Available online at www.sciencedirect.com
ScienceDirect
Energy Reports 6 (2020) 142–147
www.elsevier.com/locate/egyr

4th Annual CDT Conference in Energy Storage and Its Applications, 2019, University of Southampton, U.K.

Flash phenomena in lime-stabilised zirconia oxide ion conductor

Julia Ramírez-González*, Anthony R. West*

Department of Materials Science and Engineering, The University of Sheffield, Mappin Street, Sheffield S1 3JD, UK

Received 14 February 2020; accepted 5 March 2020

Abstract

Flash sintering is a novel technique that allows a decrease in the sintering time (from hours to seconds) and furnace temperature for the densification of ceramics. In order to find out if calcia-stabilised zirconia (15mol% CaO) can be flashed sintered, samples were first characterised by XRD and impedance spectroscopy, to confirm that the powder was single phase cubic and pellets were ionically conducting. During the flash experiments, the samples showed two of the "*flash event*" characteristics: increased conductivity and emission of light, but not densification. This shows that is possible to have the luminescent aspect of flash without sintering, as suggested by Raj.

Peer-review under responsibility of the scientific committee of the 4th Annual CDT Conference in Energy Storage and Its Applications, Professor Andrew Cruden, 2019.

Keywords: Flash sintering; Calcia-stabilised zirconia; Emission of light; Oxide ion conduction; *dc-bias phenomena*

1. Introduction

In recent decades, different sintering techniques have been developed to reduce the energy consumption during sintering of ceramics; among them, the electric current assisted/activated sintering techniques also aim to reduce the processing time [1]. Flash sintering, which belongs to this category, is able to sinter samples in less than a minute, after reaching an onset temperature (T_{onset}) and at the same time as samples are subjected to an electric field [2]. The shrinkage process is accompanied by power dissipation, non-linear increase in conductivity and emission of light; therefore, this stage of the process is known as the *"flash-event"*.

The first material to be flash sintered was the oxide ion conductor 3 mol% yttria stabilised zirconia (3YSZ) by Cologna et al. [3]. The furnace temperature was reduced from 1450 °C to ∼900 °C and the densification duration from hours to seconds, in comparison with conventional sintering, by applying 100V/cm during heating.

Calcia-stabilised zirconia (CSZ) is also an oxide ion conductor [4], with the difference that twice as many oxygen vacancies are introduced per acceptor dopant in comparison to YSZ, Eqs. (1) and (2).

$$ZrO_2 \xrightarrow{CaO} Ca''_{Zr} + V_O^{\bullet\bullet} + 2O_O^x \tag{1}$$

* Corresponding authors.
E-mail addresses: jramirezgonzalez1@sheffield.ac.uk (J. Ramírez-González), a.r.west@sheffield.ac.uk (A.R. West).

https://doi.org/10.1016/j.egyr.2020.03.008

Peer-review under responsibility of the scientific committee of the 4th Annual CDT Conference in Energy Storage and Its Applications, Professor Andrew Cruden, 2019.

$$ZrO_2 \xrightarrow{Y_2O_3} 2Y'_{Zr} + V_O^{\bullet\bullet} + 2O_O^x \quad (2)$$

The aim of this work is to find out whether CSZ behaves in a similar matter to YSZ during the flash sintering process.

2. Methodology

Powder with composition $Ca_xZr_{1-x}O_{2-x}$; x: 0.15, was prepared by solid-state reaction using $CaCO_3$ (99%, Fisher Chemical) and ZrO_2 (99%, Aldrich Chemistry), which were dried overnight at 180 °C and 1000 °C, respectively prior to weighing. The mixture was manually ground with acetone using a pestle and mortar, then fired to decarbonate and start the reaction at 1150 °C. Subsequently, the powder was re-ground and heated at 1500 °C for 8 h.

The resulting product was analysed by X-ray powder diffraction using a Stoe Stadi P diffractometer (Darmstadt, Germany) using Cu $K\alpha_1$ radiation. Data were collected from $2\theta = 20$ to 80° and compared to the diffraction pattern of cubic zirconia (PDF card:01-070-7361) using the JCPDS database.

2.1. Conventional sintering

Pellets of 10 mm diameter were uni-axially pressed at around 98MPa, and sintered at 1600 °C for 10 h. To ensure a good electrical contact, Pt paste electrodes were applied on both sides and dried at 900 °C for 2 h. Pellet densities were ∼86%.

Electrical measurements from 350 to 650 °C were performed on conventional-sintered samples using an impedance analyser Solatron SI 1260 (measurement accuracy ± 0.1%) over the frequency range 10 mHz–1 MHz with an ac voltage of 100 mV. Measurements were corrected for the geometry of the pellets and for the blank cell capacitance, more commonly known as jig correction. ZVIEW software (ZVIEW-Impedance Software version 2.4 Scribner Associates) was used to analyse the results.

2.2. Flash sintering

Dog bone-shaped samples with 5wt% of PVA as binder, were pressed using a uniaxial press, applying 1ton. To burn out the binder, the samples were taken to 550 °C for 2 h with a heating rate of 2 °C/min, and pre-sintered at 1300 °C 1400 °C and 1500 °C for 2 h; this step was used to allow the density changes during the subsequent flash process to be measured. As with conventional-sintered samples, Pt electrodes were painted inside the holes of the dog-bones and dried at 900 °C for 2 h. The samples were suspended inside a tube furnace using Pt wires and heated from room temperature at a heating rate of 10 °C/min; a constant electric field was applied, 100 V/cm, with a current density limit set at 100 mA/mm^2.

Relative density values were calculated by comparing theoretical and measured density.

3. Results and discussion

Synthesised powder appeared to be single phase and was indexed on a cubic unit cell, space group $Fm\overline{3m}$, Fig. 1. Therefore, the cubic phase of zirconia was stabilised by adding 15 mol% of CaO, consistent with the reported phase diagram for the CaO–ZrO_2 system [5].

A representative set of impedance data, recorded at 456 °C, is shown in Fig. 2. The impedance complex plane plot (a) shows three components: one semicircle at high frequencies, another at intermediate frequencies and a spike at low frequencies. The capacitance spectroscopic plot (b) shows 2 plateaus with values of ∼1 pF/cm at high frequencies and ∼0.6 nF/cm at intermediate frequencies. These values are typical of bulk and grain boundary responses. At low frequency the capacitance dispersion reaches a value of ∼20 µF/cm, which can be related to the sample-electrode interfaces, due to ionic species creating a double layer capacitance at the electrodes. Therefore, from these capacitance values, the three components on the impedance complex plane can be identified [6].

From the impedance plots at different temperatures, the total resistances (bulk + grain boundary) were extracted from the intercepts with the Z′ axis and are shown as a conductivity Arrhenius plot, Fig. 3. The activation energy was calculated from the slope with a value of ∼1.2 eV, in agreement with values reported [7] for oxide ion conduction

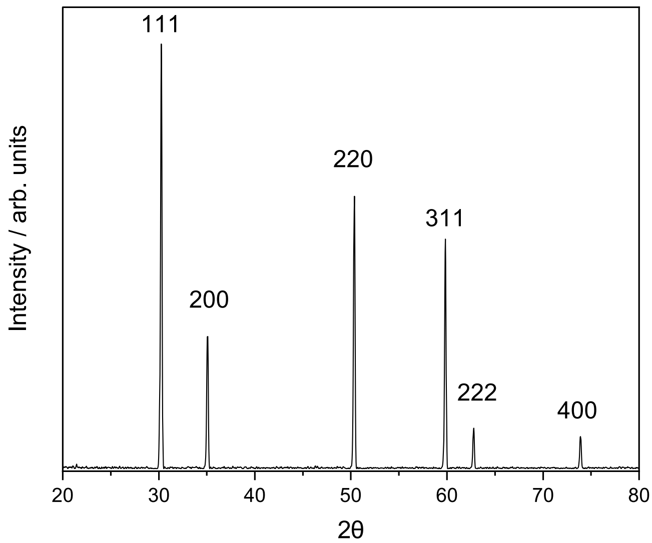

Fig. 1. XRD pattern of CSZ x:0.15.

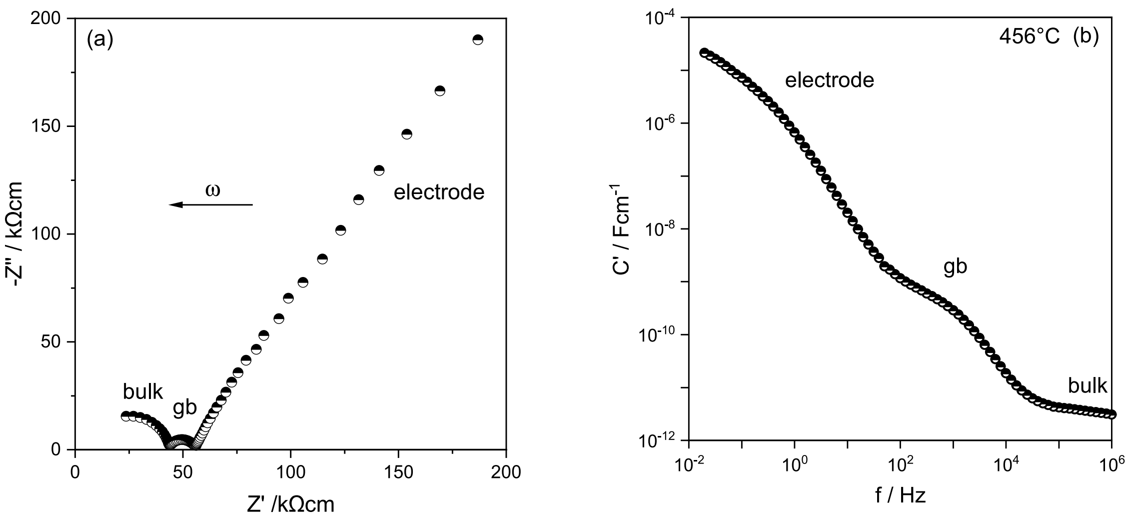

Fig. 2. Impedance complex plane plot (a) and capacitance spectroscopic plot (b) of CSZ x:0.15 at 456 °C, $\omega = 2\pi f$.

in CSZ, although there was evidence for curvature of the Arrhenius plot at high temperatures, similar to that seen for YSZ [8].

From these results, it was confirmed that the powder used for the flash sintering experiments was single phase and had the expected ionic conduction.

The samples subjected to the flash experiment showed a few of the characteristics of the *"flash event"* but not all. The conductivity increased, light was emitted, but an increase in density was not observed.

The sudden increment in the conductivity is shown in Fig. 4; the current density passing through the samples increased after reaching the flash onset temperature (T_{onset}). As the samples were heated at a constant rate, time and temperature are proportional; in this case, the results are plotted as function of time. Two types of control were used. During heating, the power supply operated in voltage control and applied a constant voltage. Once the rise in conductivity occurred, the power supply switched to current control. The samples were held between one and two minutes before turning off the power supply.

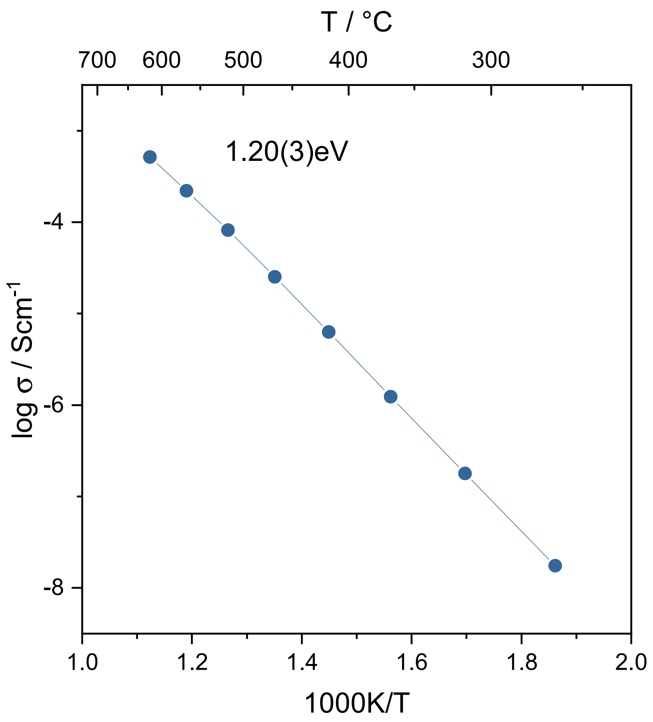

Fig. 3. Arrhenius plot of the total conductivity of CSZ.

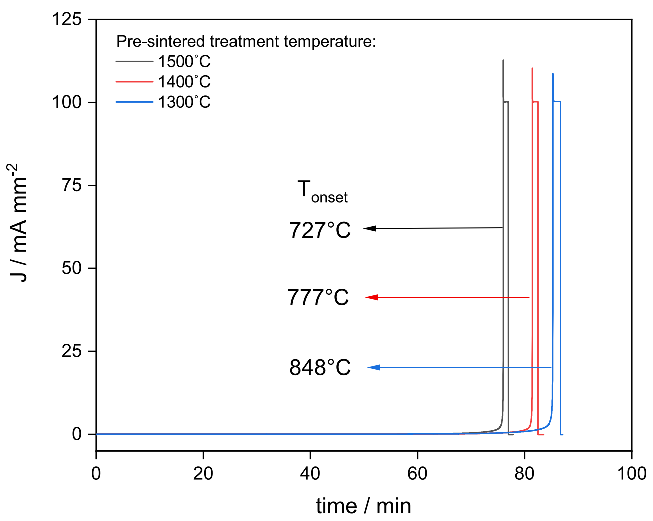

Fig. 4. Current density as a function of time during the flash sintering experiment, showing the increase in conductivity and the onset temperatures for the samples pre-sintered at different temperatures.

The onset temperature varied according to the pre-sintering heat treatment; with higher heat treatment temperatures, T_{onset} decreased. This might be due to the lower porosity achieved at higher pre-sintering temperatures, allowing the current to find more easily a conduction pathway.

Emission of light was also present in all three cases during the *flash event* and remained during the subsequent current control stage, Fig. 5.

The relative densities of the samples after flash were less than 60%, as shown in Table 1. These were significantly less than those achieved during conventional sintering.

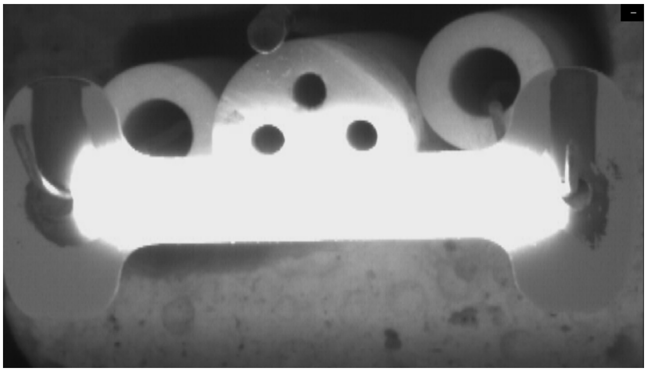

Fig. 5. Sample pre-sintered at 1500 °C during current control.

Table 1. Final densities of the samples subjected to the flash experiment.

Pre-sintering heat treatment temperature (°C)	Relative density (%) after flash
1300	53
1400	54
1500	59

The origins of densification and the emission of light are still unclear; different mechanisms that relate one to the other have been suggested by different authors. In the case of densification, Joule heating was proposed by Du et al. [9], formation of Frenkel pairs by Naik et al. [10], local overheating at grains boundaries and the interaction between electric field and space charge by Cologna et al. [11]. For the emission of light, electroluminescence, related to formation of defects, was proposed by Terauds et al. [12] and incandescence, related to Joule heating, by Biesuz et al. [13].

The results presented in this work indicate that the phenomena surrounding the *flash event* could be of different nature and that densification may be decoupled from the emission of light.

Some results in the literature could support this suggestion. Fully dense samples were flashed by Lebrun and Raj [14], in order to study the conductivity and photoemission relationship. They observed both increased conductivity and luminescence and proposed that the rise in conductivity was due to the creation of e–h pairs and the emission of light resulted from the recombination of these two electronic species. Composites of non-polar ($SrTiO_3$) and polar (0–25vol% $KNbO_3$) ceramics were flashed sintered by Naik et al. [10]. They observed that on increasing the amount of $KNbO_3$, little or no densification was achieved and the luminescence intensity decreased. The hypothesis was that defects (vacancies and interstitials), which were thought to be responsible for the densification, originated within the grains and migrated to the grain boundaries. For this reason, in pure $SrTiO_3$, full densification was achieved as the defect concentration was generated in the entire volume of the ceramic, whereas in the composites not enough defects were generated, due to the presence of the metallic interphases.

As the material used in the present study was single phase and not fully dense prior to the flash experiments, it provides a clear example of the possible decoupling of the densification and emission of light, referred to as *flash-sans sintering"* by Raj [15].

4. Conclusions

The cubic phase of zirconia can be stabilised at room temperature by adding 15 mol% of CaO. Conventional-sintered samples showed three electrical components bulk, grain boundary and sample-electrode interface, and ionic conduction with an activation energy of ~1.2 eV.

Samples subjected to the flash experiment showed an abrupt increase in conductivity and emission of light at an onset temperature between 720 °C and 850 °C depending on the temperature of pre-sintering heat treatment;

nevertheless, densification did not occur. The implication of these results is that the sintering process can be separated from the emission of light.

Further work using different experimental conditions is planned in order to gain a better understanding of the origins of the *flash event*.

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.

CRediT authorship contribution statement

Julia Ramírez-González: Investigation, Data curation, Visualization, Methodology, Validation, Formal analysis, Writing - original draft, Writing - review & editing. **Anthony R. West:** Conceptualization, Resources, Supervision, Project administration, Funding acquisition, Methodology, Validation, Formal analysis, Writing - original draft, Writing - review & editing.

Acknowledgements

We thank X. Vendrell-Villafruela for the design, F.G. Fletcher for the construction and M. McIntosh for the testing of the flash sintering apparatus. J.R.G. thanks CONACyT for a studentship grant under "Becas CONACyT al extranjero".

References

[1] Grasso S, Sakka Y, Maizza G. Electric current activated/assisted sintering (ECAS): A review of patents 1906–2008. Sci Technol Adv Mater 2009;10(5):53001–24.
[2] Yu M, Grasso S, Mckinnon R, Saunders T, Reece MJ. Review of flash sintering: materials, mechanisms and modelling. Adv Appl Ceram 2017;116(1):24–60.
[3] Cologna M, Rashkova B, Raj R. Flash sintering of nanograin zirconia in <5s at 850 °C. J Am Ceram Soc 2010;93(11):3556–9.
[4] Jing-ze S, Yu-ming W. Diffusion in Fast-ion conductor calcia stabilized zirconia: a molecular dynamics study. Chin Phys Lett 1998;15(10):727.
[5] Kown SY, Jung IH. Critical evaluation and thermodynamic optimization of the CaO-ZrO_2 and SiO_2-ZrO_2 systems. J Eur Ceram Soc 2017;37(3):1105–16.
[6] Irvine JTS, Sinclair DC, West AR. Electroceramics: Characterization by impedance spectroscopy. Adv Mater 1990;2(3):132–8.
[7] Nakamura A, Wagner JB. Defect structure, ionic conductivity and diffusion in calcia-stabilized zirconia. J Electrochem Soc 1980;127(11):2325–33.
[8] Komine S, Munakata F. Dielectric relaxation analysis for 8 mol% YSZ single crystal. J Mater Sci 2005;40(15):3887–90.
[9] Du Y, Stevenson AJ, Vernant D, Diaz M, Marinha D. Estimating Joule heating and ionic conductivity during flash sintering of 8YSZ. J Eur Ceram Soc 2016;210:86–91.
[10] Naik K, Jha SK, Raj R. Correlations between conductivity, electroluminescence and flash sitnering. Scr Mater 2016;118:1–4.
[11] Cologna M, Francis JSC, Raj R. Field assisted and flash sintering of alumina and its relationship to conductivity and MgO-doping. J Eur Ceram Soc 2011;31:2827–37.
[12] Terauds K, Lebrun JM, Lee HH, Jeon TY, Lee SH, Je JH, et al. Electroluminescence and the measurement of temperature during stage III of flash experiments. J Eur Ceram Soc 2015;35(11):2325–33.
[13] Biesuz M, Luchi P, Quaranta A, Martucci A, Sglavo VM. Photoemission during flash sintering: An interpretation based on the thermal radiation. J Eur Ceram Soc 2017;37(9):3125–30.
[14] Lebrun J, Raj R. A first report of photoemission in experiments related to flash sintering. J Am Ceram Soc 2014;97:2427–30.
[15] Raj R. Personal communication. 2019.