Ultra-rapid microwave sintering

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Abstract. The results of microwave sintering of powder materials in the regimes with high heating rates and zero hold time at maximum temperature are reported. Microwave processing of compacted samples based on Al₂O₃, Y₂O₃, MgAl₂O₄, and Yb:(LaY)₂O₃ ceramics was carried out using a 6 kW/24 GHz gyrotron system. The volumetric absorption of intense microwave radiation resulted in a very rapid densification with the duration of the high-temperature stage of sintering on the order of one to several minutes. In the rapid microwave heating regimes the effective high-frequency conductivity of the materials increased sharply at a certain threshold temperature as a result of the overheating instability, also known as thermal runaway. This suggests that the ultra-rapid sintering occurs via grain-boundary softening and formation of transient liquid phases. The indications of the presence of such phases were observed in the microstructure of the sintered samples. The absorbed microwave power density required for the transition to the ultra-rapid sintering is on the order of 10...100 W/cm³ for a broad class of the materials. The obtained results suggest that ultra-rapid microwave sintering proceeds via essentially the same mechanism as the so-called flash sintering that occurs in the presence of dc or low-frequency ac electric field.

1. Introduction
The development of sintering enhancement methods is important for the powder technology of manufacturing modern polycrystalline ceramic, composite and metallic materials. In recent decades, methods based on the use of electric and electromagnetic fields, such as FAST (Field-Assisted Sintering), PECS (Pulsed Electric Current Sintering), and SPS (Spark Plasma Sintering) have been widely developed. In these techniques, an external pressure is applied to the sample, creating an additional driving force for sintering, and the heating is produced by an electric current flowing through the mould made of an electrically conductive material and, in some cases, through the powder material undergoing sintering. Despite the significant practical successes achieved in reducing the time of densification of materials to near-theoretical density, the issue of possible activation of mass transport processes in powder materials by the electric field and the induced magnetic field remains open for discussion [1].

Recently, a considerable research interest has been attracted to an easier-to-implement method of pressureless sintering, in which an electric voltage is applied to a compacted powder sample undergoing heating in the furnace. In this case, the electric current flows directly through the sample. In the beginning of 2010 the group of Prof. R. Raj (University of Colorado Boulder, USA) discovered the effect of the so-called flash sintering [2]. At a certain combination of the furnace temperature,
voltage and current, ultra-rapid densification of powder compacts to virtually full density is observed, with a time scale of several seconds. This dramatic reduction in the duration of the high-temperature stage of sintering, from several hours to several seconds, might have a vast potential for the ceramic industry. An avalanche-like increase in the number of publications in this field in recent years confirms the growing interest to this technique. The flash sintering effect has been observed and studied by many groups on various oxide ceramics with an application of either dc or ac voltage. At present, it can be considered generally accepted that the appearance of flash sintering is due to the development of temperature instability in the material caused by a positive feedback between the Joule heating of the sample and its electric conductivity growing with temperature. However, the immediate mechanism of ultra-rapid densification, and the issues of the specific effect of current, voltage and incubation time remain the subjects of discussion.

The development of temperature instability is a well-known effect in microwave heating. It arises when there is an imbalance between the volumetric release of absorbed energy and the surface thermal loss. In experiments on the ultra-rapid sintering of ceramics, a catastrophic rise in temperature (thermal runaway), leading to destruction of the sintered sample, can be avoided using fast monitoring of the temperature of the sample and a properly coordinated control over the microwave power.

This paper presents a summary of the experimental results on the ultra-rapid microwave sintering of various oxide ceramics. Major features of the microwave power and electrical conductivity behaviour in these processes are discussed. These data, in conjuncture with the results of the study into the sintered materials microstructure allow an understanding of the mechanism of the fast microwave sintering.

2. Experimental setup
For the fabrication of the samples nanocrystalline Al₂O₃, Y₂O₃, Yb₂O₃, La₂O₃, MgO, MgAl₂O₄ powders with the grain size of 30-100 nm were used. The samples were compacted by uniaxial pressing at 200-300 MPa into the shape of disks, 10-20 mm in diameter and 2.5-3.0 mm in thickness. The compacted samples had a density of about 40-50 % of the corresponding theoretical value. The samples were heated in the applicator of a gyrotron system for microwave processing with an output power of 6 kW at 24 GHz, equipped with a feedback power control circuit [3]. Depending on composition, the samples were thermally insulated either by coarse Y₂O₃ powder filling in a quartz crucible, 110 mm in diameter and 110 mm in height (in the case of Yb(LaY)₂O₃ and Y₂O₃ samples), or by a box made of the highly porous Al₂O₃-fiber boards (in the case of Al₂O₃ and MgAl₂O₄ samples). The temperature of samples, \( T \), was measured by a B-type thermocouple with the tip embedded in a shallow hole drilled to the center of the sample – where the temperature should be maximal during the volumetric microwave heating.

At an initial stage of the process, the samples were heated in air at a rate of 10°C/min up to 800°C, and held at this temperature for one hour to remove the absorbed water and residues of the organics used in some cases to assist compaction. At this temperature no densification of samples was detected. Then the applicator was evacuated to 1-10 Pa and the samples were heated to a preset target temperature \( T_{\text{max}} \) at a preset heating rate, selected in the range 10-200°C/min. During the sintering, the time dependencies of the main parameters of the process, viz. the current temperature of the sample and the microwave power \( P_{\text{in}} \) that was automatically controlled to ensure the desired heating rate, were recorded. When the target sintering temperature was reached, the microwave power was switched off automatically and the sample cooled down along with the thermal insulation. All the experiments were performed without an isothermal hold at the maximal temperature (zero hold time).

The density of sintered samples was measured by Archimedes weighing with an accuracy of ±0.01 g/cm³. The microstructure analysis was performed using scanning electron microscopy (JEOL JSM-6390 LV, Japan), both on as-sintered and mirror polished, thermally etched surfaces. The phase composition was identified by X-ray diffraction (Ultima IV, Rigaku, Japan).
3. Results and discussion

The development of temperature instability in dielectrics heated volumetrically (by internal thermal sources) and cooled from the surface is a well-known effect [4, 5]. In the practice of microwave sintering of ceramics this effect, known as thermal runaway, is usually considered a negative factor that may lead to destruction or melting of the sintered body. However, the undesired increase in the temperature and its adverse consequences can be avoided by a proper control over the process of microwave heating.

R. Raj in his paper [6], having analyzed the results obtained by many research groups on dc and ac flash sintering of a broad range of oxide systems, concluded that the transition to a highly nonlinear rise in electrical conductivity – a signature event for the onset of the flash – occurs within a narrow range of power density of Joule heating, about 10-50 W/cm³. In our recent experiments on ultra-rapid microwave sintering of several types of oxide ceramics, it was determined that the temperature instability takes place when the microwave power density absorbed in a sample, \( p_{abs} \), exceeds several tens watts per cubic centimeter [7, 8]. Based on the coincidence between the critical values of the power density corresponding to different types of heating, it can be assumed that the major factor for the development of instability is the deposited power rather than the characteristics of the electric field (field strength, electric current, frequency) or the type of conductivity of materials. Naturally, the exact value of \( p_{abs} \) and the onset temperature of the instability may depend on the material properties such as composition, porosity, thermal diffusivity, size and shape of the sample, environment, etc.

A simple way to control the process of ultra-rapid microwave sintering is to switch the microwave power off automatically upon reaching a preset maximal temperature of heating. As an example, shown in figure 1 is a result obtained in the experimental study of the microwave sintering of Nd:Y₂O₃ laser ceramics undertaken by the authors in 2006-2007 jointly with the group of the Institute of Electrophysics (Ekaterinburg, Russia). The maximal temperature in these experiments was set at 1600°C. Shown on the left is the sample sintered in the process in which the runaway occurred. The temperature and the microwave power recorded at the high-temperature stage of this experiment as a function of time are presented in figure 2. The temperature runaway happened at a temperature of about 1100°C, and the total time of densification was slightly more than 15 s. The sample shown on the right in figure 1 was microwave sintered in a long process, similar to conventional vacuum sintering of Nd:Y₂O₃ laser ceramics, viz. heating at a rate of 5°C/min to 1750°C and hold at this temperature for 10 hr. It is seen that the fast-sintered sample is rather transparent (although the transparency of the other sample is better) which proves the high density of the fast-sintered material (over 99.5% of the theoretical value). However, despite the achieved reduction in the sintering time by a factor of more than 2000, this method of ultra-rapid microwave sintering cannot be adopted as a practical one because of the occasional character of the runaway occurrence.

Much more practical is another approach that involves high heating rate, high microwave power density absorbed in the sample and zero hold time, which is based on the use of a closed feedback-loop control over the microwave power [7]. This approach involves, as an integral part, an estimate of the energy balance in each particular process implementation.

The microwave power absorbed in a sample increases its temperature and compensates the heat losses. In sintering processes with zero hold time, the microwave power absorbed per unit volume, \( p_{abs} \), can be roughly estimated using the energy balance equations applied immediately before and after the time instant when the microwave power is switched off:

\[
\begin{align*}
p_{abs} = \rho C \left( \frac{dT}{dt} \right) + p_{hl} = \rho C \left( \frac{dT}{dt} \right),
\end{align*}
\]

where \( \rho \) is density, \( C \) is specific heat capacity of the material of the sample, \( p_{hl} \) is the power in heat losses, per unit volume of the sample, \( (dT/dt) \), and \( (dT/dt) \) are the rates of heating and cooling before and after the microwave power switchoff, respectively.
The applicator of the gyrotron system is a super-multimode unturned cavity. The microwave power density absorbed in a sample heated in such applicator, \( p_{\text{abs}} \), is proportional to the input power \( P_{\text{in}} \) [9]:

\[
p_{\text{abs}} \approx \frac{Q}{\varepsilon_0 V} \sigma_{\text{eff}} P_{\text{in}},
\]

where \( Q \) is the quality factor of applicator, \( V \) is its volume, \( \omega \) is the angular microwave frequency, \( \varepsilon_0 \) is the electric constant, \( \sigma_{\text{eff}} \) is the effective microwave conductivity of the sample. Thus, in order to implement the ultra-rapid sintering regime it is necessary to provide adequate heating and cooling rates of the sample, that would be sufficient for the development of thermal instability.

![Figure 1](image1.png)

Figure 1. Nd:Y\(_2\)O\(_3\) sample microwave sintered in a runaway process with total densification time \( \sim \)15 s (left) and a similar sample microwave sintered in a 10-hour process (right).

![Figure 2](image2.png)

Figure 2. Temperature and the microwave power recorded at the high-temperature stage of the sintering process for the sample shown on the left of figure 1.

As an example of this method implementation, we consider here ultra-rapid microwave sintering of an Al\(_2\)O\(_3\)-based ceramic sample. Shown in figure 3 are the preset temperature-time heating schedule, the actual measured temperature of the sample and the recorded microwave power, \( P_{\text{in}} \), which sustained the heating. At the final, high temperature stage of heating the preset heating rate was chosen equal to 100°C/min, and the thermal insulation was arranged so as to provide the cooling rate of about 250°C/min. As seen in figure 3, initially \( P_{\text{in}} \) increases with temperature due to an increase in the thermal losses from the sample. Then, at a temperature of about \( T \approx 1400^\circ \text{C} \) the value of the actual temperature begins to exceed the value that was preset for this particular time. The power control system starts to reduce \( P_{\text{in}} \) in such a way that the sample continues to be heated at the preset heating rate. The reduction in the automatically controlled power \( P_{\text{in}} \) concurrent with the growth of both the temperature and the thermal losses, can only result from a sharp increase in the conductivity due to the development of thermal instability, causing an increase in the microwave power density absorbed in the sample, \( p_{\text{abs}} \). In this example the temperature runaway occurred at \( T \approx 1400^\circ \text{C} \) and \( p_{\text{abs}} \approx 12 \text{ W/cm}^2 \); the sample was sintered to a density of above 95% of the theoretical value in 11 minutes (from 900 to 1500°C) without isothermal hold.

A faster-than-Arrhenius growth of conductivity was observed in separate experiments on the measurements of the dc resistivity in the microwave heated samples compacted of Yb\(_2\)(LaY)\(_2\)O\(_3\) with platinum electrodes imposed on them. A low dc voltage of 1 V (stabilized) and a low current not
exceeding 10 mA were used in order to make the Joule heating negligible. A sharp increase in the current, seen in figure 4, and a deviation from the Arrhenius dependence of the conductivity, shown in figure 5, take place at a temperature $T \approx 1150^\circ\text{C}$. It should be noted that the Arrhenius dependence of conductivity on temperature is typical of dielectrics in the solid state. The deviation from this dependence observed during microwave heating at high levels of the power $P_m$ suggests that the phase state of the material is changed at the temperature $T^*$, and a highly electrically conductive, (quasi-)liquid phase is formed in the sample. The effect of a sharp increase in the high-frequency electric conductivity associated with the liquid phase formation was observed earlier in the studies of microwave heating of alumina ceramics with minor additions of TiO$_2$ and Na$_2$O [10, 11].

![Figure 3](image-url)

**Figure 3.** The preset temperature-time heating schedule, the actual measured temperature of the sample and the microwave power recorded during the ultra-rapid microwave sintering of an Al$_2$O$_3$-based ceramic sample.

A mechanism of ultra-rapid (“flash”) sintering driven by the electrically triggered thermal instability was suggested in [7, 8]. Given a volumetric heating and surface thermal loss, the temperature distribution in the sample is non-uniform, with a maximum in its core. When the temperature and the deposited power density are high enough, the softening and melting of grain surfaces can start at a temperature which can be noticeably lower than the melting point of the bulk material due to the elevated density of defects and impurities near the surfaces. The dissolution of the material of grains into the liquid and enhanced mass transport through the liquid layer produce rounded shape and smooth surface of particles. The (quasi-)liquid phase wets the grains completely due to the affinity of the chemical compositions. The capillary attractive force arising in the liquid layer causes particle rearrangement by rotation and sliding of small-size grains relative to each other which eventually results in fast densification. The densification, which starts in the hottest core, propagates to the periphery of a sample following the liquid phase that is squeezed out into the porous peripheral region. The region of the maximum deposition of the power moves along with the liquid phase due to the enhanced electric conductivity of the latter (which also limits the thermal runaway).

Different oxide ceramics – Al$_2$O$_3$, Y$_2$O$_3$, MgAl$_2$O$_4$, and Yb:(LaY)$_2$O$_3$ – were sintered to densities 98–99% of the theoretical value ($\rho_{th}$) within minutes or even fractions of a minute, without a hold stage, using the described method of ultra-rapid microwave sintering [7, 8]. The Al$_2$O$_3$ powder compacts were sintered to a density of (0.98...0.99) $\rho_{th}$ using microwave heating at rates in the range 50-250°C/min to the temperature 1600-1650°C. The microwave power deposited per unit volume of the sample, $P_{abs}$, was 15-100 W/cm$^3$. The density of the MgAl$_2$O$_4$ samples microwave heated at rates in
the range 100-200°C/min to a maximum temperature of 1700 °C was over 0.99 \( \rho_{th} \). This was markedly larger than the density of the samples heated at a lower rate of 6°C/min to the same temperature with a 2-hour hold (about 0.97 \( \rho_{th} \)). \( Y_2O_3 \) samples with densities over 0.98 \( \rho_{th} \) were obtained using a heating rate of 100°C/min and maximum temperatures 1600-1700°C, with the values of \( \rho_{th} \) being above 40 W/cm³. The density of the samples sintered in these regimes was higher than the density of the samples obtained by a slower-rate (10°C/min) microwave heating process with a 15 min isothermal hold at the maximum temperature.

Many characteristic features of the microstructure in the sintered samples provide evidence in support of the suggested transient liquid-phase mechanism acting in ultra-rapid microwave sintering. Among them are frozen traces of liquid on the surface of the sintered \( Yb:(LaY)2O3 \)-ceramics [7], formation of interparticle layers and the kinetics of fast grain growth in the same material [8], the bimodal grain size distribution, abnormal grain growth and fast segregation of cations during the sintering of \( MgAl2O4 \) [12]. It should be noted that all mentioned phenomena proceed at rates that are 2–3 orders of magnitude larger than the typical rates for conventional solid state sintering.

Since the temperature distribution in the samples flash sintered under a dc or ac electric field is determined by the volumetric Joule heating and surface thermal loss, and since the deposited power density is similar for the dc or ac field-assisted flash sintering and ultra-rapid microwave sintering it can be argued that the mechanisms of sintering are identical for these two methods.

4. Conclusion
Ultra-rapid microwave sintering of different oxide ceramic materials in minutes’ time to virtually full density has been demonstrated. The absorbed microwave power density at high-temperature stage of sintering was 15-100 W/cm³. The proposed mechanism of rapid densification based on transient liquid phase formation should be equally applicable to both ultra-rapid microwave and dc or ac electric field-assisted flash sintering.

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