

AC Electric Field Assisted Pressureless Sintering Zirconia: 3 mol% Ytria Solid Electrolyte

Sabrina G. M. Carvalho, Eliana N. S. Muccillo, and Reginaldo Muccillo*

3 mol% yttria ionic conductors are sintered by applying AC electric fields with frequencies in the 0.5–1.0 kHz range at 1100 °C. The sintering experiments are conducted in pressed pellets positioned between platinum electrodes inside a dilatometer furnace. The dilatometer is modified in order to allow for the simultaneous monitoring of thickness shrinkage, electric voltage, and current across the pellet. The results show that the higher the frequency of the electric field, the higher the attained shrinkage and the apparent density of the pellets. Increasing the frequency of the applied electric field leads to an increase in the Joule heating promoted by the electric current pulse through the polycrystalline ceramic sample. A higher frequency therefore leads to higher amount of thermal energy delivered to the sample, favoring enhanced densification. The ionic resistivity decreases in pellets sintered with increasing frequency of the applied electric field. We suggest that Joule heating favors pore elimination and the removal of chemical species at the space charge region, inhibiting the blocking of oxide ions at the interfaces.

1. Introduction

Pressureless electric field-assisted sintering of ceramic materials consists in applying an electric field to a green (or pre-sintered) compact, either while it is being heated up to a temperature below the conventional sintering temperature (dynamic procedure), or while it is undergoing a fixed temperature (isothermal), until an electric current pulse occurs following an incubation period.^[1–4] Under some experimental conditions reliant on the temperature and the magnitude of the electric field, an yttrium-stabilized zirconia-based solid electrolyte can be sintered to near full density in a few seconds. This method is called flash sintering.^[4] Many experiments have collected data in order to

help understand the mechanisms that are responsible for flash sintering, which is a method that causes densification under an electric field in relatively short periods of time. It has been suggested that Joule heating, point defects creation, interaction between the external field and the space-charge field, Joule heating causing melting of the particle surfaces, and nucleation of Frenkel pairs are the main mechanisms that explain that there is a fast densification without any considerable grain growth.^[5–13]


There are many parameters to be taken into account in the experimental procedure for the flash sintering of ionic conductors: on the one hand the average particle size, particle size distribution of the powder,^[14] specimen shape and size, and packing density were all considered, because these may all modify the pathways through which the electric current flows; on the other hand, electrical characteristics (ionic conductivity at the temperature at which the electric field is

applied,^[15,16] electric field frequency, electric field and current amplitudes,^[17–22] time elapsed during the application of the electric field, electric current limitation), the temperature and heating rates,^[18] and the number of electric current pulses were also considered, because these may all influence the delivered power.

In order to scale this new sintering technique up from the lab to a pilot scale and further to the industrial segment, protocols must be established. To this end, many experiments have been carried out to determine the suitable parameters for a successful sintering. The reliance on the applied electric field, the limiting electric current, the particle size distribution, and the specimen's apparent density (green x pre-sintered) were already reported.^[1,16,19–21] Flash sintering with DC and with 60 Hz AC electric fields did not show any difference in densification and inhibition of grain growth in the $ZrO_2: 3 \text{ mol\% } Y_2O_3$ (3YSZ) ionic conductor.^[22,23] Microstructure differences in 3YSZ were already reported after flash sintering with DC and with AC electric fields, the grain size distribution being heterogeneous in the former and homogenous in the latter.^[24] Here, we report our research on sintering 3YSZ solid electrolytes by applying AC electric fields at a same temperature but at different frequencies. We looked at how different frequencies of the electric field influence the sintering behavior of a zirconia-based solid electrolyte.

S. G. M. Carvalho, Prof. E. N. S. Muccillo, Prof. R. Muccillo
Center of Science and Technology of Materials
Energy and Nuclear Research Institute
05508-900 S. Paulo, Brazil
E-mail: mucillo@usp.br

Prof. R. Muccillo
CECS
Federal University of ABC
09210-580 Santo André, Brazil

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/pssa.201700647>.

DOI: 10.1002/pssa.201700647

2. Experimental Section

(ZrO₂)_{0.97}(Y₂O₃)_{0.03} (3YSZ Tosoh TZ-3YBE, Japan) ceramic powders were cold-pressed both uniaxially in a metallic cylindrical die ($\phi 5 \times 5$ mm² pellet size) at 50 MPa and isostatically at 200 MPa (National Forge Co., USA). Green geometrical densities were in the range of 45–50% of the theoretical density. Apparent densities were evaluated with the Archimedes method using distilled water as the liquid medium.

The experimental setup for sintering green pellets under an electric field consisted of a vertical dilatometer (model 1161, Anter, USA). The sample holder was connected, via alumina-insulated platinum wires, either to a homemade AC power supply designed to apply voltages of up to 70 V in 500–1100 Hz frequency range or to a commercial Sorensen XG100-15 DC programmable power supply. The AC power supply operated in current limit control, providing a preset voltage (0–70 V) that turned off when the electric current reached a preset value (0.5 to 6 A). The maximum upper power limit supplied was 300 W. The DC power supply operated under current control mode, changing the voltage when changing the charge (sample) resistance. Subsequent voltages could be applied to produce as many electric current pulses as required in order to increase densification. As the sample was located 5 mm from the tip of the alumina tube-enclosed Pt-Pt10%Rh thermocouple of the dilatometer, the monitored temperature may have been underestimated by a few degrees. Further details can be found in previous papers.^[25,26]

In this paper the experimental procedure for electric current-assisted pressureless isothermal sintering (hereafter called flash sintering) consisted in i) heating the sample positioned inside the dilatometer furnace at 10 °C min⁻¹ to 1100 °C, and ii) either applying a given electric field at a chosen frequency in the 500–1000 Hz range, or a DC electric field, limiting the electric current's amplitude to the 0.5–6.0 A range. The electric field was applied until an electric current pulse occurred, at which it was kept on for 5 min. The shrinkage level was monitored accurately (1 μm) on the dilatometer's digital gauge, as was the temperature using a Pt-Pt10%Rh thermocouple whose tip was positioned close to the specimen. Data from both the electric voltage V and electric current I were monitored with two Fluke 8050A multimeters and collected in a data logger. A typical example of the collected V and I values is shown in **Figure 1**: 100 V cm⁻¹ electric field was applied 20 s after the sample reached 1100 °C. After a delay of 55 s, known as the incubation time,^[22] an electric current pulse was triggered, and the electric field was switched off when the current reached the preset limit value (1.1 A).

The ionic resistivity of the sintered zirconia was measured via the impedance spectroscopy technique, which consists in applying a low amplitude AC electric signal, measuring the corresponding electric current, and determining the impedance $[Z(\omega) = \text{Re } Z(\omega) - i \text{Im } Z(\omega)] \equiv [Z'(\omega) - i Z''(\omega)]$, where $\omega = 2\pi f$ and f is the frequency of the AC signal.^[27] A typical $[-Z''(\omega) \times Z'(\omega)]$ impedance diagram of a 3YSZ polycrystalline ceramic is composed of high (HF) and low (LF) frequency semicircles caused, respectively, by the contribution of the bulk (grains) and the interfaces (mainly grain boundaries) to the ionic resistivity. The resistance is determined at the intersection of the semicircle with the Z' axis. With $\omega_0 = 2\pi f_0$ and R determined, the

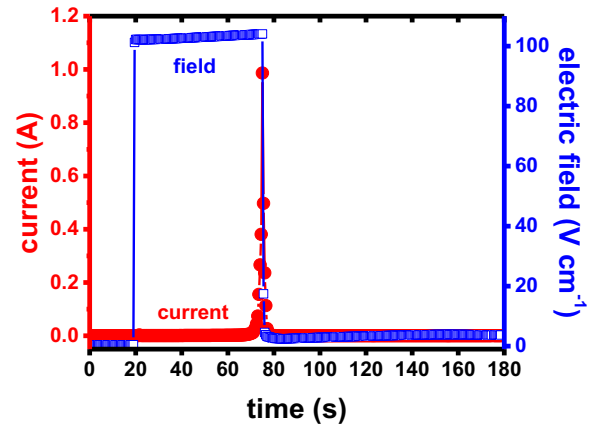


Figure 1. Applied electric field and current pulse during AC electric field-assisted pressureless (flash) sintering.

frequency at semicircle's apex enables the determination of the capacitance via $\omega_0 R C = 1$. Assuming that they form a parallel plate capacitor, the average distance between two grains, known as the intergranular distance, can be estimated after evaluating the grain boundary capacitance.^[27]

Impedance spectroscopy measurements were carried out in sintered specimens using an impedance analyzer (Hewlett Packard 4192A, USA) connected to a controller (Hewlett Packard 360, USA) from 5 Hz to 13 MHz, at 20 frequencies per decade, with a 200 mV input signal. The samples were spring-loaded, in groups of three, between two Pt disks inside an inconel 600 sample chamber. The Pt disks were connected with Pt wires to Bayonet Neill-Concelmann (BNC) connectors located on the top flange of the chamber, which was inserted in a programmable furnace. The $[-Z''(\omega), Z'(\omega), f = \omega/2\pi]$ data were collected and the $[-Z''(\omega) \times Z'(\omega)]$ diagrams were deconvoluted to obtain the grain boundary and the bulk electrical resistivities.^[28]

3. Results and Discussion

Figure 2 shows the dilatometric curves of 3YSZ green pellets heated from room temperature to 1100 °C, submitted for 5 min at 1100 °C to 100 V cm⁻¹ AC fields of 500, 750, and 1000 Hz frequencies, with a current limitation of 1 A. We also plotted the shrinkage curve of a similar pellet submitted to a 100 V cm⁻¹ DC field as well as a shrinkage curve obtained without application of the electric field (conventional sintering). The specimen heated to 1100 °C reaches a 4.3% shrinkage. Applying electric fields (for a sample diameter of 5 mm and a thickness of 5 mm, the delivered power is at approximately 2.5 W mm⁻³) at selected frequencies enhances shrinkage to 6.2, 13.9, and 20.1% for 500, 750, and 1000 Hz, respectively. The higher the frequency, the higher the final shrinkage. The easiest path for the evolution of an electric current through a polycrystalline ceramic is assumed to be the intergranular (interfaces/grain boundary) region, which is the same path that is traveled by scattered charge carriers in the dielectric breakdown phenomenon.^[29] Here we assume that the charge carriers of the electric current pulse that results from the

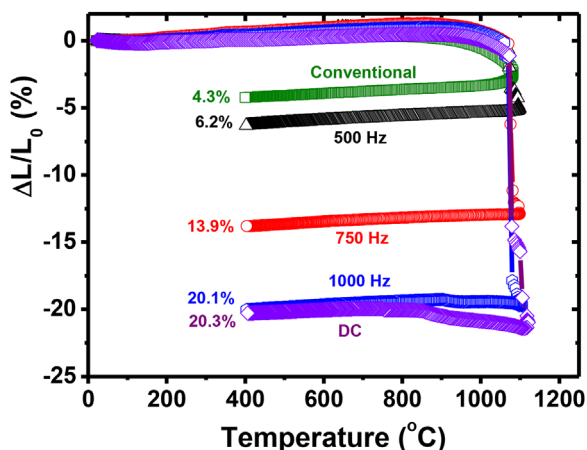


Figure 2. Dilatometry curves of conventional sintering (RT–1100–400 °C) and flash sintering of $\text{ZrO}_2: 3 \text{ mol\% Y}_2\text{O}_3$ powder compacts with the application of 100 V cm^{-1} DC electric field and 100 V cm^{-1} AC electric field at 500, 750, and 1000 Hz for 5 min. Sample thermocouple temperature: 1100 °C. The delivered power is assumed to be higher for DC field.

application of the electric field, collide with ions at the surfaces of the grain boundaries, thereby generating Joule heating and melting. This mechanism was recently proposed by Narayan.^[8,9] Moreover, the Joule heating could diffuse the depleted chemical species located in the space charge region adjacent to the grain boundaries back to the bulk.^[30,31]

When compared to AC flash sintering, DC flash sintering promotes the upper shrinkage limit reached by the sample. This results from the larger power delivery applying DC electric field, given by $P_{\text{DC}} = V \cdot I$. For the AC electric field, $P_{\text{AC}} = V \cdot I \cos(\phi = 2 \cdot \pi \cdot f \cdot t)$, that is, $0 \leq P_{\text{AC}} \leq P_{\text{DC}}$.^[32]

The above reasoning is the main point that this report wishes to emphasize. To date it has not been considered, and this is because there are no reported experiments on flash sintering with AC fields within a wide frequency range.

The electrical conductivity of polycrystalline ceramics depends on porosity, with the pores acting as insulating inclusions that inhibit the transport of charge carriers.^[33] **Figure 3** shows impedance spectroscopy diagrams of 3YSZ, measured at 450 °C, sintered (a) by heating to 1100 °C (a); (b) by applying a 100 V cm^{-1} AC field at 500 Hz; (c) at 750 Hz; (d) at 1000 Hz, and by applying a 100 V cm^{-1} DC field (e).

All the diagrams are visibly composed of two contributions: one, at high relaxation frequencies (HF) that corresponds to the electrical response of the bulk; and another, at low relaxation frequencies (LF) that corresponds to the blocking of oxide ions at interfaces. The deconvolution of these diagrams allowed us to evaluate the intragranular and intergranular components of the total resistivity: at 500 Hz, 9.3 kOhm.cm and 28.9 kOhm.cm for the intragranular and the intergranular components, respectively; at 750 Hz, 5.0 kOhm cm and 12.1 kOhm cm; at 1000 Hz, 4.1 kOhm cm and 5.2 kOhm cm; and for DC, 4.1 and 10.9 kOhm cm; and for conventional sintering, 5 and 50 kOhm cm. There is, in flash sintered samples, an evident decrease of the intergranular contribution to the total resistivity. This shows the electric current pulse's effect through the decrease of the pore fraction (major effect) and the interface thickness (minor effect). The

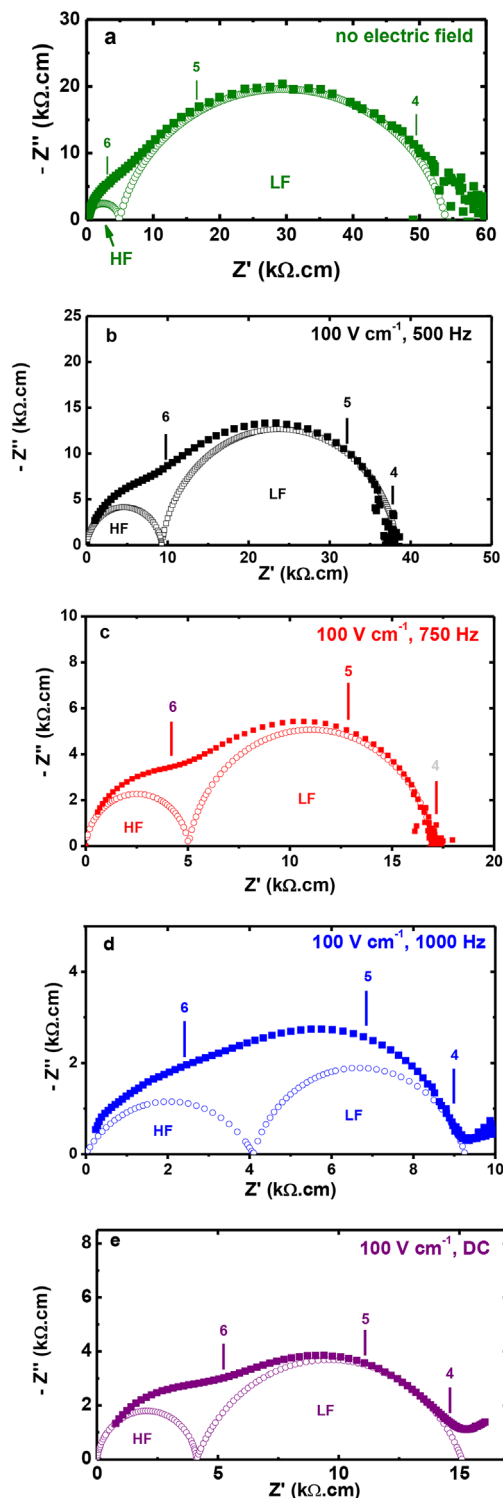


Figure 3. Impedance spectroscopy diagrams measured at 450 °C of flash sintered $\text{ZrO}_2: 3 \text{ mol\% Y}_2\text{O}_3$. Experimental conditions: without application of electric field (a); with application of 100 V cm^{-1} at 500 Hz (b), 750 Hz (c) 1000 Hz (d), and with application of 100 V cm^{-1} DC electric field. Sample thermocouple temperature: 1100 °C. Numbers stand for log f (f: Hz, relaxation frequency). All figures show also the high (HF) and low (LF) frequency deconvoluted diagrams. Apparent densities (% of the theoretical density): a) 52.3, b) 55.2, c) 65.7, d) 88.8, and e) 86.2.

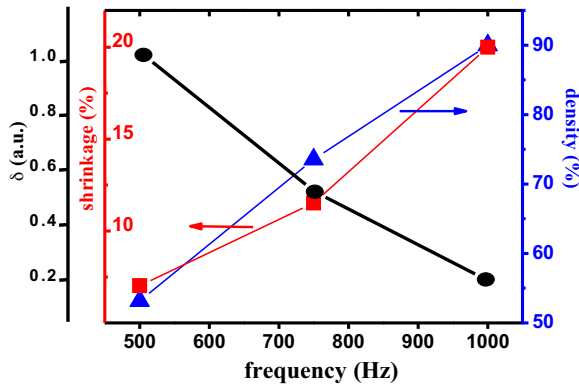


Figure 4. Final shrinkage level (square), apparent Archimedes density (triangle) and relative average intergranular distance δ (circle) of ZrO₂: 3 mol% Y₂O₃ flash sintered pellets as a function of frequency of the applied electric field, 100 V cm⁻¹. Sample thermocouple temperature: 1100 °C.

capacitances C_{LF} associated with the LF contribution to the electrical resistivity were evaluated using the equation $2\pi f_0 R_{LF} C_{LF} = 1$, where f_0 is the frequency at the apex of the LF semicircle and R_{LF} is the resistance measured at the intersection of that semicircle with the real axis.^[34] The average intergranular distance δ , plotted in **Figure 4**, was evaluated using the equation $[C_{LF} = \epsilon \cdot \epsilon_0 \cdot S/\delta]$, $\epsilon_0 \cong 8.854 \times 10^{-12} \text{ F m}^{-1}$,^[27] $\epsilon = 35$,^[35] Here, S is the sectional area of the sintered 3YSZ.

In **Figure 4** the shrinkage values and the apparent Archimedes density are plotted as a function of the frequency. The trend is similar for both parameters. The intergranular average distance δ , derived from the impedance spectroscopy diagrams, is also plotted. As expected, this parameter decreases when shrinkage and density increase. The typical apparent density (90% T.D.) of the high-density sample is similar to reported values.^[15,17,18]

4. Conclusions

We provide experimental evidence regarding the dependence of the shrinkage level of 3 mol% yttria-stabilized zirconia on the frequency of the AC electric field in electric field-assisted pressureless (flash) sintering. Sintering similar samples at the same temperature, under the same electric field amplitude, promotes higher final shrinkage levels for higher frequencies. Moreover, there is an increase of the total electrical conductivities. We proposed an explanation based on the rate of the inelastic collisions of charge carriers with defects located at the interfaces (grain boundaries), which increases with an increasing frequency. Those collisions generate Joule heating, which is the primary effect resulting from the application of an electric field to the zirconia polycrystalline ceramics. This additional heat may promote the diffusion to the bulk of depleted charged species located in the space charge region, which decreases the blocking of oxide ions at the grain boundaries. DC electric fields produce denser samples because the corresponding power delivered to the specimen is higher than the power delivered with AC electric fields at the same amplitude.

Acknowledgments

We are grateful to the Comissão Nacional de Energia Nuclear – CNEN, Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq (Procs. 470952/2013-0 and 303483/2013-0) and Fundação de Amparo à Pesquisa do Estado de São Paulo – FAPESP (Proc. 2013/07296-2) for their financial support. One of the authors (SGMC) acknowledges Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the doctorate scholarship.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

flash sintering, impedance spectroscopy, ionic conductors, solid electrolytes, zirconia

Received: August 28, 2017
Revised: December 7, 2017
Published online: January 24, 2018

- [1] S. Ghosh, A. H. Chokshi, P. Lee, R. Raj, *J. Am. Ceram. Soc.* **2009**, 92, 1856.
- [2] D. Yang, H. Conrad, *Scripta Mater.* **2010**, 63, 328.
- [3] R. Muccillo, M. Kleitz, E. N. S. Muccillo, *J. Eur. Ceram. Soc.* **2011**, 31, 1517.
- [4] R. Raj, *J. Eur. Ceram. Soc.* **2012**, 32, 2293.
- [5] K. S. Naik, V. M. Sglavo, R. Raj, *J. Eur. Ceram. Soc.* **2014**, 34, 2435.
- [6] M. Cologna, B. Rashkova, R. Raj, *J. Am. Ceram. Soc.* **2010**, 93, 3556.
- [7] R. Muccillo, E. N. S. Muccillo, *J. Electroceram.* **2017**, 38, 24.
- [8] M. Yu, S. Grasso, R. McKinnon, T. Saunders, M. J. Reece, *Adv. Appl. Ceram.* **2016**, 99, 1534.
- [9] C. E. J. Dancer, *Mater. Res. Express* **2016**, 3, 1.
- [10] J. Narayan, *Scripta Mater.* **2013**, 68, 785.
- [11] J. Narayan, *Scripta Mater.* **2013**, 69, 107.
- [12] J.-C. M'Peko, J. S. C. Francis, R. Raj, *J. Am. Ceram. Soc.* **2013**, 96, 3760.
- [13] A. L. G. Prette, M. Cologna, V. Sglavo, R. Raj, *J. Power Sources* **2011**, 196, 2061.
- [14] M. Cologna, J. S. C. Francis, R. Raj, *J. Eur. Ceram. Soc.* **2011**, 31, 2827.
- [15] R. Chaim, *Materials* **2016**, 9, 280.
- [16] J. S. C. Francis, M. Cologna, R. Raj, *J. Eur. Ceram. Soc.* **2012**, 32, 3129.
- [17] D. Liu, J. Liu, Y. Gao, F. Liu, K. Li, J. Xia, Y. Wang, L. An, *Ceram. Int.* **2016**, 42, 19066.
- [18] W. Ji, B. Parker, S. Falco, J. Y. Zhang, Z. Y. Fu, R. I. Todd, *J. Eur. Ceram. Soc.* **2017**, 37, 2547.
- [19] R. I. Todd, E. Zapata-Solvas, R. S. Bonilla, T. Sneddon, P. R. Wilshaw, *J. Eur. Ceram. Soc.* **2015**, 35, 1865.
- [20] J. A. Downs, V. M. Sglavo, *J. Am. Ceram. Soc.* **2013**, 96, 1342.
- [21] R. Baraki, S. Schwartz, O. Guillon, *J. Am. Ceram. Soc.* **2012**, 95, 75.
- [22] J. S. C. Francis, R. Raj, *J. Am. Ceram. Soc.* **2013**, 96, 2754.
- [23] H. Conrad, J. Wang, *Scripta Mater.* **2014**, 72-73, 33.
- [24] W. Qin, H. Majidi, J. Yun, K. van Benthem, *J. Am. Ceram. Soc.* **2016**, 99, 2253.
- [25] R. Muccillo, E. N. S. Muccillo, *J. Eur. Ceram. Soc.* **2014**, 34, 3871.
- [26] R. Muccillo, E. N. S. Muccillo, *J. Eur. Ceram. Soc.* **2014**, 34, 915.
- [27] E. Barsoukov, J. R. Macdonald, *Impedance Spectroscopy, Theory, Experiment, and Applications*, Wiley-Interscience, USA **2005**.

- [28] M. Kleitz, J. H. Kennedy, *Fast Ion Transport in Solids*, P. Vashishta, J. N. Mundy, G. K. Shenoy (Eds.), Elsevier/North-Holland, The Netherlands **1979**, pp. 185.
- [29] M. Biesuz, P. Luchi, A. Quaranta, V. M. Sglavo, *J. Appl. Phys.* **2016**, 120, 145107.
- [30] J. Maier, *J. Appl. Phys.* **2002**, 92, 6819.
- [31] X. Guo, W. Sigle, J. Fleig, J. Maier, *Solid State Ionics* **2002**, 154-155, 555.
- [32] J. R. Reitz, F. J. Milford, R. W. Christy, *Foundations of Electromagnetic Theory*, Pearson/Addison-Wesley, USA **2009**.
- [33] R. Muccillo, *J. Mater. Res.* **2009**, 24, 1780.
- [34] M. Kleitz, H. Bernard, E. Fernandez, E. Schouler, *Science and Technology of Zirconia*, Vol. 3, A. H. Heuer, L. W. Hobbs (Eds.), American Ceramic Society, Westerville, OH, USA **1981**, pp. 310.
- [35] D. P. Thompson, A. M. Dickins, J. S. Thorp, *J. Mater. Sci.* **1992**, 27, 2267.