Journal of the European Ceramic Society 40 (2020) 3354–3357

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Short communication

Highly dense spinel ceramics with completely suppressed grain growth prepared via SPS with NaF as a sintering additive

Vojtěch Nečina*, Willi Pabst

Department of Glass and Ceramics, University of Chemistry and Technology, Prague (UCT Prague), Technická 5, 166 28, Prague 6, Czech Republic

ARTICLE INFO

Keywords:
Spinel
Spark plasma sintering (SPS)
Sintering additives
Sodium fluoride
Transparent ceramics

ABSTRACT

For the preparation of transparent spinel ceramics it is common practice to use LiF as a sintering additive to achieve transparency. However, it is well known that in this case the grain size exhibits a significant increase compared to pure spinel ceramics, which can lead to a deterioration in mechanical properties. The findings of this paper indicate that when NaF is used as a sintering additive for the preparation of spinel ceramics via spark plasma sintering (SPS) translucent materials with a high level of densification can be obtained without observable grain growth. It is shown that the grain size after SPS at 1500 °C with 1 h dwell is essentially the same as the primary particle size of the spinel powder, whereas pure spinel ceramics prepared via SPS under the same conditions exhibit grain growth by approximately a factor 5.

One of the key problems in ceramic technology in general is the tradeoff between densification and grain growth. This problem is highly acute in the context of transparent ceramics usable for impact-resistant windows because full densification is needed to ensure transparency, while small grain size is desirable from the viewpoint of mechanical strength. In this paper the effect of NaF as a sintering additive in the preparation of fully dense spinel ($MgAl_2O_4$) ceramics with almost completely suppressed grain growth is investigated. Usually LiF is utilized as a sintering additive in order to obtain highly dense, transparent spinel ceramics, e.g. via spark plasma sintering (SPS), but it is known that LiF tends to promote excessive grain growth [1,2], thus degrading mechanical properties. Contrary to LiF, it is demonstrated here that NaF not only allows full densification of spinel ceramics via SPS, but at the same time almost completely suppresses grain growth, leading to the remarkable result that the grain size is more than 5 times smaller compared to pure spinel ceramics (without LiF or any other sintering additive) prepared under the same conditions. The material thus prepared is highly translucent.

Both samples (with or without NaF) were prepared from commercially available magnesium-aluminum spinel ($MgAl_2O_4$) powder (S25CRX, Baikowki, France) and extra pure NaF (Carl Roth, Germany) as a sintering additive. The spinel powder was homogenized together with 1 wt.% of NaF in ethanol suspension by ball-milling for 24 h, followed by 24 h drying at 80 °C. The resulting powder was crushed and subsequently sieved to avoid large agglomerates. The particle size distributions of the pure powder and the powder with NaF addition (after ball-milling) were measured by laser diffraction (Particle Sizer Analysette 22 Nanotec, Fritsch, Germany).

Sintering was conducted in a spark plasma sintering furnace (HP D 10-SD, FCT Systeme, Germany). A sintering schedule which is commonly utilized for the preparation of transparent spinel ceramics with the addition of LiF [3] was adapted. Samples (20 mm in diameter) were prepared by pouring 3.5 g of powder into a graphite die lined with graphite paper and insulated by carbon felt. Heating up to 1100 °C at a rate of 25 °C/min was followed by 30 min dwell, whereby the initial pressure of 10 MPa was raised up to 80 MPa within 1 min after the first 15 min of the dwell. After the dwell the temperature was raised up to 1500 °C at the same heating rate (25 °C/min), followed by 1 h dwell. Cooling was performed at a rate of 50 °C/min, with continuous reduction of the pressure down to a minimal value of 10 MPa at 600 °C.

After sintering the samples were polished to a 1 μm diamond finish. The in-line transmittance of samples was measured using a spectrophotometer (UV-2450, Shimadzu, Japan). Thermal etching was performed at 1400 °C for 1 h. Thermally etched surfaces were observed by scanning electron microscopy (SEM Lyra 3, Tescan, Czech Republic). Mean chord lengths and Jeffries sizes of grains were determined on SEM

* Corresponding author.
E-mail addresses: necinav@vscht.cz (V. Nečina), pabstw@vscht.cz (W. Pabst).

https://doi.org/10.1016/j.jeurceramsoc.2020.03.005
Received 27 January 2020; Received in revised form 2 March 2020; Accepted 3 March 2020
Available online 04 March 2020
0955-2219/

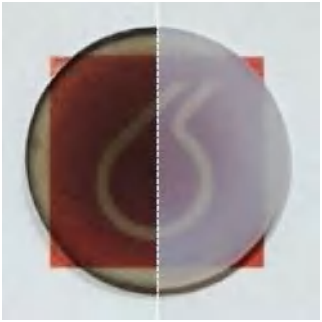

Fig. 1. Macroscopic appearance of spinel ceramics prepared via SPS from pure powder (left) and powder with 1 wt.% addition of NaF (right); the thickness of both samples is approximately 1.7 mm.

micrographs by stereology-based image analysis [4]. In both cases the same positions on the samples were analyzed (i.e. at 3 mm distance from the sample periphery).

The macroscopic appearance of the polished samples is shown in Fig. 1. The sample prepared from pure spinel powder is characterized by black discoloration, caused by carbon contamination, which is typical for spinel ceramics prepared via SPS [5] and closely related to temperature gradients [6]. On the other hand, the sample with NaF addition does not exhibit any black discoloration, which indicates that also NaF prevents carbon contamination in spinel ceramics, similar to LiF [3,7], where the liquid layer of sintering additive inhibits the deposition of carbon and the evaporation of sintering additive can create turbulences which prevent even the contact of carbon with the sintering material. However, the sample with NaF addition is characterized by a white haze, which may indicate Rayleigh scattering at small pores, probably as a result of a small amount of residual porosity. Measured in-line transmittances for the two samples are displayed in Fig. 2. Obviously, the sample prepared from pure spinel powder exhibits better values throughout the whole measured spectrum (200–800 nm), but the difference is becoming smaller at larger wavelengths and tends to be very small towards the infrared region.

The microstructure of samples with or without NaF is illustrated in Fig. 3. One can clearly see that the grain size is significantly smaller in the case of the sample with NaF addition. The corresponding mean chord lengths and Jeffries sizes of grains are displayed in Table 1, where it is evident that the grain size of the sample with NaF addition is more than 5 times smaller compared to the pure one. It has to be emphasized that for obtaining comparable values it is highly recommended (and in some cases essential) to measure the grain size at the same distance

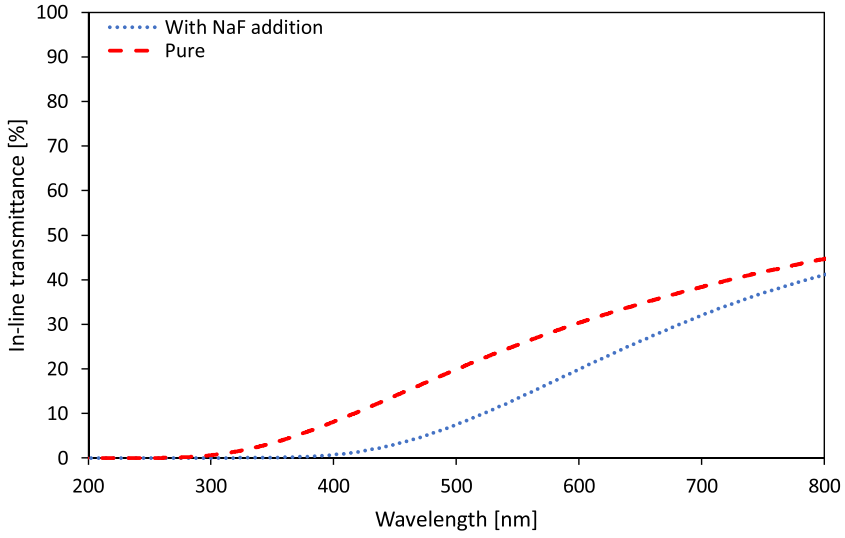

Fig. 2. In-line transmittance of polished samples prepared from pure spinel powder (dashed curve) and powder with 1 wt.% addition of NaF (dotted curve); all values are valid for 1.7 mm thickness.

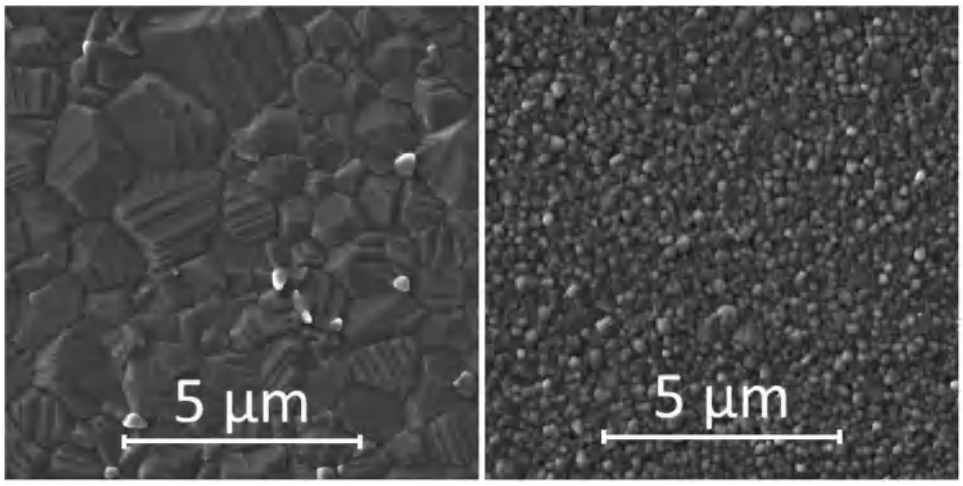

Fig. 3. Microstructure of spinel ceramics prepared via SPS from pure powder (left) and powder with 1 wt.% addition of NaF (right).

Table 1
Mean chord lengths and Jeffries sizes of grains of spinel ceramics prepared via SPS from pure powder and powder with 1 wt.% addition of NaF, determined at the same distance from the periphery (for calculation of errors see [4]).

Sample	Mean chord length [nm]	Jeffries size [nm]
Pure	952 ± 48	979 ± 40
With NaF addition	179 ± 8	186 ± 4

(here 3 mm) from the sample periphery, see the discussion in [8].

The grain growth of the sample is in fact almost negligible, when the original particle size is considered. In Fig. 4 results of laser diffraction are displayed for both powders. The results are very similar, with median sizes of 247 and 233 nm for the pure (as-received) and powder with NaF addition (after homogenization by ball-milling), respectively. Obviously the large-size modes (at around 1.07 μm for both powders) correspond to agglomerates of primary particles[1].

The progress of sintering (temperature and relative densification[2] versus time) is illustrated in Fig. 5, where an earlier onset of densification at approximately 830 °C can be identified for the sample with NaF addition (the melting point of NaF is 993 °C), i.e. the shift of the densification onset temperature compared to the pure sample is approximately 160 °C. Surprisingly, NaF accelerates the densification of spinel at low temperature (area A in Fig. 5), but decelerates it at high temperature (area B in Fig. 5). In fact, in area B the densification of the pure spinel powder accelerates (steep densification rate) and overrides the relative densification of the powder with NaF addition, so that the densification of the former is practically finished (documented by the translucency on the left hand side of Fig. 1) at an earlier stage (slightly more than 60 min), and a crossover of the two densification curves results. Now it is well known that grain growth dominates in the final stage of sintering, in particular when second-phase inclusions or pores are absent. Therefore, in the case of the pure spinel grain growth is expected to accelerate immediately after densification, while in the case of the powder with NaF addition, where full density is achieved only asymptotically (as documented by the translucency on the right hand side of Fig. 1), grain growth is inhibited or even suppressed by a very small amount of residual pores and/or possibly by another effect that is related to NaF enrichment at the grain boundary (the explanation of which is of course unclear so far and would require further investigation). This corresponds well with the observed difference in grain size.

The combination of high temperature, pressure and prolonged time surprisingly did not result in any significant grain growth in the case of sample with 1 wt.% of NaF, even though very high densification was achieved, the temperature was high enough and the dwell time long enough for grain growth to occur. Such a dual character of a sintering additive is an unusual feature. It is clear that this pilot work requires further process optimization as well as a more thorough understanding of the mechanism by which NaF influences the densification of spinel ceramics. It is known e.g. that NaF is also a useful processing additive for the synthesis of spinel from alumina and magnesia [10,11], but the connection of this fact with the findings of the present work is unclear. In any case, the combination of a very fine microstructure and reasonable transparency is more than appealing as a target for spinel ceramics, especially for applications in which high strength is required. It is clear, therefore, that future efforts concerning spinel ceramics

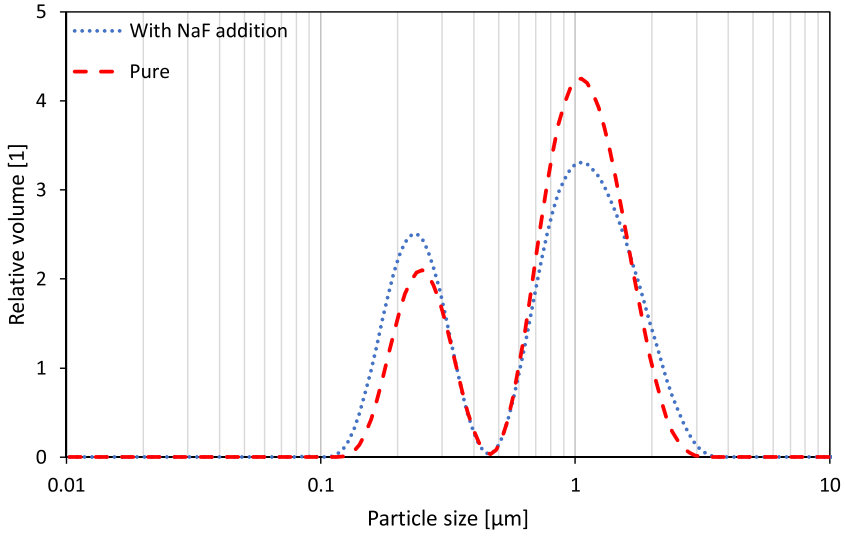

Fig. 4. Particle size distributions (volume-weighted probability density curves) obtained by laser diffraction (evaluated via Mie theory) for pure spinel powder (dashed curve) and powder with 1 wt.% addition of NaF (dotted curve).

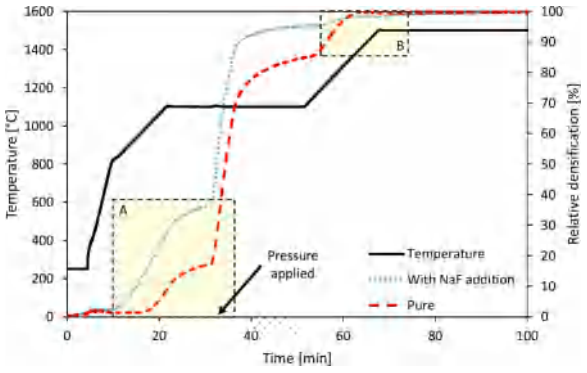

Fig. 5. Relative densification of pure spinel powder (dashed curve) and powder with 1 wt.% addition of NaF (dotted curve).

[1] The fact that the grain size determined for the sample with NaF addition is even lower than the median size of the primary particles of the original powder is of course a consequence of the fact that the particle size distributions measured by laser diffraction are volume-weighted and concern equivalent sphere diameters, whereas image analysis yields statistical grain size measures that are based on arithmetic means of number-weighted distributions. The quantitative comparison of these results is highly non-trivial [9].

[2] In the context of this study, relative densification is defined as $\frac{D}{D_{max}} \cdot 100$, where D is the piston displacement and D_{max} is the piston displacement at the end of sintering, i.e. at 1500 °C (at the end of second dwell).

prepared with NaF as a sintering aid must primarily focus on improving the transparency by process optimization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is part of the project “Partially and fully sintered ceramics – processing, microstructure, properties, modeling and sintering theory” (GA18-17899S), supported by the Czech Science Foundation (GAČR). V. N. also acknowledges support from Specific University Research (MSMT No. 20-SVV/2019).

References

[1] 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.

[2] 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 (2) (2009) 358–364.

[3] Goldstein, J. Raethel, M. Katz, M. Berlin, E. Galun, Transparent $MgAl_2O_4$/LiF ceramics by hot-pressing: host–additive interaction mechanisms issue revisited, J. Eur. Ceram. Soc. 36 (2016) 1731–1742.

[4] W. Pabst, E. Gregorová, T. Uhlířová, Microstructure characterization via stereological relations – a shortcut for beginners, Mater. Charact. 105 (1) (2015) 1–12.

[5] K. Morita, B.-N. Kim, H. Yoshida, K. Hiraga, Y. Sakka, Assessment of carbon contamination in $MgAl_2O_4$ spinel during spark-plasma-sintering (SPS) processing, J. Ceram. Soc. Jpn. 123 (10) (2015) 983–988.

[6] V. Nečina, W. Pabst, Reduction of temperature gradient and carbon contamination in electric current assisted sintering (ECAS/SPS) using a “saw-tooth” heating schedule, Ceram. Int. 45 (2019) 22987–22990.

[7] L. Esposito, A. Piancatelli, P. Miceli, S. Martelli, A thermodynamic approach to obtaining transparent spinel ($MgAl_2O_4$) by hot pressing, J. Eur. Ceram. Soc. 35 (2015) 651–661.

[8] V. Nečina, W. Pabst, Influence of the heating rate on grain size of alumina ceramics prepared via spark plasma sintering (SPS), J. Eur. Ceram. Soc. (submitted).

[9] W. Pabst, S. Hříbalová, Mean values, moments, moment ratios and a generalized mean value theorem for size distributions, Ceram. Silik. 63 (4) (2019) 419–425.

[10] S. Shimada, R. Furuichi, T. Ishii, Effects of additives on solid state reaction. I. A kinetic study of the effects of halides of the formation of $MgAl_2O_4$, B. Chem. Soc. Jpn. 47 (8) (1974) 2026–2030.

[11] S. Shimada, R. Furuichi, T. Ishii, Effects of additives on solid state reaction. II. A thermoanalytical study of the effect of fluorides on the formation of $MgAl_2O_4$ in initial stage, B. Chem. Soc. Jpn. 47 (8) (1974) 2031–2035.