Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 38 (2012) 131–140
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Fine-grained transparent $MgAl_2O_4$ spinel obtained by spark plasma sintering of commercially available nanopowders

Guillaume Bonnefont [a], Gilbert Fantozzi [a,*], Sandrine Trombert [b], Lionel Bonneau [b]

[a] INSA-Lyon, MATEIS UMR CNRS 5510, Bât. Blaise Pascal, 7 Av. Jean Capelle, 69621 Villeurbanne, France
[b] Baikowski, Les Marais Noirs Ouest-BP501, 74339 La Balme de Sillingy, France

Received 31 May 2011; received in revised form 21 June 2011; accepted 23 June 2011
Available online 29th June 2011

Abstract

A high transmittance/small grain size combination for pure spinel ceramics from commercially available nanopowders without sintering aids can be obtained by SPS sintering. By using a low heating rate $\leq$10 °C/min and a sintering temperature $\leq$1300 °C, a transparent polycrystalline $MgAl_2O_4$ spinel was fabricated by SPS with an in-line transmission of 74% and 84% for 550 nm (visible) and 2000 nm (NIR) wavelengths respectively. A small average grain size of about 250 nm was obtained and the pores located at the multiple grain junctions have a mean size of about 20 nm. The high in-line transmission is linked not only to the low residual porosity but particularly to the very small size of pores.

Keywords: Spinels; Spark plasma sintering; Transparent ceramics

1. Introduction

Elaboration of transparent polycrystalline ceramics is a significant technological challenge because single crystals exhibit a high transparency but a low mechanical performance [1–3].

Transparent ceramics must be fully dense with a porosity lower than 0.1% and a pore size as low as possible (<100 nm). Furthermore, ceramics must be single phase materials. For cubic ceramics like spinel a microstructure with a small grain size is not requested for transparency. But in order to improve the mechanical properties (strength and hardness), it is important to obtain a microstructure as fine as possible (with a grain size lower than 1 μm).

Among the cubic transparent ceramics, $MgAl_2O_4$ spinel presents a good interest for several structural applications because it has a high optical real in-line transmission and it is relatively hard [3–5]. However the availability of commercial powders is low as compared to alumina powders [1].

In order to obtain transparent $MgAl_2O_4$ spinel, very pure powders must be used [1,4,6] and furthermore, in order to reach a fine grain size after sintering, it is preferable to start with nanopowders which allows a low temperature sintering to limit the grain growth. But as shown by Krell et al. [4], the presence of strong agglomerates in the nanopowders green bodies must be avoided if a good sintering activity must be obtained at low temperature. Several commercial spinel nanopowders can be used, some of them being exploratory as emphasized by Krell et al. [4].

Sintering of spinel powders can be realized by using different sintering techniques such as hot pressing (HP) [7,8], hot isostatic pressing (HIP) post-sintering [4–6,9–12] and spark plasma sintering (SPS) [13–19].

Hamano and Kanzaki [7] have obtained by reactive hot pressing at 1400 °C/1 h/75 MPa a light transmission at 1.2 mm thickness of about 50% for a wavelength of 550 nm with a grain size of 1–2 μm. Gilde et al. [8], using a commercial powder with addition of 0.75 wt% LiF hot pressed at 1650 °C/3 h/20 MPa have measured a transmittance at 6 mm thickness of about 40% for a wavelength of 500 nm with a grain size higher than 100 μm.

The most used sintering technique is HIP. A lot of results have been obtained by many authors and a summary of these results is given below.

Gilde et al. [8] have HIPed (1900 °C/6 h/200 MPa) the precedent hot pressed spinel ceramics and have obtained a high

* Corresponding author.
E-mail address: gilbert.fantozzi@insa-lyon.fr (G. Fantozzi).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.06.045

transmittance (82.5% at 632 nm) but with a large grain size (200–300 μm). Tsai et al. [9] have used a commercial powder from Baikowski (S30CR) with an average particle size of 60 nm, sintered by HP at 1500 °C/2 h/40 MPa, followed by HIP 1500 °C/2 h/200 MPa. They have measured a transmittance at 2 mm thickness of about 72% for a wavelength of 700 nm and an average grain size of ∼2 μm. Tsukuma [10] has sintered by HIP (1300 °C/1 h/150 MPa) another commercial powder (Taimei Chemical Industry) with an average particle size of ∼150 nm and with a small addition of 0.15 wt% B_2O_3: the transmittance at 550 nm with a 1 mm thickness is ∼81% and the grain size is 1–2 μm. Goldstein et al. [11] has studied an exploratory nanopowder from Nanocerox with a particle size of ∼20–50 nm (with the presence of soft agglomerates of ∼0.8 μm) which gives after air sintering 1400 °C/80 h and HIP 1700 °C/3 h/200 MPa a real in-line transmission of about 75% at 550 nm and a grain size of ∼17 μm. Further, by using a similar powder, Goldstein et al. [5] have made a low temperature sintering (air pressureless sintering 1280 °C/3 h and HIP 1320 °C/3 h/200 MPa) and have found an in-line transmission of ∼75% at 550 nm (2 mm thickness) with an average grain size of 0.45 μm. It is the first high transmittance/small grain size combination obtained for pure spinel ceramics. Recently, Goldstein et al. [12] have shown that it is possible to obtain transparent polycrystalline spinel parts with a fine grain size (∼2.5 μm) and a high in-line transmission (72% at 550 nm, 1.7 mm thickness) after air sintering 1470 °C/3 h plus HIP 1520 °C/3 h/200 MPa of a commercially nanopowder (SCR30 from Baikowski). A higher transmission (80%) can be reached by making the HIP at higher temperature (1580 °C) with a light increase of the grain size (3.5 μm). So, it is possible to elaborate transparent polycrystalline spinel parts with high performance by using moderate cost powder and relatively low cost processing.

At present the best results obtained are those of Krell et al. [3,4]: they have investigated different undoped spinel nanopowders either commercial or exploratory. The powders were pressureless presintered in order to close the porosity and hipped in argon for 15 h with a pressure of 200 MPa. The following real in-line transmission measured at 640 nm wavelength and grain size were found: for a nanopowder with ∼50 nm particle size presintered at 1240–1260 °C and hipped at ∼1260 °C, a transmission of 84% (3.9 mm thickness) with an average grain size of 0.3 μm was obtained; for another commercial powder with ∼60 nm particle size (not too expensive), a transmission of 81–82% with an average grain size of 1.4–2.2 μm was measured after presintering at 1470 °C and hipping at 1430–1450 °C.

Another technique for obtaining transparent ceramics is SPS [20] which allows to elaborate fully dense fine-grained ceramics by sintering at lower temperature than for conventional sintering.

The first results were presented by Frage et al. [13]. They have used a commercial powder CERALOX with a medium particle size of 0.78 μm doped with 1 wt% LiF and sintered by SPS (8 °C/min/1600 °C/30 min/64 MPa). They have obtained an in-line transmittance of ∼65% at 550 nm wavelength (2.7 mm thickness) with a grain size higher than 20 μm. After this result, Meir et al. [16] have elaborated transparent polycrystalline spinel ceramics by SPS (100 °C/min/1600 °C/30 min/64 MPa, pressure applied at 1600 °C) using a reactive sintering and a sintering aid (1 wt% LiF). They attain a transmittance of ∼68% at 550 nm (thickness 2.1 mm) with a grain size of ∼10 μm.

At the same time, Morita et al. [14,15] have sintered, without sintering aid, transparent spinel polycrystal by SPS processing (1300 °C/20 min/80 MPa) of commercial powder (Taimei) with ∼360 nm particle size. By using low heating rates (<10 °C/min), the spinel exhibits an in-line transmittance of 47% at 550 nm (1.8 mm thickness) with a grain size of 0.45 μm. By using a preheating of the powder in air (3 h at 1100 °C), Kim et al. [19] have improved the transmittance (55% at 550 nm) with the same powder and the same SPS cycle. If the sintering temperature is higher than 1300 °C, precipitation of second phases consisting essentially of Mg and/or Cl occurs and degrades the transparency.

Bernard-Granger et al. [17] have investigated the transmittance of transparent spinel sintered by SPS (100 °C/min/∼1400 °C/60 MPa) from the commercial powder S30CR from Baikowski: an in-line transmittance of 46% is measured at 550 nm (1.185 mm thickness) with a grain size of ∼530 nm.

Wang and Zhao [18] have used a two-step pressure profile to sinter by SPS, at 1300 °C for 3 min, the same powder S30CR and have shown that with a low pre-load pressure (5 MPa), a heating rate of 100 °C/min and a final pressure of 100 MPa an in-line transmission of 51% at 550 nm (1.8 mm thickness) is obtained with a mean grain size of 600–700 nm.

All the main results (real in-line transmission and mean grain size) obtained by HP, HP + HIP, HIP or SPS sintering are summarized in Tables 1–3 in order to make easier a comparison between the different results.

The goal of this work is to show that it is possible to reach a high transmittance/small grain size combination for pure spinel ceramics from commercially available and not expensive powders by using the SPS sintering.

2. Experimental procedure

Different commercially available high-purity $MgAl_2O_4$ spinel powders (Baikowski, La Balme de Sillingy, France) were selected as the starting material: S30CR, S30XCR, SA30XCR. These powders are prepared from pure aluminium

Table 1
Real in-line transmission and grain sizes of spinel ceramics sintered by HP or HP + HIP.

Sintering technique	HP	HP	HP + HIP	HP + HIP
Temperature of sintering (°C)	1400	1650	1900	1500
Additive (wt%)		0.75 LiF	0.75 LiF	
RIT (%)	50	40	82.5	72
(Thickness, mm)	(1.2)	(6)	(6)	(2)
Wavelength (nm)	550	500	632	700
Average grain size (μm)	1–2	100	200–300	∼2
Reference	[7]	[8]	[8]	[9]

Table 2
Real in-line transmission and grain sizes of spinel ceramics sintered by HIP.

Sintering technique	HIP	HIP	HIP	HIP	HIP	HIP
Temperature of sintering (°C)	1300	1700	1320	1520	1580	1260
Additive (wt%)	0.15 B_2O_3					
RIT (%)	81	75	75	72	80	84
(Thickness, mm)	(1)	(2)	(2)	(1.7)	(1.7)	(3.9)
Wavelength (nm)	550	550	550	550	550	640
Average grain size (μm)	1–2	~17	0.45	2.5	3.5	0.3
Reference	[10]	[11]	[5]	[12]	[12]	[3,4]

Table 3
Real in-line transmission and grain sizes of spinel ceramics sintered by SPS.

Sintering technique	SPS	SPS	SPS	SPS	SPS	SPS
Temperature of sintering (°C)	1600	1600	1300	1300	1400	1300
Additive (wt%)	1 LiF	1 LiF				
RIT (%)	65	68	47	55	46	51
(Thickness, mm)	(2.7)	(2.1)	(1.8)	(1.8)	(1.2)	(1.8)
Wavelength (nm)	550	550	550	550	550	550
Average grain size (μm)	>20	~10	0.45	0.45	0.53	0.65
Reference	[13]	[16]	[14,15]	[19]	[17]	[18]

and magnesium salts using wet chemistry followed by calcination and milling. Some variations in synthesis process lead to differences of powder properties, especially concerning specific surface area and residual agglomerates quantity and cohesion. The main impurities contained in the three powders (in weight ppm) and the specific surface area measured by BET (Micromeritics) are given in Table 4. The average size of the elemental crystallites is in the range of 50–80 nm. The powders have a composition corresponding to a ratio MgO/Al_2O_3 equal to ~1. Scanning electron microscopy (SEM, Zeiss Supra 55VP, Germany) examination shows the presence of agglomerates with variable sizes formed by diffusion during the powder synthesis (Fig. 1). The powder particles (agglomerates) size distribution was measured with a classical laser diffraction apparatus (Horiba LA-920, Japan) and the results are shown in Fig. 2. It can be observed that the three powders do not present the same distribution of the agglomerates size. The values of the different particles diameters d10, d50, d90 and d100 are given in Table 5.

Measurements of pore size distribution were made by using the mercury intrusion equipment Autopore III (Micromeritics, USA). From the pressure dependence of the intruded mercury volume, the pore size distribution is obtained. Either the incremental pore volume or the cumulative pore volume can be plotted in the range of 5–1000 nm. The measurements were made on green samples obtained after uniaxial pressing of the powders at 72 MPa in the SPS equipment.

The powders were sintered by using a SPS equipment HPD 25/1 (FCT, Germany). The following sintering parameters have been used:

- *General conditions*: a graphite die with an internal diameter of 20 mm and a wall thickness of 10 mm was used with 2 g of powder. A constant pressure of 72 MPa is applied from the start up of the cycle to the end of the holding time, all the experiments are made under a vacuum of about 1 Pa. The following pulse sequence was chosen: 10 ms of pulsed current followed by 5 ms of current without pulse. At the end of the holding time, an annealing of 10 min at 1000 °C is performed. The cooling rate between the end of the holding time and the annealing and after the subsequent annealing is 100 °C/min.
- *Heating rates and sintering temperatures*: the following temperature cycle was used: 100 °C/min up to 800 °C, then 10 °C/min up to 1100 °C then 1 °C/min up to 1250–1320 °C, generally without holding time and with a subsequent annealing at 1000 °C for 10 min.

The microstructure was observed on the polished surface after chemical etching (concentrated phosphoric acid 120 s at the boiling temperature) using a scanning electron microscope (Zeiss Supra 55VP, Germany). The average grain size was measured using a line-intercept method, taking into account at least 200 grains and with a three-dimensional correction factor of 1.225 [21]. The residual porosity was very low and was

Table 4
Investigated spinel powders.

	SSA (m^2/g)	Na (ppm)	K (ppm)	Fe (ppm)	Si (ppm)	Ca (ppm)	S (ppm)
S30CR	31	13	35	1	36	<1	~600
S30XCR	21.7	18	34	2	6	5	~300
SA30XCR	28.2	19	26	7	6	10	~400

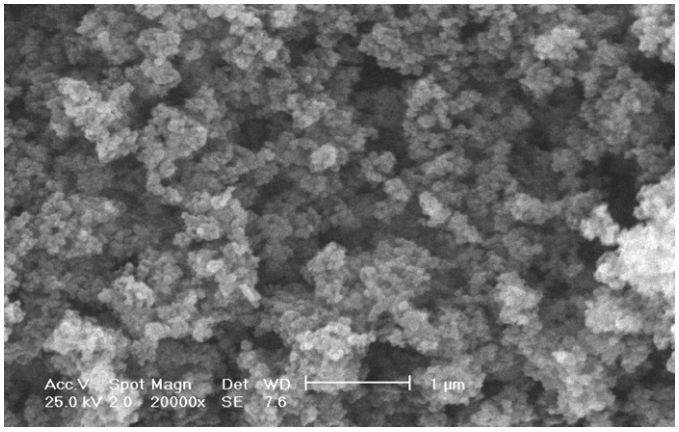

Fig. 1. Typical scanning electron microscopic image of the S30CR powder.

measured by using the SEM. The pore size and the average area fraction of pore A_p were measured directly in the SEM images with a resolution limit <15 nm.

Specimens for optical measurements were prepared by polishing the samples with 0.2 μm diamond paste to about 3 mm thickness. The real in-line transmission (RIT) was measured with a spectrophotometer UV-Vis/NIR V-670 (Jasco, Japan) as a function of the wavelength λ in the visible and near-IR range 300–3000 nm.

The hardness HV3 was measured using a Vickers hardness tester FV-700 (Future Tech Corporation, Japan) with a standard Vickers diamond indenter with a load of 3 kgf (∼30 N).

Table 5
Particle diameters of powders.

	d10 (μm)	d50 (μm)	d90 (μm)	d100 (μm)
S30CR	0.21	1.12	3.96	10.08
S30XCR	0.20	0.32	1.37	4.47
SA30XCR	0.3	1.92	5.34	13.23

3. Results and discussion

Fig. 3 shows an example of profile of the main process parameters (temperature, pressure, displacement of the upper punch) used during the SPS sintering. According to the data of Fig. 3, the apparent densification begins near 870 °C and is almost complete at around 1200 °C.

All sintered samples exhibit a relative density higher than 99.95% measured by the Archimedes method in water. The sintering cycle has been chosen taking into account the results obtained by Morita et al. [14,15] who have shown that the residual porosity and the pore size can be reduced by using low heating rates (≤10 °C/min) without significant grain growth. By comparison with the Taimei commercial powder [14,15], the densification of the Baikowski powders occurs at lower temperature (of about 100 °C). The sintering temperatures leading to the best real in-line transmission were determined for each powder: 1300 °C, 1300 °C, 1280 °C for the S30CR, S30XCR, SA30XCR powders respectively.

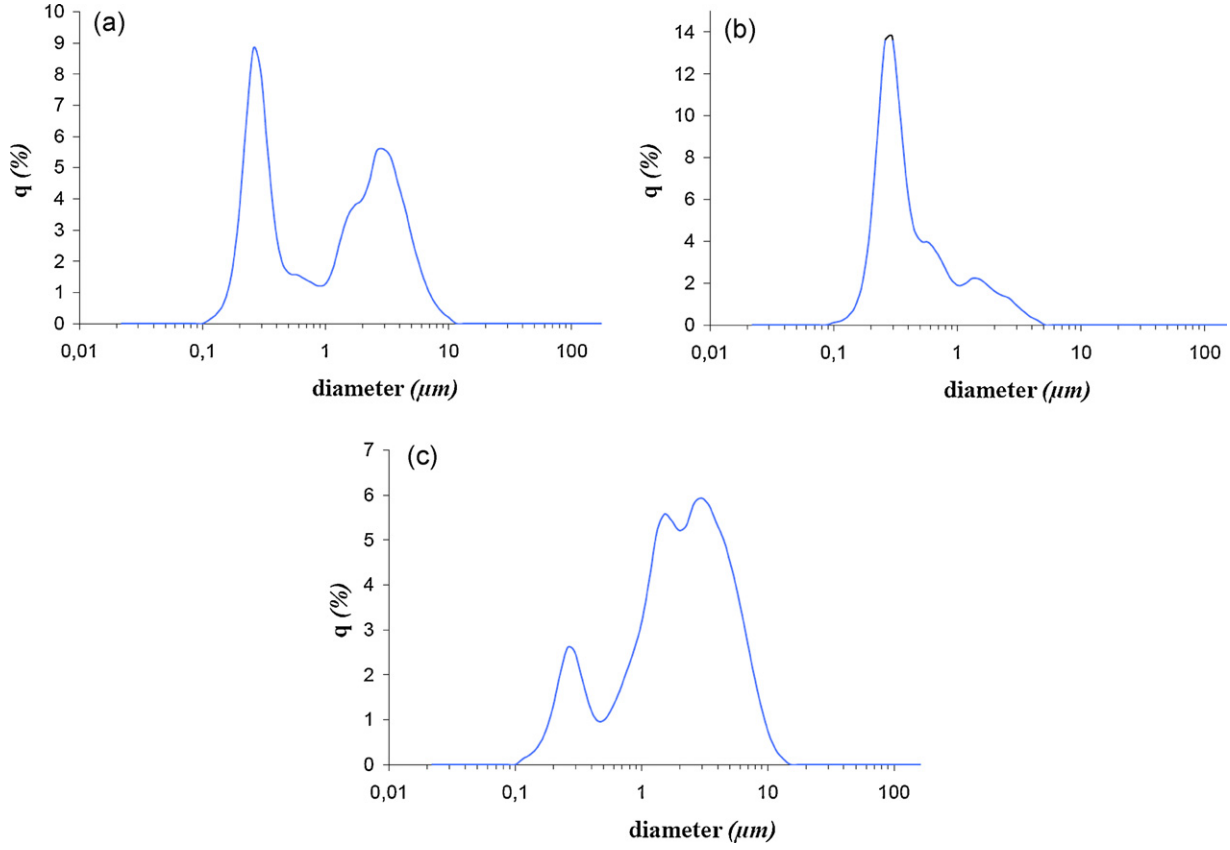

Fig. 2. Particles size (volumetric) distribution of spinel powders: (a) S30CR, (b) S30XCR and (c) SA30XCR.

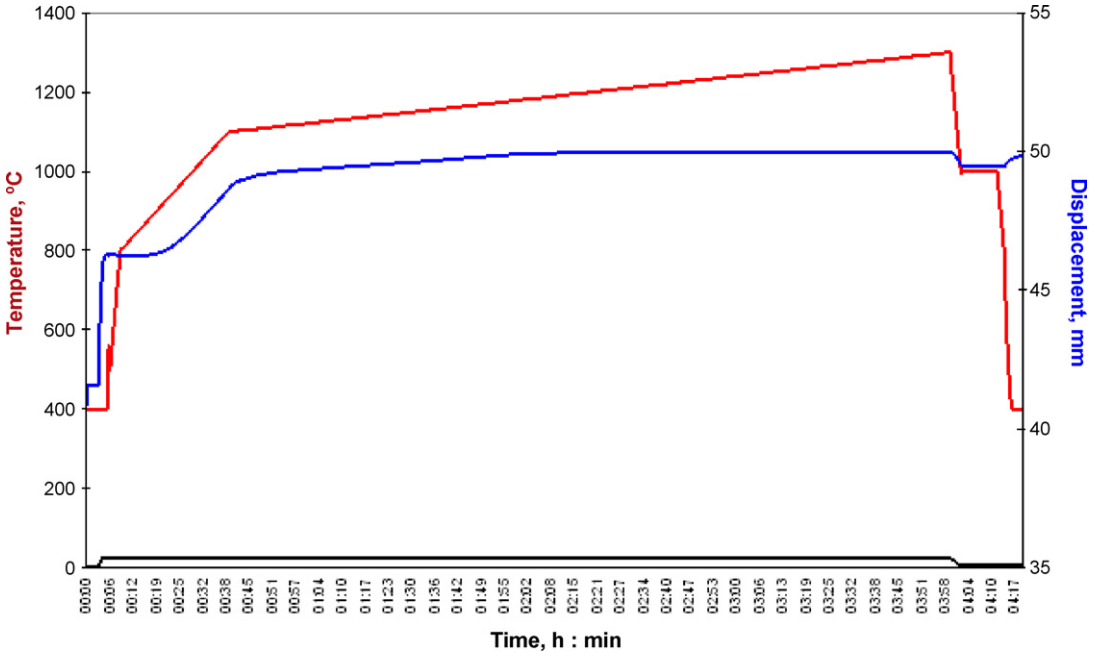

Fig. 3. Temperature, pressure and punch displacement profiles during a SPS cycle.

The microstructure of the SPS samples is shown in Fig. 4. The mean measured grain size is about 250 nm and the area fraction of pore A_p is smaller than 0.4% for the S30CR spinel. This fine grain size is due to the low temperature of sintering which was used during the SPS processing. The fine pores are essentially located at the multiple grain junctions and their mean size is about 20 nm (the maximum size is ~50 nm). The presence of fine particles of second phases (consisting of Mg and/or Cl) as seen by Morita et al. [15] for sintering at high temperature was not observed for our specimens. So, our samples exhibit a very fine-grained microstructure with a low residual porosity and a size of pores lower than 50 nm. The small sizes of the pores must be linked to the limitation of the grain growth and consequently to the agglomeration of fine pores [15]. The S30XCR spinel exhibits about the same microstructure as the S30CR spinel: the grain size is slightly higher (350 nm against 250 nm). On the other hand, the SA30XCR presents a microstructure with a higher grain size (mean grain size of ~450 nm) and particularly bigger pores sizes (mean pores size of ~120 nm as shown in Fig. 4c and d)

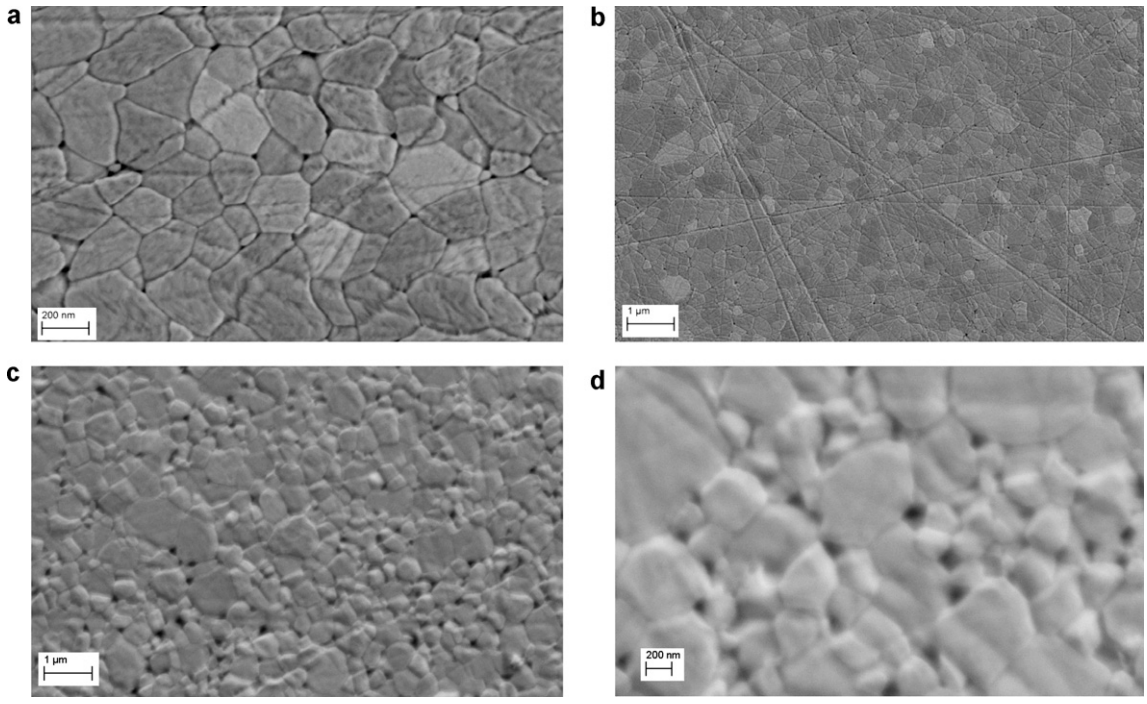

Fig. 4. Scanning electron microscopic images of the S30CR (a and b) and SA30XCR (c and d) spinels after sintering up to 1300 °C and 1280 °C respectively.

Fig. 5. Visual appearance of the S30CR spinel sample sintered up to 1300 °C (2.3 mm thickness) (the left sample is 30 mm above the printed text).

compared to the two other spinels. The area fraction of pores A_p is about 1% for the SA30XCR.

The Vickers hardness was measured for the sintering temperatures corresponding to the best results in transmission. The following results were obtained: HV3 = 16 GPa, HV3 = 15 GPa, HV3 = 15 GPa for the S30CR, S30XCR, SA30XCR powders respectively. The high value of hardness is due to the very small grain size of our sintered spinels as expected from the study of Krell and Bales [22] on the grain size dependence of transparent spinel. The S30CR has a slightly higher value of hardness due to its very small grain size.

Fig. 5 shows the visual aspect of the S30CR spinel sample sintered by SPS (2.3 mm thickness). Our sample appears transparent in the visible range, with a very small brown coloration. The in-line transmission spectra obtained for the three powders are shown in Fig. 6. In order to make a comparison with the results obtained by other researchers, the RIT measured at two wavelengths (550 nm for the visible range and 2000 nm for the IR range) is evaluated for the three powders for a same thickness $d_2 = 1.8$ mm by using Eq. (1)

$$\mathrm{RIT}(d_2) = (1 - R_S)\left(\frac{\mathrm{RIT}(d_1)}{1 - R_S}\right)^{d_2/d_1} \quad (1)$$

where R_S is the total normal surface reflectance (≈0.14) and $\mathrm{RIT}(d_1)$ is the in-line transmission for a sample thickness d_1 (the real thicknesses of the samples were the followings: 2.3 mm for the S30CR and SA30XCR powders and 2.25 mm for the S30XCR powder).

For λ = 550 nm, the following values are found: S30CR 74%, S30XCR 71%, SA30XCR 62%; for λ = 2000 nm, the transmittance is: S30CR 82%, S30XCR 84%, SA30XCR 77%. For the S30CR and S30XCR powders, the IR in-line transmission approaches the theoretical transmission which is ∼87%. In the visible range, the in-line transmission is sensitive to the SPS conditions as shown by Morita et al. [15], Wang and Zhao [18] and depends also on the powder used. The SA30XCR powder which has the larger particles or agglomerates size exhibits the most important fraction of large particles (Fig. 2b) and the less good in-line transmission for all the wavelength range. This result must be related to a decrease of the sintering activity when the powder has a more significant aggregation as pointed out by Krell et al. [4]. Indeed, the SA30XCR contains a high amount of hard agglomerates which cannot be totally eliminated by pressing and sintering. The higher residual porosity and the higher pore size observed for this powder (Fig. 4) is responsible for the lower values obtained in both visible and IR ranges. The difference of behaviour of the two other powders can be also related to the particles size distribution and to the cohesion of the agglomerates: the residual agglomerates of S30CR and S30XCR are soft. The S30CR powder exhibits a larger fraction of large particles compared with the S30XCR powder (Fig. 2) but has a higher specific surface area (31 m^2/g against 21.7 m^2/g). The S30XCR is better des-agglomerated than S30CR, but its reactivity during

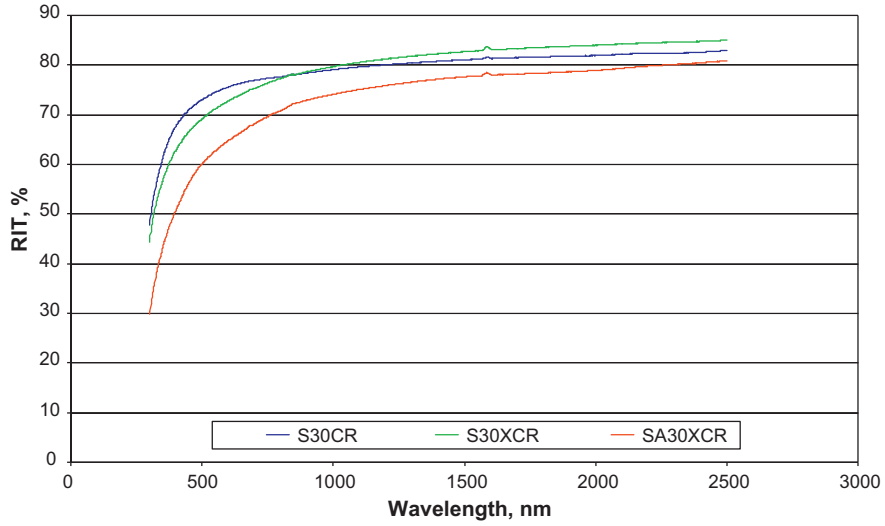

Fig. 6. In-line transmittance (evaluated for a thickness of 1.8 mm) as a function of the wavelength λ of the different polycrystalline spinels after sintering up to 1300 °C: (a) S30CR (2.3 mm), (b) S30XCR (2.25 mm) and (c) SA30XCR (2.3 mm).

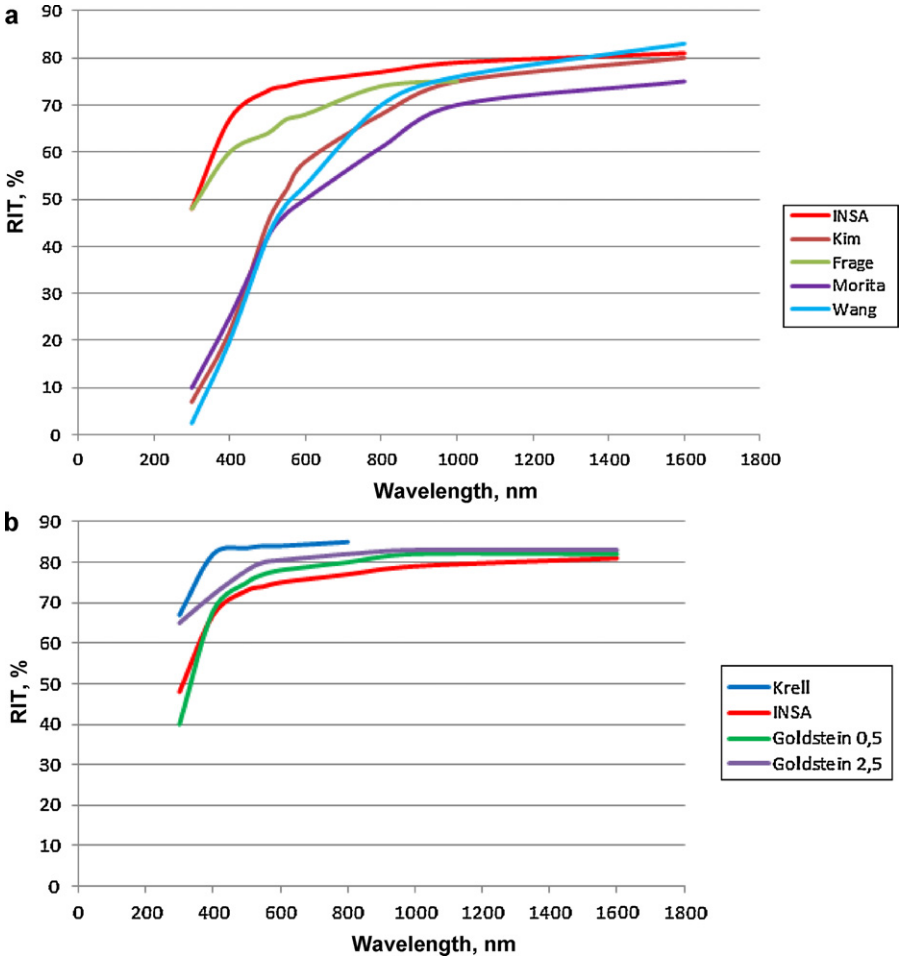

Fig. 7. In-line transmittance as a function of the wavelength λ for polycrystalline spinels obtained by different authors: (a) by SPS: Frage et al. [13], Morita et al. [15], Kim et al. [19], Wang and Zhao [18] and (b) by HIP: Krell et al. [4], Goldstein et al. [5] (0.5 μm), Goldstein et al. [12] (2.5 μm).

sintering is lower, due to lower specific surface area. That might induce some slight differences in pore amount and pore size in sintered S30CR and S30XCR and explains their behaviour.

It is interesting to compare our results with those obtained by the different authors who have used SPS for sintering the spinel polycrystal. This comparison is made in Fig. 7a. For the transparent spinel sintered with pure nanopowders without sintering additive, our results are clearly better than the in-line transmittance results reported previously. For the wavelength λ = 550 nm, a maximum value of 74% is measured against 55% for Kim et al. [19] and 50% for Wang and Zhao [18]. Our results show that a two-step pressure procedure as used by Wang and Zhao is not indispensable in order to obtain a very good transmittance and furthermore no graphite contamination was observed contrarily to the results of Bernard-Granger et al. [17]. Wang and Zhao assumed that the observed darker discoloration for high pre-load pressure is due to an increase of the dislocation density during the fast densification process in SPS. This hypothesis is not confirmed by our results and furthermore, the transmission electron microscopic observations made by Morita et al. [15] do not confirm the presence of dislocations after SPS sintering of the transparent $MgAl_2O_4$ spinel polycrystal. Concerning the graphite contamination, it can be effectively avoided by making careful experiment [18].

If a sintering additive is added (1 wt% LiF) like reported by Meir et al. [16], the transmittance is higher (68% at 550 nm) but still lower than our result. Another important point concerns the grain size: for the pure powders, the grain size is between 450 and 700 nm against 250 nm for our samples; for the doped powder, the grain size is higher than 10 μm.

It is important also to compare our results with the best results obtained after a HIP sintering (Fig. 7b). Goldstein et al. [5,12] have measured at 550 nm the following transmittance: 75% with a grain size of 450 nm and by using the S30CR commercial powder 72% and 80% with a grain size of 2.5 and 3.5 μm respectively. Krell et al. [3,4] have attained the best in-line transmission of about 83% at 550 nm with a small grain size of about 0.3 μm.

In summary, our results show clearly that it is possible to reach a high transmittance/small grain size combination for pure spinel ceramics from commercially available powders by using the SPS sintering which is more rapid than the HIP processing.

These results can be understood if the scattering sources for high purity ceramics are taken into account and particularly the

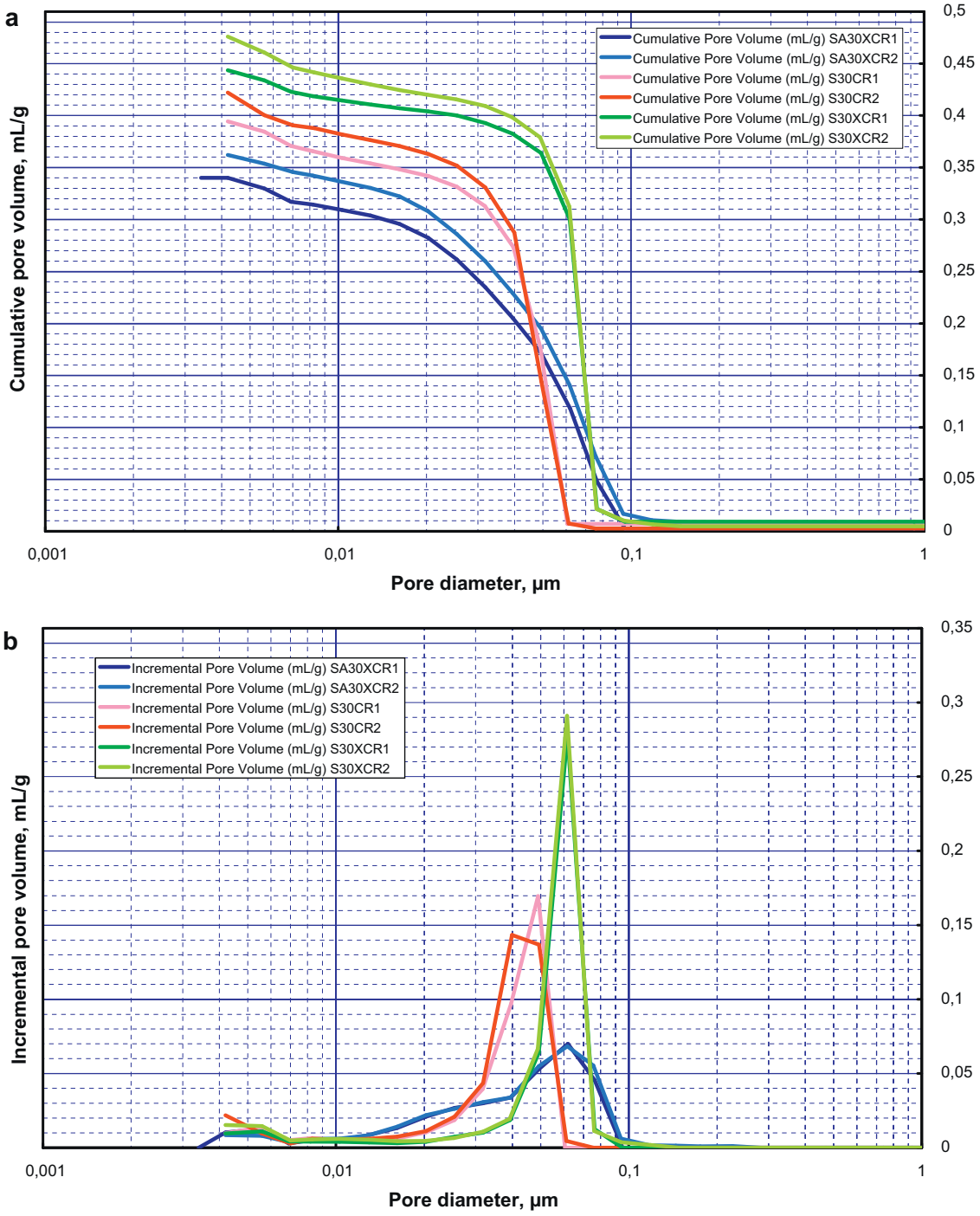

Fig. 8. Pore size distribution of green samples after uniaxial pressing at 72 MPa for the three powders: (a) cumulative pore volume and (b) incremental pore volume.

presence of pores. Indeed for cubic ceramics with clean grain boundaries, the grain size has no influence on in-line transmission and the in-line transmission is essentially controlled by the residual pores.

As shown by Krell and Klimke [23], the pore size distribution does not change substantially between the green state and the intermediate sintering stage. So, in order to obtain a very high density after sintering with a good homogeneous densification, it is important to have green samples after uniaxial pressing with a narrow distribution of the pore size and the absence of large pores (agglomerates).

Fig. 8 presents the pore size distribution obtained after uniaxial pressing for the three powders. The obtained results which exhibit a good reproducibility show that the two powders S30CR and S30XCR display a much narrow width of the pore size distribution compared to the SA30XCR powder. Furthermore, the maximum pore sizes obtained are the following: ~60 nm for the S30CR powder, ~75 nm for the

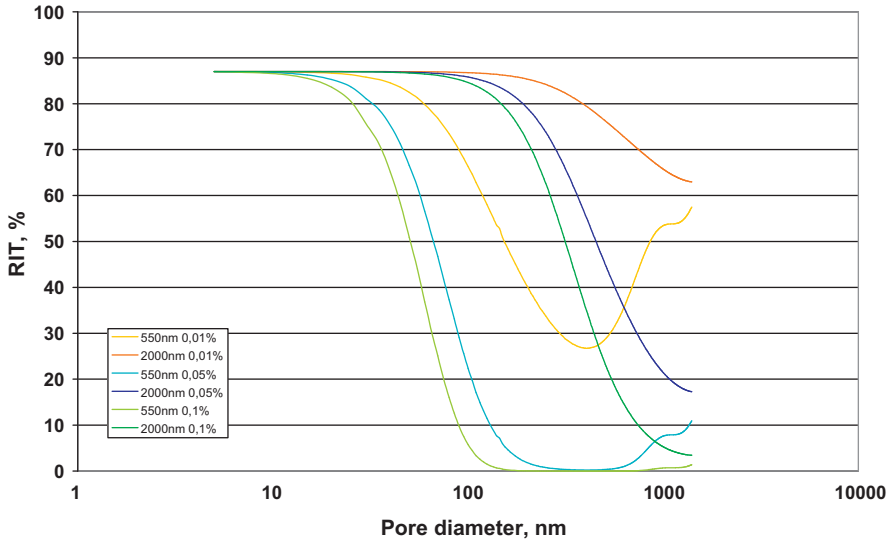

Fig. 9. Effect of pore size on the in-line transmission for wavelengths of 550 and 2000 nm, with porosities, $p = 0.01$, 0.05 and 0.1% (thickness 1.8 mm).

S30XCR powder and about 100 nm for the SA30XCR which presents a broader distribution. So, the two powders S30CR and S30XCR exhibit a better homogeneous particle coordination and so a better sintering densification.

The effect of the pore size distribution on the in-line transmission can be examined. Indeed, the RIT is given by the Beer–Lambert law and decreases exponentially with the thickness d as follows:

$$\mathrm{RIT} = (1 - R_s)\exp(-\gamma d) \tag{2}$$

with R_s is the reflection losses on the two surfaces ($\approx$0.14) with a normal incidence; R_s the $2R'/(1 + R')$; R' the $(n - 1)^2/(n + 1)^2$; n the refractive index of the ceramic; γ the total scattering coefficient; $\gamma = \gamma_{gb} + \gamma_p$ with γ_{gb} the grain boundary contribution and γ_p is the pore contribution.

The grain boundary contribution to scattering for cubic polycrystalline ceramics can be neglected and the pore-scattering contribution is the more important. The pore contribution is given by [21]:

$$\gamma_p = \frac{3pC_{sca}}{4\pi r^3} \tag{3}$$

with p is the total porosity; r the radius of the pores and C_{sca} is the scattering cross section of one spherical pore.

C_{sca} can be calculated numerically using the Mie scattering theory [21,24,25]. The scattering cross section of pores C_{sca} has been determined for incident light with two wavelengths 550 and 2000 nm as a function of the pore size by using the computer program given by Bernhard [25]. From the calculation of C_{sca}, the scattering coefficient due to the pores can be determined and so, the in-line transmission is determined as a function of the pore size for the two wavelengths for different amounts of porosity and for a sample thickness of 1.8 mm. The obtained results presented in Fig. 9 are very similar to those of Morita et al. [15] and show clearly that the in-line transmission depends not only on the porosity but is very sensitive to the pore diameter. When the pore size becomes of the same order of magnitude of the wavelength of the incident light, the transmission reaches a minimum. So, for the wavelength 550 nm, the transmission decreases significantly if the pore size exceeds about 40–50 nm whereas for $\lambda = 2000$ nm, this decrease occurs for a pore size higher than about 300 nm. On the other hand, the measured transmission of 74% for our S30CR samples can be explained by the very small size of the essentially intra-agglomerate pores: the pore diameter of the S30CR is lower than 50 nm. This size is lower than the pore diameter range (50–300 nm) obtained by Morita et al. The pore diameter of our spinels typically ranges from 20 to 100 nm. So, the higher in line transmission measured for the S30CR and S30XCR spinels can be explained by the smaller pores size observed for these two materials. The same observation has been made from the measurements of pore size distribution after uniaxial pressing: the S30CR spinel presents the lower maximum pore size ~60 nm and the S30XCR has a slightly larger maximum pore size (~75 nm). So, the microstructures of the S30CR and S30XCR spinels being very similar, their transmissions are relatively close as observed in Fig. 6. Concerning the SA30XCR spinel, it exhibits a mean pore size of about 120 nm which leads to a decrease of the real in-line transmission as observed in Fig. 6 and as shown in Fig. 9. So, the SA30XCR spinel has a lower real in-line transmission in the visible and in the NIR wavelengths compared to the S30CR and S30XCR spinels.

4. Conclusion

In summary, the present study successfully showed that a high transmittance/small grain size combination for pure spinel ceramics from commercially available nanopowders without sintering additives can be obtained by SPS sintering. By using low heating rate as proposed by Morita et al. [15], transparent polycrystalline $MgAl_2O_4$ spinel with an in-line transmission of 74% and 84% for the wavelengths in the visible (550 nm) and in the near infrared (2000 nm) respectively, was fabricated by SPS

sintering at temperatures lower than 1300 °C. A small average grain of about 250 nm was obtained and the pores are located at the multiple grain junctions with a mean size of about 20 nm. The high in-line transmission is linked not only to the low residual porosity but particularly to the very small size of pores which can be achieved by the low heating rate and the low temperature SPS processing.

Acknowledgements

The authors are grateful to the financial support of the ANR CERATRANS and to all the gathered participants, Lucile Lallemant (INSA) for the measurements of pore volume and SEM observations, Bernard Durand (Université Paul Sabatier), Johan Petit (ONERA), Stéphane Chaillot (BOOSTEC) and Denis Langlade (BTS Industrie).

References

[1] A. Krell, T. Hutzler, J. Klimke, Transparent ceramics for structural applications, Ceram. Forum Int. (Ber Dt Keram Ges), 84 (2007) E41–E50.
[2] A. Krell, T. Hutzler, J. Klimke, Transparent compact ceramics/inherent physical issues, Opt. Mater. 31 (2009) 1144–1150.
[3] A. Krell, T. Hutzler, J. Klimke, Transmission physics and consequences for materials selection, manufacturing, and applications, J. Eur. Ceram. Soc. 29 (2009) 207–221.
[4] A. Krell, T. Hutzler, J. Klimke, A. Potthoff, Fine-grained transparent spinel windows by the processing of different nanopowders, J. Am. Ceram. Soc. 93 (2010) 2656–2666.
[5] A. Goldstein, A. Goldenberg, M. Hefetz, Transparent polycrystalline $MgAl_2O_4$ spinel with submicron grains, by low temperature sintering, J. Ceram. Soc. Jpn. 117 (2009) 1281–1283.
[6] I. Reimanis, H.-J. Kleebe, A review on the sintering and microstructure development of transparent spinel ($MgAl_2O_4$), J. Am. Ceram. Soc. 92 (2009) 1472–1480.
[7] K. Hamano, S. Kanzaki, Fabrication of transparent spinel ceramics by reactive hot-pressing, J. Ceram. Soc. Jpn. 85 (1997) 225–230.
[8] G. Gilde, P. Patel, P. Patterson, D. Blodgett, D. Duncan, D. Hahn, Evaluation of hot pressing and hot isostatic pressing parameters on the optical properties of spinel, J. Am. Ceram. Soc. 88 (2005) 2747–2751.
[9] D.S. Tsai, C.T. Wang, S.J. Yang, S.E. Hsu, Hot isostatic pressing of $MgAl_2O_4$ spinel infrared windows, Mater. Manuf. Proc. 9 (1994) 709–719.
[10] K. Tsukuma, Transparent $MgAl_2O_4$ spinel ceramics produced by HIP post-sintering, J. Ceram. Soc. Jpn. 114 (2006) 802–806.
[11] A. Goldstein, A. Goldenberg, Y. Yeshurun, M. Hefetz, Transparent $MgAl_2O_4$ spinel from a powder prepared by flame spray pyrolysis, J. Am. Ceram. Soc. 91 (2008) 4141–4144.
[12] A. Goldstein, A. Goldenberg, M. Vulfson, Development of a technology for the obtained of fine grain size, transparent $MgAl_2O_4$ spinel parts, J. Ceram. Sci. Technol. 2 (2011) 1–8.
[13] N. Frage, S. Cohen, S. Meir, S. Kalabukhov, M.P. Dariel, Spark plasma sintering (SPS) of transparent magnesium-aluminate spinel, J. Mater. Sci. 42 (2007) 3273–3275.
[14] K. Morita, B.-N. Kim, K. Hiraga, H. Yoshida, Fabrication of transparent $MgAl_2O_4$ spinel polycrystal by spark plasma sintering processing, Scripta Mater. 58 (2008) 1114–1117.
[15] K. Morita, B.-N. Kim, K. Hiraga, H. Yoshida, Spark-plasma-sintering condition optimization for producing transparent $MgAl_2O_4$ spinel polycrystal, J. Am. Ceram. Soc. 92 (2009) 1208–1216.
[16] S. Meir, S. Kalabukhov, N. Froumin, M.P. Dariel, N. Frage, Synthesis and densification of transparent magnesium aluminate spinel by SPS processing, J. Am. Ceram. Soc. 92 (2009) 358–364.
[17] G. Bernard-Granger, N. Benameur, C. Guizard, M. Nygren, Influence of graphite contamination on the optical properties of transparent spinel obtained by spark plasma sintering, Scripta Mater. 60 (2009) 164–167.
[18] C. Wang, Z. Zhao, Transparent $MgAl_2O_4$ ceramic produced by spark plasma sintering, Scripta Mater. 61 (2009) 193–196.
[19] B.-N. Kim, K. Morita, J.-H. Lim, K. Hiraga, H. Yoshida, Effects of preheating of powder before spark plasma sintering of transparent $MgAl_2O_4$ spinel, J. Am. Ceram. Soc. 93 (2010) 2158–2160.
[20] J.R. Groza, Field assisted sintering, Powder Metall. 7 (1998) 583–589.
[21] R. Apetz, M.P.B. van Bruggen, Transparent alumina: a light-scattering model, J. Am. Ceram. Soc. 86 (2003) 480–486.
[22] A. Krell, A. Bales, Grain size-dependent hardness of transparent magnesium aluminate spinel, Int. J. Appl. Ceram. Technol., in press.
[23] A. Krell, J. Klimke, Effects of the homogeneity of particles coordination on solid-state sintering of transparent alumina, J. Am. Ceram. Soc. 89 (2006) 1985–1992.
[24] J.G.J. Peelen, R. Metselaar, Light scattering by pores in polycrystalline materials: transmission properties of alumina, J. Appl. Phys. 45 (1974) 216–220.
[25] M. Bernhard, http://www.lightscattering.de/MieCalc/index.html.