

## Microwave Flash Sintering

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In recent years, significant interest has been attracted to the studies of very rapid ("flash") sintering of ceramics under a DC or low-frequency AC voltage applied to the samples undergoing heating<sup>1</sup>. The common feature attributed to flash sintering of various materials is fast densification (within several seconds to minutes) occurring at a certain threshold temperature of the furnace that depends on the product of the applied voltage and current. The densification is accompanied by a sharp increase in electrical conductivity of the samples undergoing sintering.

To date, it is almost generally agreed that a primary role in the initiation of flash sintering is played by the thermal instability associated with the Joule heating by the electric current flowing through the sample. The development of an instability in dielectrics heated volumetrically by internal thermal sources was described as early as in 1928 by V.A. Fock<sup>2</sup>. An increase in the electrical conductivity with temperature, inherent in most dielectric materials, can lead to a disbalance between the power deposited in the bulk of a sample and the heat loss from its surface.

The thermal instability also known as thermal runaway is a widely discussed issue in microwave processing of materials. As a rule, thermal runaway

is viewed as one of the main shortcomings of the use of microwave heating for high-temperature processing of materials. However, we have recently demonstrated<sup>3, 4</sup> how the controlled development of the thermal instability is used advantageously for ultra-rapid microwave sintering of oxide ceramic materials ( $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgAl}_2\text{O}_4$ , and  $\text{Yb}:(\text{LaY})_2\text{O}_3$ ). In the experiments, the samples were sintered in the applicator of a gyrotron system with a microwave power of up to 6 kW at a frequency of 24 GHz equipped with a computerized feedback power-control circuit<sup>5</sup>. The samples were heated at various constant ramp-up rates up to the preset temperatures  $T_{\text{max}}$ . The microwave power switched off automatically upon achieving  $T_{\text{max}}$ , and the sample cooled down along with the thermal insulation surrounding it.

Detailed results of the experimental studies on flash microwave sintering of oxide ceramics have been previously published<sup>3,4,6</sup>, and only a brief account is presented here. The results of the flash microwave sintering of various ceramic materials are presented in Table 1. Ceramic samples in densities of 98-99 % have been obtained in the processes with a zero hold time, and the total duration of the high-temperature stage of the sintering process not exceeding several minutes.

**Table 1.** Results of flash microwave sintering experiments

Ceramic	Relative density [% th. d.]	$T_{\text{max}}$ [C]	Heating rate [°C/min]	$P_{\text{abs}}$ [W/cm <sup>3</sup> ]
Yb: (La <sub>0.1</sub> Y <sub>0.9</sub> ) <sub>2</sub> O <sub>3</sub>	98.5	1500	50	15
	98.5	1500	150	22
	98.0	1300	1350	120
Al <sub>2</sub> O <sub>3</sub>	98.6	1600	200	100
Y <sub>2</sub> O <sub>3</sub>	98.3	1600	100	40
3YSZ	95.8	1100	50	80
	81.3	1300	50	7 (< 10)
	98.8	1300	50	87
MgAl <sub>2</sub> O <sub>4</sub>	98.5	1780	150	25
MgAl <sub>2</sub> O <sub>4</sub> +1wt.% Y <sub>2</sub> O <sub>3</sub>	99.1	1780	150	27

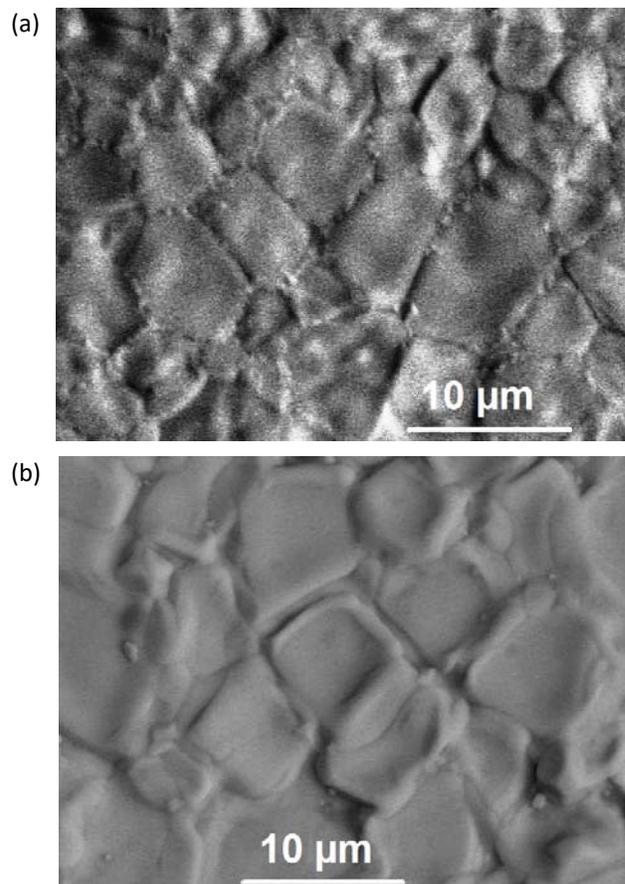
The microwave power absorbed in the sample undergoing heating increases its temperature and compensates the heat losses from it. The microwave power absorbed per unit volume of the sample,  $P_{\text{abs}}$ , can be estimated using the energy balance equations<sup>3</sup>. We have demonstrated that, similar to the DC/AC flash sintering studies,  $P_{\text{abs}}$  is a critical parameter that determines the onset of the flash sintering effect under microwave heating<sup>4</sup>. Interestingly, the critical value of  $P_{\text{abs}}$  for microwave flash sintering happens to be of the same order of magnitude (10-40 W/cm<sup>3</sup>) as that determining the onset of flash sintering under the applied DC/AC electrical voltage<sup>7</sup>.

Despite the growing number of publications on the DC/AC flash sintering, the mechanism responsible for the effect of fast densification remains a subject for discussion. As follows from estimates<sup>8</sup>, the increase in the temperature in the bulk of the samples during the development of the thermal instability may reach 800°C relative to the temperature before the onset of flash sintering. However, such an increase is insufficient to explain the observed ultra-rapid sintering by the enhanced rates of thermally activated solid-state diffusion mass transport processes. The exponential growth of the conductivity *per-se* does not explain the accelerated sintering<sup>8</sup>.

Our results of the microstructure characterization of the samples of various composition, microwave flash sintered in different heating regimes, revealed the features that are characteristic of the process of ceramic sintering in the presence of the liquid phase. The SEM studies of microwave sintered Yb:(La<sub>0.1</sub>Y<sub>0.9</sub>)<sub>2</sub>O<sub>3</sub> samples revealed traces of the (quasi-) liquid phase in the microstructure. At relatively low temperatures and/or heating rates, spherical tiny droplets were seen at grain boundaries of the sintered samples (Fig. 1a). With an increase in the heating rate (and hence in the microwave power absorbed in the sample), liquid phase surrounded the grains which acquired a concave shape (Fig. 1 b).

The kinetics of grain growth under microwave heating of Yb:(La<sub>0.1</sub>Y<sub>0.9</sub>)<sub>2</sub>O<sub>3</sub> samples is typical of liquid-phase sintering, and the average grain size is several times higher than the grain size obtained under conventional heating<sup>3</sup>. Fast segregation of dopants (La and Y, respectively) to the grain

boundaries is observed in Yb:(La<sub>0.1</sub>Y<sub>0.9</sub>)<sub>2</sub>O<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub>+1wt.% Y<sub>2</sub>O<sub>3</sub> samples. The microstructure of the sintered samples depends strongly on the material composition. The Yb:(La<sub>0.1</sub>Y<sub>0.9</sub>)<sub>2</sub>O<sub>3</sub> sintered samples have uniform density and grain size profile across the sample diameter, despite strong temperature gradients existed in the samples during sintering<sup>3</sup>. On the other hand, a pronounced bimodal grain size distribution and abnormal grain growth are characteristic for MgAl<sub>2</sub>O<sub>4</sub>+1wt.% Y<sub>2</sub>O<sub>3</sub> samples sintered to high density (Fig. 2).



**Figure 1.** SEM images of the surfaces of flash microwave sintered Yb:(La<sub>0.1</sub>Y<sub>0.9</sub>)<sub>2</sub>O<sub>3</sub> samples: (a) heating rate 50 °C/min, maximum temperature 1500 °C; (b) heating rate 200 °C/min, maximum temperature 1500 °C.

Based on the analysis of the results of experiments with various materials, the following mechanism of flash sintering has been suggested<sup>4</sup>. Due to the abundance of impurities and defects in the near-boundary regions of particles, the melting temperature of the surface / boundary can differ noticeably from the melting point of pure solid material. Provided that the temperature and the density of deposited power are high enough, the

particle surface pre-melting occurs well below the melting point of the bulk of grains, and a (quasi-) liquid phase with a low viscosity surrounds the grains. The liquid phase wets the particles completely due to the affinity of their chemical compositions. The capillary pressure attracts the adjacent particles together, and causes their rearrangement via rotation and sliding. The resulting densification is enhanced by particle shape accommodation due to fast diffusion mass transport through the quasi-liquid phase.

During volumetric heating, the highest temperature arises in the core of the sample and the process of particle surface melting starts from that position. In the course of densification, the liquid phase is extruded out into the more porous peripheral structure and contributes to its densification. Melting of particle surfaces results in a very sharp growth of absorption because the conductivity of the liquid phase is much higher than the conductivity of the solid material. In

effect, a densification front, coinciding with the region of the maximum deposition of the microwave power, propagates from the core of the sample to its periphery, producing a fully dense ceramic material within a very short time.

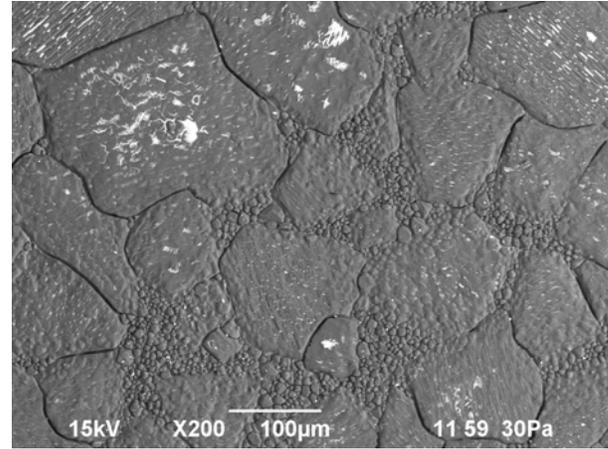


Figure 2. SEM image of the surface of MgAl<sub>2</sub>O<sub>4</sub>+1wt.% Y<sub>2</sub>O<sub>3</sub> sample microwave sintered at 1780 °C with zero hold time.

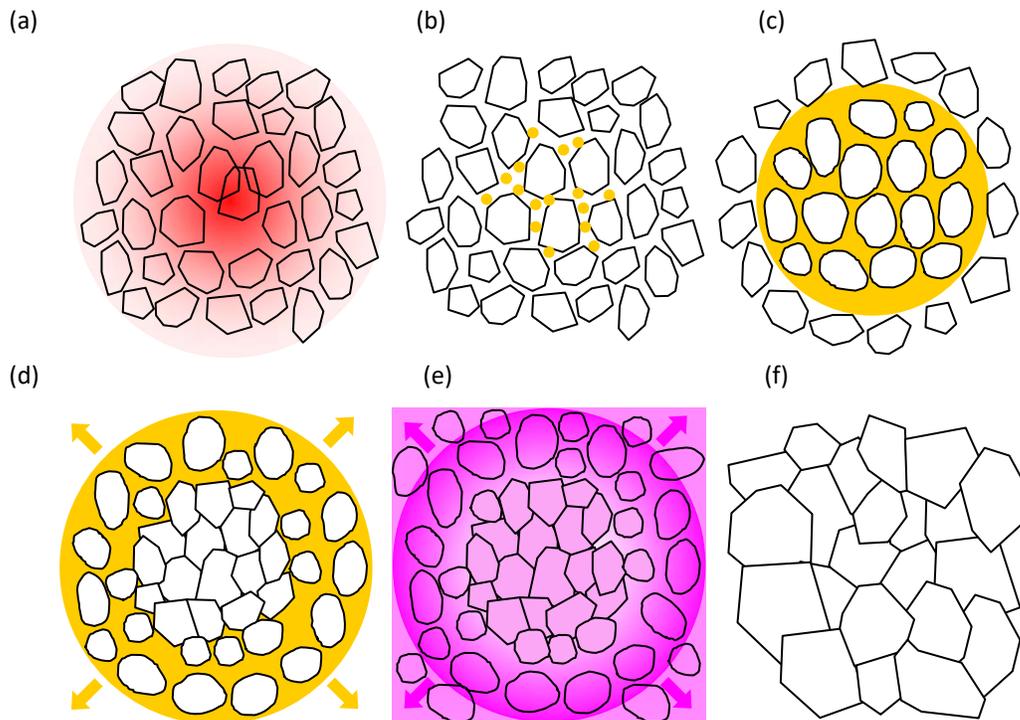


Figure 3. Illustration of the mechanism of flash sintering under volumetric heating: (a) volumetric heating creates a non-uniform temperature distribution with the core of the sample being the hottest; (b) droplets of liquid phase begin to form at particle surfaces; (c) liquid phase surrounds particles, the particle shape becomes rounded, particles rotate and slide relative to each other; (d) after rapid local densification liquid phase is squeezed from the core region towards the periphery of the sample; (e) the region of maximum power absorption propagates along with the liquid phase due to the elevated effective conductivity of the latter; (f) the propagation of the densification front results in achieving full density throughout the sample with a concurrent grain growth.

The volumetric energy deposition and surface thermal loss are characteristic of both the DC/AC and microwave flash sintering processes. However, it should be emphasized that from the potential applications standpoint the latter process has an obvious advantage as it requires no electrodes to supply the power to the articles undergoing sintering. Further research is necessary in order to optimize such factors as the properties of powder materials, materials composition, geometrical limitations imposed on the configuration of the sintered products, structural, functional properties, and performance of the materials obtained by flash sintering.

#### For further reading:

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#### About the Authors

The team of Laboratory for Microwave Processing of Materials at the Institute of Applied Physics (IAP), Russian Academy of Sciences, has been active in the field of microwave processing research for more than 25 years. The two main lines of the team's efforts are (1) design and development of systems for high-temperature processing of materials based on gyrotron millimeter-wave sources, and (2) investigation of the physical mechanisms underlying the interaction of microwave fields with materials. The gyrotron systems developed at IAP are currently in operation at a number of laboratories in Germany, Japan, China, and the United States.

Over the past decades, the team accomplished experimental studies of microwave sintering of a wide range of ceramic and composite materials. In recent years, the research carried out at the laboratory was focused on metal-ceramic functionally graded materials and transparent ceramics for laser applications. A theoretical study of the ponderomotive effect of the microwave electromagnetic field on the mass transport in solids has been accomplished, and novel models of effective microwave properties of conductive powder materials have been developed. An important recent development was the world's first demonstration of an ultra-rapid ("flash") sintering of oxide ceramic materials when heated by high-power microwave energy.

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