J Mater Sci (2007) 42:3273–3275
DOI 10.1007/s10853-007-1672-0

LETTER

Spark plasma sintering (SPS) of transparent magnesium-aluminate spinel

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Received: 5 February 2007 / Accepted: 8 March 2007 / Published online: 7 April 2007

Transparent ceramics are of great current interest on account of their versatile optoelectronic properties and their potential for transparent armor related applications. Foremost candidates for structural transparent ceramic armor materials are cubic aluminum oxynitride, known under the trade name ALON, cubic magnesium-aluminate spinel and sapphire. The latter has a non-cubic crystal structure and is currently manufactured and used only in the form of single crystals, whereas cubic, isotropic ALON and spinel can be processed as polycrystalline materials. The raw material powders for ALON are proprietary and expensive. Spinel powders can be purchased from commercial suppliers and their synthesis is relatively simple. The critical properties for the preparation of bulk transparent spinel are related to the purity, morphology and size of the starting powder. The consolidation into bulk solids is performed at elevated temperatures conjointly with the application of high pressure either as hot pressing (HP) or as hot isostatic pressing (HIP). Optical requirements dictate the elimination of all second phase particles and of residual porosity. Thus the end product of the consolidation process must be a fully dense solid.

The conditions for fabrication of transparent spinel using HP and HIP were reported in [1–4]. A sufficient optical transparency up to 80% was achieved only upon addition of 1 wt.% LiF to high purity spinel powder containing less than 5 ppm impurities [1].

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Spark plasma sintering, SPS, is a relatively recent consolidation technique that relies on the simultaneous application of axial pressure and elevated temperature, generated by a high current flow. The Joule energy released by the current raises the temperature in the graphite dies enclosing the sample, or within samples that display some electrical conductivity. When a pulsed current is applied, sparking in the powder sample and alleged plasma generation may involve some surface activation and promote consolidation and densification. Whatever the exact mechanism, empirically it has been convincingly shown, that SPS consolidation provides significant advantages both by lowering the required sintering temperature, shortening its duration and generally providing high quality samples with elevated density values.

Even though SPS has been applied to a long list of ceramic materials, most often with positive results, the reported data on its utilization for the fabrication of transparent ceramics is limited. Wu and Li [5] reported results of spark plasma sintered of transparent lanthanum-doped lead zirconate titanate (PLZT) ceramics at 900 °C for 10 min to achieve 31% transmittance. Chaim et al. [6] succeeded in reaching 60% transmittance in the red wavelength range by spark sintering MgO nano-powder at 800 °C for 5 min under150 MPa pressure, while Xiong et al. [7] reached a maximal transmittance of about 50% in the mid infrared after having spark plasma sintered of AlN at 1,900 °C for 1 h. The present communication is concerned with the spark plasma sintering of commercial magnesium aluminate powder, the effect of LiF additions and the resulting optical properties of the consolidated transparent solid.

The magnesium aluminate powder (spinel) was purchased from CERALOX, with the main impurities, as

determined by ICP, in ppms: Si-13, Fe-7, Ca-9 and Zr-10. The surface area as determined by BET was about 17 m^2/g and the medium particle size 0.78 μm. Two sets of samples, the one as received and the other with 1 wt.% LiF were inserted in the 20 mm diameter bore of a graphite die of the SPS apparatus (FCT Systeme GmbH). The main process parameters, including the displacement of the upper punch, which reflects the shrinkage, i.e., densification of the sample, are summarized in Fig. 1. Identical parameter profiles were applied to both sets of samples to allow a simple identification of the effect of the LiF additive presence. At the outcome of the SPS treatment, the density of the samples was determined by the liquid displacement method. X-ray diffraction revealed the exclusive presence of the spinel diffraction peaks, and metallographic and scanning electron microscopy put in evidence the significant difference in the microstructure of the undoped and the LiF-doped spinel.

Contraction of the sample (Fig. 1), i.e. its densification, started at 950 °C and continued monotonously until application of the external pressure at 1,220 °C. Concomitantly with the application of the pressure, a discontinuous and quasi-instantaneous contraction took place. Further increase of the temperature did not cause any additional densification and only normal thermal expansion was detected. The discontinuous density increase with applied pressure is an irreversible effect since the sample maintained its state of full density after the pressure release.

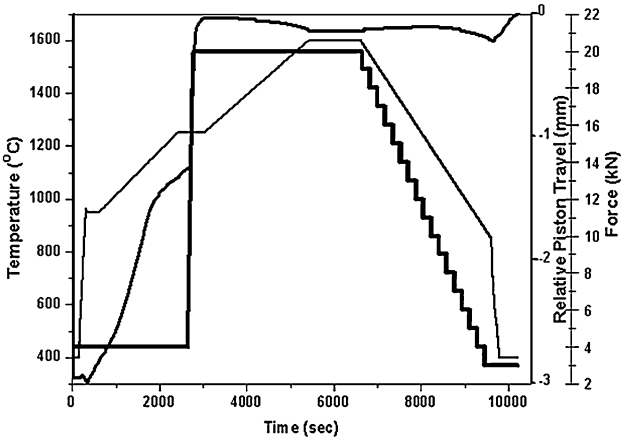

Fig. 1 The thinnest line shows the evolution of the temperature, as determined by a pyrometer focused on the upper graphite punch. The intermediate thickness line describes the location of the punch which follows the changes that take place in the height of the sample as the result of the thermal expansion and the dimensional changes induced by the sintering. The resolution is much lower than that of a dilatometer and consequently, thermal expansion effects are difficult to discern. The thickest line describes the evolution of the force (axial pressure) applied to the sample. Notice the discontinuous contraction which occurs approximately at 1200 °C upon applying the external pressure

Table 1 Properties of the samples after the SPS cycle

Property	Relative density	Elastic modulus (GPa)	Hardness (HV)
Value	99.5 ± 0.5	289 ± 10	1,300 ± 50

Both the doped and the undoped samples reached full density and have the identical mechanical properties within the experimental error at the outcome of the SPS cycle. The density values, the elastic moduli (ultrasonic sound velocity measurements) and hardness values of the consolidated samples attained after the SPS cycle are given in Table 1.

The difference between the undoped samples and those that had been doped with 1%LiF shows up dramatically in the microstructures, shown in Figs. 2, 3.

Both pictures in Fig. 2 are at the same magnification and illustrate the dramatic effect of the doping by LiF on the microstructure. The average grain-size in the doped sample is significantly larger than in the undoped one. Noteworthy are the well-defined and straight grain boundaries in the doped sample. SEM micrographs of the fracture surfaces of the undoped and doped spinel samples are shown in Fig. 3.

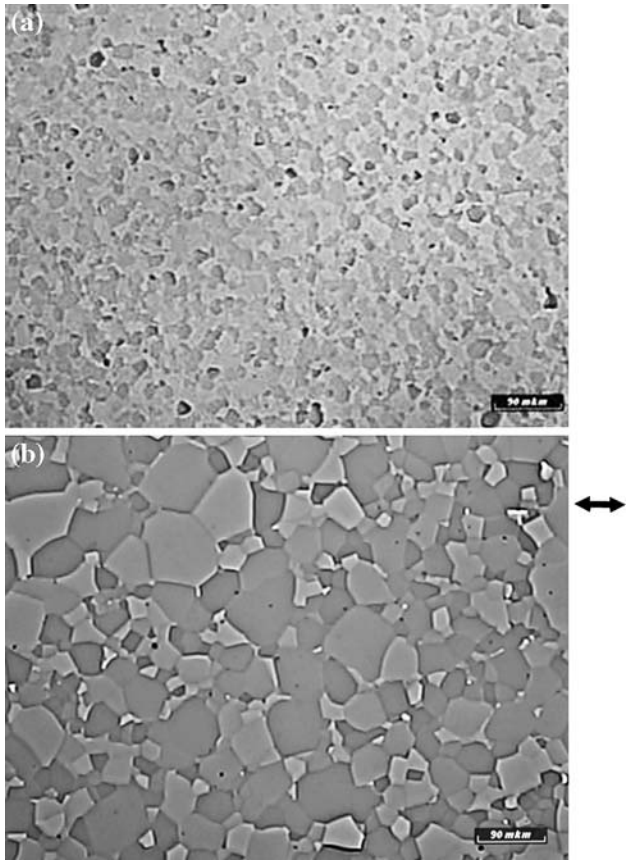

Fig. 2 Optical micrographs of the undoped (**a**) and LiF-doped (**b**) spinel after the SPS treatment

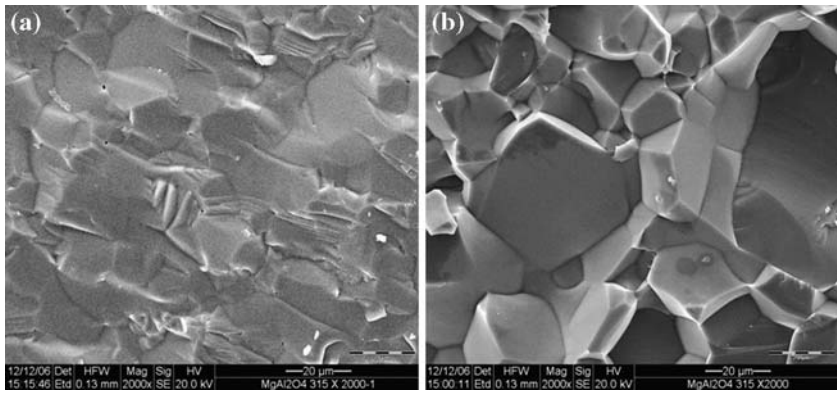

Fig. 3 SEM secondary electron micrographs of the fracture surface of the undoped spinel sample (left figure) and the sample doped with 1 wt.%LiF. Notice some residual pores (pointed at by arrows in the undoped sample)

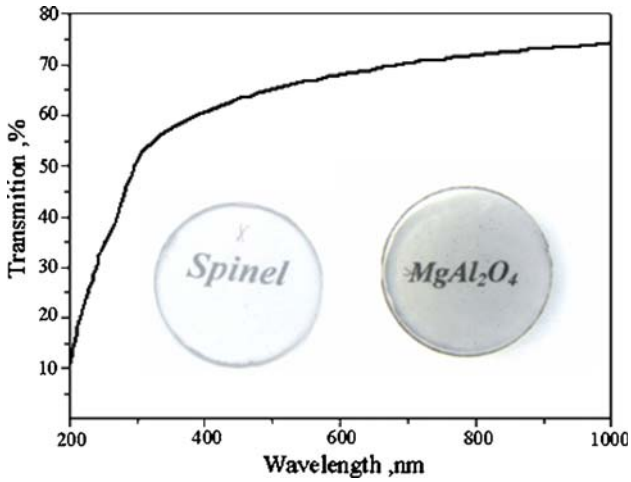

Fig. 4 Optical transmission of a spinel sample doped with 1 wt.% LiF as a function of the incident light wavelength. Insert –sintered samples of 2.7 mm width with (right) and whithout LiF addition

Whereas the fracture surface has mostly an intergranular appearance in the sample doped with LiF, it is significantly different in the undoped sample. In Fig. 3 a few residual pores are distinguishable, with many more present in the undoped sample.

A critical parameter of transparent ceramics is their light transmission characteristics. This is shown in Fig. 4 for the doped sample in which light transmission reached close to 75%. Light transmission was below 50% in the undoped sample that had undergone a similar SPS treatment.

The results that have been presented underscore two important aspects of the process described in the present communication:

1. The SPS consolidation treatment allows achieving full densification of the commercially available spinel powder.
2. The presence of 1 wt.% LiF dopant affects dramatically the spinel morphology, leads to the formation of large well-defined grains, eliminates residual boundary phases and allows achieving relatively high levels of light transmission.

The details of the LiF doping effect during SPS treatment will be further investigated.

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