

Combined Microwave-Laser Processing for Sintering of Oxide Ceramics

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The technique of combined microwave and laser treatment of samples was developed and used for preparation of dense ceramics of various oxide compounds, including individual oxides and multicomponent cobaltites and manganites. It was found that simultaneous application of microwave and laser irradiation allows shortening of sintering time by orders of magnitude and leads to the formation of dense (up to 99% relative density) ceramics with uniform grain size distribution.

Introduction

Microwave treatment possesses many advantages in comparison with conventional heating methods, including higher velocity of heating, homogeneity of heat distribution and lower power inputs [1]. One of the main problems of microwave treatment is the fact that many compounds, for example most dielectric materials, are poor microwave absorbers at room temperature. Previously we, as have other researchers dealing with microwave synthesis and sintering, have used either “hybrid” microwave heating with SiC, carbon, copper oxide, etc. as initial microwave absorbers [2], or we have used *ex situ* samples pre-heating in a conventional furnace. Both of these techniques have significant disadvantages. In the case of a ‘hybrid’ microwave heating technique it is very hard to establish contributions of microwave heating on the one side and conventional heat transfer on the other. Also, contamination by the absorbing material is almost inevitable. On the other hand, pre-heating leads to unpredictable changes in temperature during sample transfer and therefore irreproducible results. Laser treatment also allows us to obtain a very high temperature (>3000°C) in a rather tight heating zone. Unlike thermocouples, ceramic heaters, etc., laser beam use does not affect the distribution of the electromagnetic field in a microwave cavity and therefore cannot interfere with microwave heating.

A combination of microwave treatment with laser treatment enables us to carry out *in situ* pre-heating of the sample to the desired temperature and enables us to control the sample condition throughout the entire heating process. In the present work we have developed a technique of combined microwave and laser treatment of samples and used it for preparation of dense ceramics of various oxide compounds, including iron oxide (Fe₂O₃, test sample), zirconia (ZrO₂), multicomponent cobaltites for solid oxide fuel cells (La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_z and Nd_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_z) and CMR-manganites (La_{0.6}Sr_{0.4}MnO_{3-z} and Nd_{0.6}Ba_{0.4}MnO_{3-z}).

Technique

As starting materials, corresponding metal nitrates (reagent grade) were used. Nitrates (or stoichiometric nitrate mixtures) were annealed at high temperatures (900°C for most samples) in order to obtain oxide powders. Phase composition of the obtained powders was controlled by



Fig. 1. Device for simultaneous laser and microwave treatment.

means of powder XRD-analysis. Only single phase powders were used for microwave-laser sintering. The resulting powders were ground in a planetary mill (700 RPM / 30 min.) with the addition of 1 mass % of polyvinyl alcohol as a plasticizer and then pressed into pellets of 8 mm diameter and 2 mm height using cold isostatic pressing.

The device used for simultaneous laser and microwave treatment is shown in Fig. 1. We used a Balay 3WM 1918 domestic microwave oven (650 W, 2.45 GHz) and a Rofin-Sinar CO₂-laser (300 W, wavelength = 10.6 μm) with a parabolic focusing mirror. The laser beam was delivered to the sample through a copper attenuator by means of a system of copper mirrors. In the carrying out preliminary experiments the following regimes of laser operation were used: focused in the pulsed regime, focused in the continuous regime, defocused in the continuous regime. To determine optimal conditions the power of the laser and the impulse length in the pulsed regime varied. As a result of preliminary experiments, it was established that the continuous regime with the unfocussed beam is the optimal source of laser emission for sintering of ceramic materials.

Samples were placed into the special container made of porous alumina (Fig. 2). In order to avoid the mechanical destruction of pellets in the beginning of the sintering process, the power of the laser smoothly increased from the minimum possible (5 W) to the working value with a velocity of 0.5 W/min. The power of microwave treatment was always 650 W, sintering temperature varied from 1000 to 1200°C, and duration of the process of sintering varied from 15 to 90 minutes. Temperature of the samples was measured by means of a specially calibrated IR-pyrometer.



Fig. 2. Container with sample under laser and microwave treatment.

Results

Experiments on sintering of iron oxide pellets allow us to establish that the optimal regime for treating the tablets of Fe_2O_3 is 25 % of the maximum power of the laser. Subsequently the optimal power for treating the remaining substances was established by a similar method. The optimal power of the laser for ZrO_2 was found to be 20 % of the maximum; for manganites – 20 %, and for cobaltites – 25 %. This data could be an additional argument in favor of the use of a gas laser, since the effectiveness of the radiation absorption of diode and solid-state lasers is determined by the color of the treated substance.

Study of the processes of densification of compacted powders of oxides (Fig. 3) allows us to establish that the optimal regime for sintering Fe_2O_3 and manganites is 2 hours at 1100°C ; to achieve maximum density of cobaltite pellets, it is optimal to sinter samples for the same amount of time at $1,200^\circ\text{C}$. These results are in the good agreement with the earlier-obtained data concerning sintering of these compounds under microwave treatment without the use of laser of processing.

Fig. 4 shows the time dependence of densification of manganite samples at optimal temperature (1100°C). A clear break of the curve can be seen after 60 min. of laser-microwave sintering. This break is indicative of the transition of the sintering process into its final stage, namely grain growth and curing of isolated porosity. The developed method of sintering is thus most likely optimal, and further increase of final ceramic density will be possible only through modification of the morphology of starting powder.

However, in the case of sintering of cobaltites there is no such break of the densification curve, and therefore to obtain higher densities it is necessary to increase either the duration or the temperature of sintering. Unfortunately, for us it is not possible technically to increase the duration of the process, since the magnetron of microwave oven is not designed for such a long period of continuous operation.

Comparing densification curves for manganites and cobaltites with those for zirconia and iron oxide, one can conclude that in contrast with microwave sintering without laser treatment

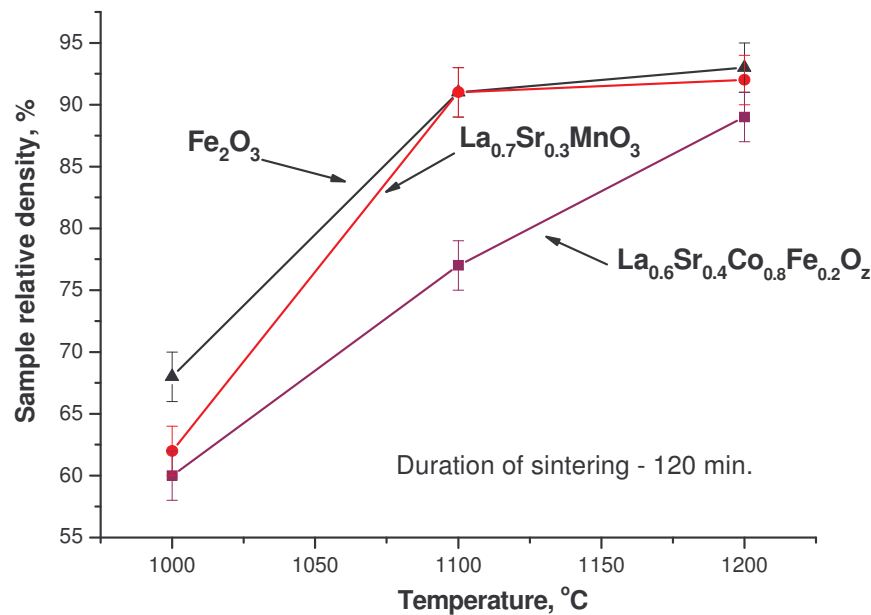


Fig. 3. Temperature dependence of densification of oxide samples.

[3], laser-microwave treatment is not very sensitive to electric conductivity of treated compounds.

Evidently this effect is connected with the intensive heat supply from the laser beam, which largely neutralizes the difference in absorption of microwaves by different compounds. Thus, it is possible to note higher flexibility of the laser-microwave technique of sintering in comparison with microwave sintering without the application of additional treatment.

Study of the microstructure of sintered samples allows us to establish that, similarly to “pure” microwave sintering, the process of grain growth during laser-microwave sintering is very slow and densification of samples is largely associated with grain gliding and grain-boundary diffusion. In complete agreement with the data of geometric density measurements, it is possible to isolate three stages of the sintering process.

During the first stage, formation of the isthmuses between the particles of sintered powder occurs. In this stage the shrinkage of the sample is small and occurs mostly due to reorientation and gliding of grains. In the second stage of sintering, we observe intensive binding of grains due to intergranular mass transfer.

The second stage is characterized by the most rapid shrinkage of samples due to the removal of intergranular porosity. At this stage only a insignificant increase in grain size occurs. Of the greatest interest from the point of view of comparison of thermal, microwave, and laser-microwave sintering is the third and final stage of the process of sintering, during which the final removal of porosity and grain-growth occurs. As is well known from literature [3-5], the specific effects of microwave processing consist of decreased velocity of grain growth due to an increase in the intergranular diffusion. It was found that under combined laser and microwave irradiation, the velocity of grain growth is also rather low. Generally we may conclude that microstructures of ceramics sintered under “pure” microwave and combined laser-microwave treatment are very

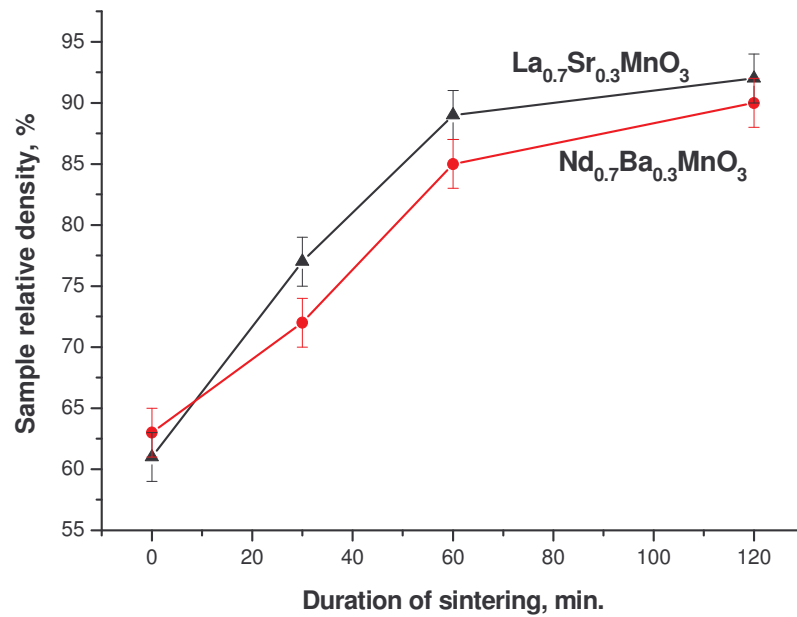


Fig. 4. Time dependence of densification of manganite samples.

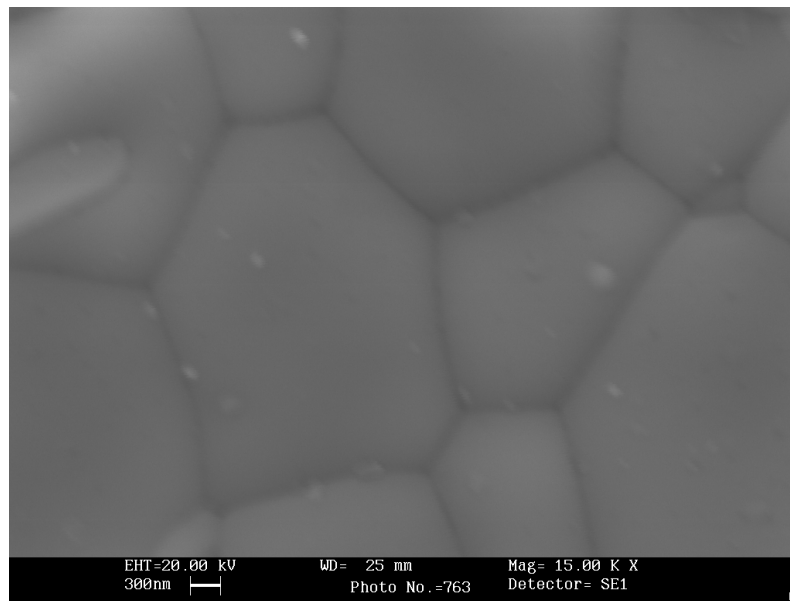


Fig. 5. Microstructure of La_{0.6}Sr_{0.4}MnO_{3-x} sintered at 1100°C for 2 hours.

similar. Nevertheless, as is clearly seen from Fig. 5, using simultaneous laser and microwave actions it is possible to obtain ceramics, which are characterized by high density and high uniformity of microstructure.

Conclusion

Techniques for simultaneous laser and microwave treatment of solid materials were developed. Using these techniques, samples of highly dense ceramics of individual (Fe_2O_3 , ZrO_2) and multicomponent (manganites and cobaltites) oxides were synthesized. Results obtained allow us to draw conclusions about the expediency of utilizing simultaneous laser and microwave treatment for sintering highly dense ceramic materials with uniform microstructure.

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