# Spark Plasma Sintering of transparent spinel ceramics.

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*Highlights*

- Commercial and self-synthesized spinel powders were sintered via SPS.

- To be determined: best powder and cycle for fine-grained transparent spinels.

## 1. Introduction

Transparent ceramic materials are intriguing because of their wide range of applications anywhere from laser optics to dentistry. We are interested in the future application of dense (and transparent) small-grained ceramics as radiation resistant materials. Although well researched, results on the effect of starting powder characteristics and chosen sintering cycle on the final properties of spark plasma sintered (SPS) ceramics vary. Fine-grained translucent alumina and spinel ceramics have been received using both, low ($\leq$10°C/min)[1, 2] and high ($\geq$100°C/min)[3, 4] heating rates and pressures. Sintering additives and post-SPS secondary sintering have also been proposed to keep the microstructure of sintered ceramic as fine as possible. With the assorted choice of commercial SPS set-ups and the randomness of current paths in the sample, local temperatures can be much higher than the average temperature of the sample. Starting powder morphology becomes important here since so-called hot spots tend to form at grain boundaries of the powder. Thus one way to reduce the randomness of heating is to use a homogeneous fine-grained starting powder for all of the experiments.

## 2. Methods

This work was carried out using different powders based on ultraporous alumina (UPA)[5], using them as a base for adding ZnO/MgO and receiving doped alumina or Zn/Mg aluminate spinel after SPS. In comparison, sintering was also carried out using commercially available spinel powders. To receive $Al_2O_3$:MgO (1:1) oxide mixture for sintering $MgAl_2O_4$ spinel ceramics, we started from UPA calcined to alpha phase and carried out multiple cycles of impregnation with $Mg(NO_3)_2$ water solution, until desired $Al_2O_3$:MgO ratio was reached. Alternatively, the addition of ZnO or MgO to $Al_2O_3$ was done via modified polyol process[6], starting from UPA calcined to alpha phase and dispersed in polyol before starting the ZnO/MgO synthesis. The powders were consolidated without any pretreatment using a SPS apparatus under 20 Pa vacuum. Standard pulse pattern 12:2 (on-off) with pulse duration of 3.4 ms was used. About 1.5 g of powder was poured into graphite paper insulated die with an inner diameter of 15 mm, the die was then covered by carbon felt to suppress heat loss from the die surface. The temperature was measured using an optical pyrometer focused on a small hole in the graphite die. Samples were held in vacuum at 600°C for 10 min in the beginning of the sintering cycles to remove adsorbed water. Before characterization, all ceramics were polished using diamond solutions and paste down to crystallite size of 0.25 μm. The phase composition of the starting powders and received ceramics were determined by X-ray diffraction patterns. The grain sizes of received ceramics were measured from backscattered electron images from scanning electron microscope. The density of received ceramics was measured by a He pycnometer.

## 3. Results and discussion

First results of this study are presented on Figure 1. Figure 1 shows that lowering commercial spinel powder (crystallite size 115 nm) sintering temperature from 1450°C to 1300°C decreases the grain size from 4,3 *μm* to 1,1 *μm*, while maintaining high density and translucency. Using stoichiometric $Al_2O_3$:MgO (300 nm: 50 nm) mixture received via impregnation as a starting powder for sintering (reactive SPS consolidation) results

in monophasic spinel ceramic with grain size of about 15 $\mu m$ after sintering. The huge grain size in comparision to commercial powder sintered at the same conditions arises from the reactive nature of the sintering, where MgO consumes the $Al_2O_3$ to form the spinel phase. In contrast, it is known that in the case
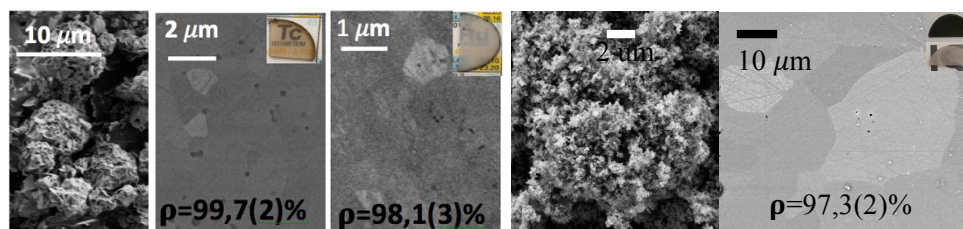


**Figure 1.** *1: received spinel powder; 2: ceramic sintered at 1450°C (grain size 4,3(2) um); 3: ceramic sintered at 1300°C (grain size 1,08(2) um; 4: (1:1) mixture of $Al_2O_3$:MgO obtained as described above; 5: ceramic sintered from this mixture at 1450°C (grain size 15 um).*

of lower concentration (ppm range)[7], Mg(O) acts as a grain growth inhibiting and transparency increasing secondary phase inside $Al_2O_3$. Additional boost to grain growth might have emerged from the bi-sized crystallites of the oxide mixture (300 nm alumina vs 50 nm magnesia).

To better the homogenity of the oxide mixture received by impregnation and stabilize the grain growth during sintering, we look to modify polyol process to include alumina as a base for synthesizing MgO/ZnO. Polyol process is wellknown as a relatively cheap and fast soft chemistry route to receive several grams of homogeneous nanopowders. Thus we will receive a homogeneous mixture of alumina and MgO/ZnO, for the latter of which we can modify the particle size to find an optimal powder for obtaining dense transparent small-grained spinel ceramics via reactive SPS. A homogeneous mixture of small particles will allow us to use less severe sintering conditions and hence not enter into the rapid grain growth conditions. As a last aid, we will use $Ta_2O_5$ to suppress the grain growth during sintering.

## 4. Conclusions

In this communication we use ultraporous alumina as a base to produce zinc oxide and magnesia doped dense ceramics and compares them to ceramics produced from commercially available powders to analyze the effect of different phases and morphologies of starting powder. We focus on improving the transparency and decreasing the grain size of sintered ceramics. In this work we will discuss the benefits and drawbacks of using reactive sintering instead of sintering powders already in the desired final phase. Microstructural properties, phase composition and transparency of received ceramics will be compared and interpreted in the light of the elaboration process used as well as the morphomology of the sintered powders. The challenge of this work will be to obtain dense transparent ceramics while keeping the grain size minimal.

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## Keywords
Spark Plasma Sintering; transparent ceramics; microstructure; sintering cycle engineering