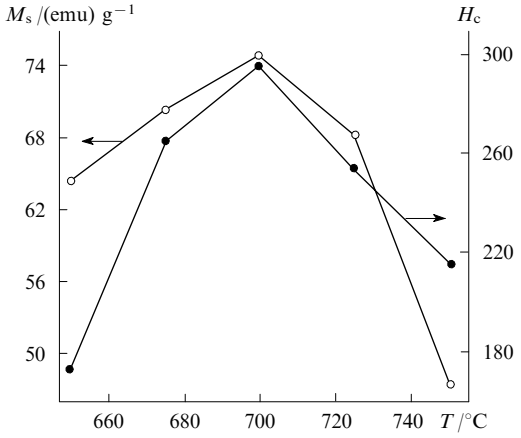


Figure 14. Saturation magnetisation (M_s) and coercive force (H_c) for $Ni_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ samples synthesised in a microwave field *vs.* temperature of their subsequent heat treatment.[150]

The synthesis of layered aluminium and zinc double hydroxides with intercalated sodium dodecyl sulfate molecules has been reported.[151] Crystallisation in the microwave field proceeded much faster than that with the use of conventional heating (1–2 h instead of 2–3 days). In addition, crystallisation induced by microwave heating enhances the intercalation of the organic anion into the hydroxide matrix, and thus the starting concentration of sodium dodecyl sulfate can be reduced. The product consists of smaller crystallites with a narrower size distribution than the sample prepared by the conventional heating.

The results of synthesis of the ferrite $Co_{1-x}Zn_xFe_2O_4$ ($0 \leqslant x \leqslant 0.8$) by precipitation of hydroxides from solutions of the corresponding salts by a solution of KOH in ethylene glycol under microwave treatment followed by separation of the precipitate and annealing at a temperature above 500 °C have been reported.[152] The influence of the solution pH and the duration of boiling on the micromorphology of the resulting powders has been studied. It was shown that with an increase in

the pH, the particle size of the powder increases and the degree of agglomeration simultaneously decreases. The addition of ethylene glycol to the solution led to a decrease in agglomeration of the powders.

High-temperature solvolysis of solutions of barium, lead, titanium and zirconium salts in ethylene glycol gave the double oxides $BaTiO_3$, $BaZrO_3$, $PbTiO_3$ and $Ba_6Ti_{17}O_{40}$ in the nanocrystalline state.[153] A specific feature of the synthesis is that the use of ethylene glycol, which functions simultaneously as a solvent, a complexing agent and a surfactant, allows one to vary the powder composition and morphology over a broad range. Note that with the use of microwave heating, it is possible to eliminate a key drawback of the synthesis of oxide phases from solutions in ethylene glycol, *i.e.*, the low reaction rate.

V. Conclusion

The range of physicochemical problems solved successfully by means of microwave radiation is exceptionally broad. This review covers only a small portion mainly related to the synthesis of oxide materials. Not only studies dealing with the synthesis of sulfides,[80–84] nitrides,[50,154] selenides[155] or silicides,[156] but also the applications of microwave treatment such as organic synthesis,[4,7,157–159] analytical chemistry[4,160–162] and so on remained beyond the scope of the review. Each of these fields deserves separate consideration and comprises an extended subject matter.

Nevertheless, a general problem should be considered, namely, the possibility to control the processes taking place during microwave treatment of chemical systems, and a closely related problem of evaluating the efficiency of microwave treatment.

Evidently, a satisfactory solution to this problem can now be obtained only for the microwave heating of very simple, more precisely, single-phase systems the physicochemical state of which is not changed much during heating. A good example of such process is the preparation of dense ceramics by sintering of compacted powders, because only the sample morphology is changed most often during compaction, which undoubtedly affects the absorption capacity but this effect is slight and can be taken into account. Similar conditions exist during solution treatment, because these processes usually take place in a rather narrow temperature range and the physicochemical properties of the system do not change much. This range can be supplemented by reactions in inert matrices the specific features of which caused by microwave heating have been poorly studied. In the case of multicomponent systems, it is rather difficult to control the results of microwave treatment due to the large number of processes taking place simultaneously, each affecting significantly the absorption capacity of the whole system. The only practicable way is to accumulate the empirical information on the behaviour of various systems under microwave heating. This would provide an at least qualitative estimate for the efficiency of using such heating. Therefore, systematisation of the accumulated experimental data appears a topical task, which was fulfilled, to some extent, by this review.

Thus, to be able to control the microwave heating in the synthesis or sintering, one should choose systems with the smallest number of components or attain artificially a greater system uniformity by diluting it with a inert matrix or a 'buffer' component the absorption capacity of which depends slightly on the processes that take place. This type of microwave treatment has much in common with the above-mentioned 'hybrid' microwave heating; however, in this case, the added inert component not only enhances the absorption of radiation, but also allows one to control the microwave heating. Thus, the buffer medium should satisfy the same requirements, namely, it should be chemically inert, absorb efficiently the microwave radiation and be easily separable from the synthesis products after heating has been completed. This route seems especially attractive, as in the future, it may be extended to a rather broad range of physicochemical processes.

This review was written with the financial support of the Russian Foundation for Basic Research (Project No. 06-03-33042), the programme 'Development of the Scientific Potential of Higher School' (government contract No. RNP 2.1.1.1205), the Complex Scientific Research Program of the RAS and the Foundation for the Support of Russian Science. The authors are grateful to Doctor of Science (Physics and Mathematics) V E Semenov for the assistance and valuable remarks made during preparation of the review and to the staff of the Laboratory of Chemical Synergetics of the Institute of General and Inorganic Chemistry of the RAS and the Laboratory of Inorganic Materials Science of the Department of Chemistry, Moscow State University, for fruitful discussion on the issue.

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