TRANSPARENT ALUMINA /CERIA NANOCOMPOSITES BY SPARK PLASMA SINTERING.**

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The influence of oxides (such as MgO, TiO₂, CaO, etc) on the transparency of polycrystalline alumina compacts are largely studied in the literature. In the present work, a completely different approach is developed, consisting in precipitating 0.5 wt% CeO₂ nanoparticles (< 5 nm) on the surface of the starting alumina nanopowder (d₅₀ ~170 nm) using cerium (III) acetate as precursor. It is proved that the ceria nanoparticles strongly enhance the transparency of the Spark Plasma Sintered (SPSed) compacts due to: i) the ceria nanoparticles act as powder lubricant, increasing around 15% the initial density of the powder in the Spark Plasma Sintering (SPS) die, and ii) the CeO₂ nanoparticles, with a very low solid solubility in the alumina grains, are located at grain boundaries, hindering the alumina grain growth by pinning during SPS sintering at 1430°C, 80 MPa for 2 min. This

effect is found to be effective only under SPS vacuum conditions. In order to explain the light scattering behavior in the near-infrared and visible range, a light scattering model under the Rayleigh-Gans-Debye approximation for polycrystalline alumina is used. This model offers an additional and simple tool for a completed bulk evaluation of the SPS compacts microstructure.

1. Introduction

It is well known that obtaining transparent alumina is of special interest for applications that require the combination of optical and mechanical properties. Sapphire and polycrystalline alumina are being used in industrial and military applications such as armour parts, discharge lamps, airborne infrared sensors and laser.^[1] In addition, the high cost of the production of transparent sapphire crystals and the difficulties to carry out the synthesis process for large sized alumina monocrystals has focused the attention on the development of Polycrystalline Transparent Alumina Materials (PTAMs).^[2]

Obtaining PTAMs has to deal with two main challenges: i) the porosity in the final material must be lower than 0.05 vol.% to avoid scattering effects in order to achieve transparency,^[3] and ii) the birefringence character of alumina grains, which is inherent to the material and seems to be more critical for larger grains, must be balanced. In this context, the key factor to achieve PTAMs seems to be the control of the grain growth in order to decrease the flaw size (<100 nm) and, therefore, the volume of porosity, as well as to minimize the influence of birefringence in the optical properties of alumina.

Several authors have reported that the presence of second phases such as MgO, Y₂O₃, SiO₂, TiO₂, CaO, etc., modifies the grain growth rate of alumina when sintering.^[4,5,6] Nevertheless,

this is not enough to reach transparency due to the anisotropic character of alumina. Moreover, the effect of these elements on decreasing porosity is not well understood so far.

Ceria (CeO_2) is a well known oxide with a very low solid solubility in alumina ($< 0.1\%$), that is mainly used to stabilize other metastables phases in zirconia or alumina.^[7] One interesting property of this oxide is the ability to change its oxidation state with oxygen partial pressure. Hence, for low partial pressures of oxygen, Ce^{4+} will reduce to Ce^{3+} .^[8]

A singular characteristic of the alumina-ceria system is that, on one hand, Ce^{3+} can be incorporated in solid solution into the alumina crystalline structure and,^[9] on the other hand, Ce^{4+} is almost insoluble in alumina. Therefore, by controlling the SPS atmosphere it could be possible either to incorporate Ce^{3+} into the alumina lattice or to precipitate CeO_2 at the alumina grain boundaries. Consequently, in order to control the grain growth in the SPS alumina compact, the SPS atmosphere can be used as a novel tool, instead of the restrictive operating temperature ($< 1350^\circ\text{C}$), regularly used to obtain transparent alumina.^[10-13]

Furthermore, in recent papers it has been pointed out the importance of the different parameters of powder processing methods in the optical properties of SPS dense alumina compacts.^[14,15]

In the present investigation, a low fraction of a ceria precursor (0.5 wt%) has been added to the alumina powder, obtaining a nanocomposite powder which has been sintered by SPS under different conditions. The aim of this work has been to study the effect of these parameters on the transparency of the final SPSed alumina compacts.

2. Results and discussion

2.1. X-ray Photoelectron Spectroscopy (XPS) Spectra

The XPS spectra of the starting alumina/ceria powder and the sintered samples (ACe-1, ACe-2 and ACe-3) are represented in **(Fig. 1)**. In the case of the powder sample, the spectrum exhibits a clear emission at the binding energy of approx. 917 eV. The appearance of this high intensity signal is a direct evidence of the presence of Ce^{4+} . Upon detailed analysis of XPS line shape, the Ce3d spectrum consists of five 3d3/2 and 3d5/2 spin-orbit split doublets representing different 4f configurations in the photoemission final state in accordance with characteristic energy shifts reported elsewhere.^[16,17] This result confirms that the oxidation state of alumina/ceria composite powder is a mixture of the two states Ce^{3+} and Ce^{4+} . It can be estimated that the proportion of each one in the mixture is around 50%.

When this powder is partially sintered for 20 minutes in SPS in vacuum atmosphere at 1250°C and 80 MPa, a clear modification in the XPS spectrum of the surface of the sample (ACe-1) is readily observed. It not only reveals the absence of the high binding energy feature characteristic of Ce^{4+} , but it is composed of two spin-orbit split structures with peaks at well defined energies. This can be interpreted in terms of the complete reduction of Ce oxide, and the single formation of Ce^{3+} . A similar result was obtained when the powder was sintered at 1430°C and 80 MPa for 2 min in SPS with Ar/H₂ atmosphere (sample ACe-3). However, the sample ACe-2 (sintered in SPS in vacuum atmosphere and fully densified at 1430°C and 80 MPa for 2 min) showed a mixture of Ce^{3+} and Ce^{4+} very similar (55% / 45% respectively) to the starting powder.

2.1. Powder packaging

(Fig. 2) represents the packaging density of pure alumina powder with and without addition of 0.5 wt% of ceria, versus the apply load. The density measured for the alumina/ceria is higher than that of the pure alumina. As observed in the same figure, a Transmission Electron Microscopy (TEM) micrograph of the composite powder shows that the ceria nanoparticles (<20 nm) are attached at the surface of the alumina particles forming aggregates ranging from 20 to 60 nm. These aggregates act as a lubricant, improving the packaging behaviour of the alumina grains in the die, which allows to reach higher relative densities (~15%) at low load (<100 N). This fact is relevant, due to the fact that the presence of large pores in the green body is always related to a poor packaging behaviour of the starting powder.^[18] This fact is more dramatic in the particular case of transparent ceramics, where the presence of large pores can drastically decrease the transmittance value.

2.2. Microstructure of the sintered materials

The microstructure of the sintered materials can be seen in (Fig. 3). The fracture surface of the pure alumina (sample A) shows an intergranular fracture in which pores concentrate at grain boundaries and triple points. The corresponding average grain size was found to be $2.8 \pm 0.1 \mu\text{m}$.

As observed in the microstructure of the alumina/ceria nanocomposites SPSed in vacuum (samples ACe-2), small precipitates of cerium oxide (CeO_x) are mostly located at grain boundaries and triple points of alumina grains. No residual porosity was detected in the sample, at least up to a 20 nm resolution. The average grain size of alumina and CeO_x precipitates grains resulted to be $570 \pm 10 \text{ nm}$ and $30 \pm 10 \text{ nm}$, respectively.

In the microstructure of alumina/ceria nanocomposites SPSed in Ar/H_2 (samples ACe-3), ceria precipitates are also formed and tend to concentrate at grain boundaries and triple points of alumina grains. However, it can be appreciated that the fraction of those precipitates is substantially lower than in the vacuum sintered samples (ACe-2). This can be rationalized considering the higher solid solubility of Ce^{3+} vs. Ce^{4+} in the alumina lattice.^[19, 20] The average grain size of the alumina grains (470 ± 75 nm) and CeO_x precipitates (30 ± 10 nm) were found to be similar to those found in the sample sintered in vacuum.

The densities of the different samples are reported in (**Table 1**). As can be observed, the highest relative density corresponds to ACe-2, with a porosity around 0.06%, whilst pure alumina sintered under the same conditions presents a porosity of 0.09%. Therefore, by adding a small fraction of homogeneously distributed ceria nanoparticles (0.5 wt% CeO_2), it is possible to obtain near-fully dense nanostructured alumina ceramics.

The important effect of the SPS atmosphere has been studied as well. Sample ACe-2 was sintered in vacuum. In the case of sample ACe-3, SPSed under the same sintering conditions of time and pressure, but different atmosphere (Ar/H_2), a remaining and significant porosity of 0.44% was not possible to eliminate. Thus, it is clear that vacuum definitely helps to reach theoretical density in the final alumina compact.

2.3. Optical properties

The transmittance spectra of the samples are plotted in (**Fig. 4**). An important factor that must be taken into account in the transmittance analysis of the studied samples is the maximum value of this property. Nanometric flaws such as pores and grain boundaries tend to reduce the transmittance maximum because of Rayleigh light scattering processes. In the case of IR range ($\lambda > 2000$ nm), medium size defects (~ 100 nm) produce the characteristic Rayleigh

scattering, following a λ^{-4} light intensity law. In this sense, samples A and ACe-3, display much lower value of transmittance, specially for shorter wavelengths ($\lambda < 4000$ nm) and present higher porosity than ACe-2.

The poor packaging of the pure alumina powder before sintering facilitated the carbon diffusion from the graphite SPS die through the green compact in samples ACe-2 and ACe-3. Both composite samples present an additional band at 4750 nm that corresponds to a C-C bonding, indicating the presence of a carbonate material which could come from unburned residue of the ceria precursor (cerium acetate) or from black carbon from the SPS die. In this regard, it can be assumed that the ceria precursor in samples ACe-2 and ACe-3 acts as a lubricant, facilitating the initial packaging of alumina, and therefore, increasing the initial green density (Figure 2). Moreover, as suggested by Aman et al;^[14] this fact may narrow the pore size distribution and reduce the pore size.

The absorption band at 2900 nm observed in sample A corresponds to an O-H bonding. This band can be eliminated with a thermal treatment before sintering. As observed, in samples ACe-2 and ACe-3 this band was absent due to the previous thermal treatment at 800°C to burn out the organic from ceria precursor.

In order to explain the light scattering behaviour in the Near-InfraRed (NIR) and visible (VIS) range, we have used a light scattering model under the Rayleigh-Gans-Debye approximation for polycrystalline alumina.^[21] This model which is valid for small scatters with a refractive index very similar to that of the environment ($|m-1| \ll 1$ and $2\pi|m-1|a/\lambda \ll 1$, where m is the quotient between the refractive index of the scatter and that of the surrounding medium, a represents the scatter radius, and λ corresponds to the incident wavelength. The model states that the transmittance of dense alumina ceramics basically depends not only on the maximum

grain size but also on the preferential orientation of their c-axis, or texture. This model predicts an absorbance law following:

$$A_g = -\frac{6\pi^2 \langle a_g \rangle}{\lambda^2} \Delta n^2 \alpha(\xi) d \quad (1),$$

where Δn is the difference between the refraction index in the different axis, and equals to 0.008 for α -alumina. Moreover, d is the thickness of the sample. The slope of the line is proportional to the values of the texture function $\alpha(\xi)$,^[22] where ξ is the effective angle of the optical axis of a singular crystallite with the sample surface normal, and $\langle a_g \rangle$ is the average grain radius value corresponding to a volume grain distribution, defined by:

$$\langle a_g \rangle = \frac{\sum_i a_i^4}{\sum_i a_i^3} \quad (2)$$

It can be stated that, with a good degree of approximation, for heterogeneous grain size distribution, $\langle a_g \rangle$ can be considered similar to the maximum value of grain radius experimentally found.

The presence of a very small amount of CeO_2 will also contribute to light scattering. In the case of transparent matrices with CeO_2 , the refractive index of CeO_2 ($n_{\text{CeO}_2} = 2.36$) is very different from that of the alumina ($n = 1.76$) and assuming that CeO_2 grain size, a , is $a \ll a_g$ so Rayleigh scattering must be taken into account.^[23] Thus, the CeO_2 absorbance is:

$$A_{\text{CeO}_2} = -\frac{32\pi n}{\lambda} df \left(\frac{2\pi n a}{\lambda} \right)^3 \left| \frac{n_{\text{CeO}_2}^2 - n^2}{n_{\text{CeO}_2}^2 + 2n^2} \right|^2 \quad (3)$$

Therefore, the transmittance is given by the combination of grain and CeO_2 scattering as follows:

$$T = \left[1 - 2 \left| \frac{n-1}{n+1} \right|^2 \right] e^{A_g + A_{\text{CeO}_2}} \quad \alpha \quad T = T_0 e^{-\left(\frac{\kappa_{\text{CeO}_2}}{\lambda^2} + \frac{\kappa_g}{\lambda^4} \right)} \quad (4)$$

This model offers an additional and simple tool for a complete bulk evaluation of the microstructure (grain size, texturing, porosity, etc) of the sintered polycrystalline alumina samples. This bulk microstructural information is critical to fabricate transparent polycrystalline alumina compacts and cannot be obtained by conventional microstructural analysis (i.e. Transmission and Scanning Electron Microscopy, X-Ray Diffraction).

Following this theoretical model, the $\log(T)$ vs. $1/\lambda^2$ of the considered samples have been plotted in **(Fig. 5)**. It can be stated that, for the low spectral range, the experimental data fit to a straight line.

In the sample ACe-2, the line deviates from the linear fit and follows a λ^{-4} law at visible range, which implies the presence of CeO_2 . Thus, the grain size of CeO_2 in the sample ACe-2 was calculated, being 15 nm of diameter. Conversely, in the case of samples A and ACe-3, the deviation from the linear fit involves a saturation of the absorbance at shorter wavelength, anomalous diffraction regime. This is an evidence of the presence of large grain size, which reduces an anomalous diffraction scattering in perfect agreement with the microstructural analysis (Fig. 3).

According to X-Ray Diffraction data on sintered samples (data not shown), no texturing was detected. In this regard, we assigned the texture angle $\alpha(\xi)=0.277$, which corresponds to random orientation ($\xi=45$). The fit can be straightforward used to determine the average grain radius. As can be seen in (Table 1), the value of the maximum grain size corresponding to ACe-3 (alumina ceria sintered in Ar/H_2), 2900 nm, is about 3 times larger than the one corresponding to alumina ceria sintered in vacuum, 1020 nm. This can be explained considering that the fraction of ceria precipitated in the sample sintered in Ar/H_2 is

significantly smaller than in the case of the sample sintered in vacuum (Fig. 2), and then the grain size distribution for the sample sintered in Ar/H₂ is wider than in the case of the sample sintered in vacuum.

3. Conclusions

The most important results obtained in this investigation are as follows:

- 1.- The small precipitates of CeO_x on the alumina surface found in the composite powder (<20 nm), act as an inorganic lubricant, facilitating grain boundary sliding and powder packaging during the green state. In consequence, the starting porosity of the initial green compact decreases and the pore size distribution is narrower, avoiding the presence of large pores. This fact also decreases the final content of C in the SPS compact.
- 2.- During the SPS process, the Ce⁴⁺ is partially (in the case of vacuum) or totally (in Ar/H₂) reduced to Ce³⁺. This fact decreases the fraction of ceria precipitates and, consequently, increases the porosity in the sintered sample, affecting negatively to the transmittance maximum of the SPS compact.
- 3.- During the SPS process, the CeO_x nanoparticles (< 30 nm) that remain unreduced at the alumina grain boundaries, decreasing the porosity and allowing that the microstructure of the final SPSed alumina compact remains at the nanometer size (< 600 nm).
- 4.- The important effect of the SPS atmosphere has also been stated. In the case of the sample SPSed in Ar/H₂ a remaining and significant porosity level of 0.44% was not possible to eliminate. Moreover, vacuum definitely helps to reach theoretical density in the final alumina compact (0.06% porosity).
- 5.- Finally, by adding a small fraction of homogeneously distributed ceria nanoparticles (0.5 wt% CeO₂), it is possible to obtain fully dense nanostructured transparent alumina ceramics

by SPS (<0.1% porosity) at temperature higher (1430°C) than the ones required in the case of nanostructured alumina SPSed compacts (<1300°C).

4. Experimental

Al₂O₃/CeO₂ powder has been prepared with 0.5 wt% ceria following a wet-processing route.^[24] A high purity α -Al₂O₃ has been selected as starting raw material (*Taimet* TM-DAR, *Taimicrons*, average particle size ~170 nm). In order to prepare the alumina/ceria composite powder, cerium (III) acetate, (*Sigma-Aldrich*.) was diluted into an aqueous alumina suspension. Cerium acetate was diluted in deionized water and added dropwise to the Al₂O₃ suspension to reach a concentration of 0.5 wt% CeO₂. The slurry was partially dried under magnetic stirring at 60-70°C and finally dried at 120°C for 24 h to eliminate the remaining water. The obtained powder was thermally treated at 800°C during 2 h in air to eliminate the organic rests of the precursor and to form the CeO_x. The treated powder was crushed in an alumina mortar, sieved below 250 μ m and attrition milled with Al₂O₃ balls to break agglomerates. The attrition milled powder was sieved down to 63 μ m mesh.

The packaging behaviour of the composite powder and pure alumina powder was studied under low pressure conditions (<2 MPa) in a cylindrical die with 10 mm diameter using a universal testing machine *Instron* 8562. The displacement of the piston die with the applied load was registered during the test. The mass of each sample was 1g.

Subsequently, the powder was Spark Plasma Sintered (SPSed) under different conditions (Table 1) of temperature (1250°C; 1430°C), atmosphere (10⁻² mb vacuum; Ar/H₂, 5 vol% H₂) and dwell time (2 min; 20 min.). The oxidation states of CeO_x were studied on the starting powder and also under different SPS conditions. Pure alumina was studied as control.

The oxidation state of cerium in the samples was analyzed by X-ray photoelectron spectroscopy (XPS). XPS spectra were recorded with a *SPECS Phoibos150* electron spectrometer and a nine segments delay line detector, using Mg K α radiation (1253.6 eV), in an ultrahigh vacuum chamber at a base pressure of 6×10^{-10} mbar. Ce3d core-level XPS spectra were acquired with 20 eV pass energy and 0.1 eV energy step at normal emission take-off angle.

Data analysis was performed by applying a fitting line shape of XPS spectra using the *CasaXPS* processing software (Casa Software Ltd, Cheshire, UK). With this method each XPS spectrum, after Shirley background subtraction, is decomposed into several components to provide a satisfactory fit to the line shape of the experimental data. All spectra are presented as-acquired with data points represented as filled circles and synthetic peaks and envelopes using solid lines. The analysis of the spectra line shape illustrates the nature of the oxide phases formed, and it reveals the presence of Ce³⁺ and Ce⁴⁺ oxidation states. This chemical identification has been performed by the assignation of these synthetic components to different Ce oxidation states, with characteristic energy shifts, in good agreement with the values previously reported.^[12, 13] The relative intensity of the different oxidation states is determined to illustrate the influence of the processing parameters for each sample.

The microstructure of the samples was observed by Field Emission-Scanning Electron Microscopy (FE-SEM, *Zeiss Ultraplus*). The density of the different SPS samples has been calculated following the Archimedes method (ASTM C 373-88).

The surfaces of the samples were polished down to 1 μm using diamond paste to eliminate the surface roughness. The Real In-line Transmittance (RIT) spectra of the samples ACe-1, ACe-2 and ACe-3 were measured from 2.5 to 5 μm with a FTIR *Nicolet 20 SXC* (Fourier transform

infrared, FTIR). For the 0.9 to 2.5 μm range, a FTIR spectrophotometer *Bruker IFS 66V* was used. Finally, in the visible range, measurements were carried out with a spectrophotometer *JASCO V-660*.

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REFERENCES

- [1] Q. H. Yang, Z. J. Zeng, J. Xu, H. W. Zhang, and J. Ding, *Journal of Rare Earths*. **2006**, 24, 72.
- [2] J. P. Cheng, D. Agrawal, Y. J. Zhang, and R. Roy, *Materials Letters*. **2002**, 56, 587.
- [3] B. N. Kim, K. Hiraga, K. Morita, H. Yoshida, T. Miyazaki, and Y. Kagawa, *Acta Materialia*. **2009**, 57, 1319.
- [4] N. Hilli, and P. Goeuriot *Symposium on Powder Science and Technology - Powders and Sintered Material*(Elsevier Science Sa, Albi, FRANCE, **2007**), 129.
- [5] G. Bernard-Granger, C. Guizard, *Scripta Materialia*, **2007**, 56, 983.
- [6] G. Bernard-Granger, C. Guizard, A. Addad, *Journal of the American Ceramic Society*, **2008**, 91, 1703.
- [7] N. Balagopal, K. G. K. Warriar, A. D. Damodaran, and K. S. Krishnan, *Journal of the European Ceramic Society*. **1993**, 12, 449.
- [8] S. Damyanova, C. A. Perez, M. Schmal, and J. M. C. Bueno, *Applied Catalysis a-General*. **2002**, 234, 271.
- [9] A. I. Leonov, A. V. Andreeva, V. E. Shvaiko-Shvaikovskii, E. K. Keler, *Neorganicheskie Materialy*, **1966**, 2, 517.
- [10] D. Jiang, D. M. Hulbert, U. Anselmi-Tamburini, T. Ng, D. Land, and A. K. Mukherjee, *Journal of the American Ceramic Society*. **2008**, 91, 151.
- [11] D. Jiang, D. M. Hulbert, U. Anselmi-Tamburini, T. Ng, D. Land, and A. K. Mukherjee, *Window and Dome Technologies and Materials X*. **2007**, 6545, 54509.
- [12] K. Morita, B. N. Kim, H. Yoshida, and K. Hiraga, *Journal of the American Ceramic Society*. **2009**, 92, 1208.
- [13] Z. J. Shen, M. Johnsson, Z. Zhao, and M. Nygren, *Journal of the American Ceramic Society*. **2002**, 85, 1921.

- [14] Y. Aman, V. Garnier, and E. Djurado, *Journal of the European Ceramic Society*. **2009** 29, 3363.
- [15] M. Suarez, A Fernandez, J.L. Menendez, M. Nygren, R. Torrecillas, Z. Zhao , *Journal of the European Ceramic Society*, **2010**, 30, 1489.
- [16] V. Matolin, M. Cabala, V. Chab, I. Matolinova, K. C. Prince, M. Skoda, F. Sutara, T. Skala, and K. Veltruska, *Surface and Interface Analysis*. **2008**, 40, 225.
- [17] M. Romeo, K. Bak, J. Elfallah, F. Lenormand, and L. Hilaire, *Surface and Interface Analysis*. **1993**, 20, 508.
- [18] J.S. Reed, “Principle of Ceramic Processing”, John Wiley and Sons, **1994**.
- [19] A. Piras, S. Colussi, A. Trovarelli, V. Sergo, J. Llorca, R. Psaro, and L. Sordelli, *Journal of Physical Chemistry*.**2005**, B 109, 11110.
- [20] J. Z. Shyu, W. H. Weber, and H. S. Gandhi, *Journal of Physical Chemistry*. **1988**, 92, 4964.
- [21] C. Pecharroman, G. Mata-Osoro, L. A. Diaz, R. Torrecillas, and J. S. Moya, *Optics Express*. **2009**, 17, 6899.
- [22] C. Pecharroman, F. Gracia F, J.P Holgado , M. Ocana, A.R. Gonzalez-Elipe, J. Bassas, J. Santiso , A. Figueras, *Journal of applied physics*, **2003**, 93, 4634.
- [23] C.F. Bohren, D.R. Huffman, *Absorption and scattering of light by small particles*, ed. Wiley-Interscience, **1998**.
- [24] J.S. Moya, S. Lopez-Esteban y C. Pecharroman, *Progress in Materials Science*, **2007**,52, 1017-1090.

FIGURES

Fig. 1. (Ce 3d XPS spectra of alumina/ceria powder and the sintered samples)

Fig.2. (a) Relative density of the powder with and without ceria, versus the applied load; b) TEM micrograph of alumina with 0.5 wt% CeO_2 powder).

Fig.3. (FE-SEM Micrographs of the sintered materials A, ACe-2 and ACe-3.)

Fig. 4. (Experimental optical transmittance vs. wavelength for the three considered samples.; External aspect of the SPS samples ACe-2 (left) and A (right)).

Fig. 5. (Same graphic as Figure 4 but representing logarithm of transmittance (absorbance) vs. the inverse of the wavelength square .In samples A an A-Ce2, straight lines represent the linear fitting in the low wavelength region. The fit of the sample A-Ce3 is the combination of grain scattering, λ^{-2} , and CeO_2 scattering, λ^{-4}).

TABLES

Sample	CeO ₂ (wt%)	SPS conditions					Density (%, ± 0.05)	Fitting param. $2\langle a_g \rangle$ (nm)
		T max (°C)	Atmosphere	Dwell time (min)	Heating rate (°C·min ⁻¹)	Pressure (MPa)		
A	0	1430	Vac. (10 ⁻² mb)	2	50	80	99,91	6000
ACe-1	0.5	1250	Vac. (10 ⁻² mb)	20	50	80	88,31	-----
ACe-2	0.5	1430	Vac. (10 ⁻² mb)	2	50	80	99,94	1020
ACe-3	0.5	1430	Ar/H ₂ (5 vol.% H ₂)	2	50	80	99,56	2900

Table 1. (SPS conditions, density of SPS sintered samples and fitting parameter.)

This manuscript highlights the fabrication of high-performance alumina-based nanostructured materials which reach transparency. This work presents the influence of the addition of small quantities of a ceria precursor on the transparency of polycrystalline alumina-based composite materials with different sintering atmospheres by Spark Plasma Sintering. Green density and alumina grain growth inhibition promoted by CeO_x precipitates are found to be responsible for the enhancement in transmittance with respect to pure alumina.

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