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On the role of Debye temperature in the onset of flash in three oxides

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ABSTRACT

Higher electric fields lower the temperature for the onset of flash. We explore the question "what can be the lowest temperature for initiating flash?". Constant heating rate experiments at increasing electric fields reveal a surprising characteristic: the Debye temperature emerges as a the lower bound for the onset of flash. Data for flash temperature for three oxides are shown to exhibit this behavior in a universal plot.

Flash Sintering (FS) is a process whereby sintering can be achieved in mere seconds at unusually low temperatures by the application of modest electrical fields [1]. A broad class of ceramics, including ionic conductors [2–5], electronic conductors [6], insulators [7–10] and semiconductors [11,12] show this phenomenon. The process can be carried out in two ways: (i) by heating the furnace at a constant rate, at a constant applied field until the specimen flashes, or (ii) holding the specimen at a isothermal furnace temperature and applying the electric field as a step function – the specimen flashes after an incubation time which depends on the strength of the field and the temperature.

The onset of flash is signalled by a non-linear rise in conductivity; this causes a surge in power dissipation in the specimen. The electrical power to the specimen is then transitioned from voltage control to current control in order to prevent electrical/thermal runaway. This transition is accompanied by rapid densification to near full density, typically within seconds.

While the mechanisms of the flash sintering process remain under consideration, they encompass three characteristics [13,14]: (i) an abrupt increase in conductivity, (ii) electroluminescence, and (iii) rapid densification. Extensive reviews of flash have been published by Biesuz and Sglavo [19], Yu et al. [20], and Dancer [21].

The onset of the flash, that is the cusp in the increase in conductivity, is related to the applied field and the furnace temperature. It is now accepted that the flash-onset temperature is inversely related to the applied electric field [11,17,18]. The flash effect is seen not only in sintering experiments with powder-pressed specimens but also in dense polycrystals [15], and in single crystals as well [16]. It is interesting that at a given applied field the flash temperature for single crystals of cubic zirconia is lower than in dense polycrystals, which is lower than in sintering of porous samples.

The underlying mechanism of flash sintering remains unclear. A suggestion has been made that defects, in concentrations far above thermal equilibrium, are produced as a result of non-linear lattice vibrations [22]; under this hypothesis flash would be possible only at phonon wavelengths that are equal to or less than the lattice parameter. The Debye temperature (Θ_D) is defined as the temperature for the crystal's highest normal mode of vibration [23]. It follows that, under this theory, the Debye temperature would be the lower bound for the onset of the flash. Indeed, Yadav et al. [18] have shown that the onset temperature for YSZ, and titania, approaches the Debye temperature at high electric field.

Recently, the generation of an abnormal concentration of Frenkel defects has been investigated in aluminum single crystals by molecular dynamics. These simulations have confirmed that defects can be generated by the injection of phonons, but only when the specimen is at or above the Debye temperature [24].

In this letter, we further investigate the generality of the idea that Debye temperature can be the lower bound for the onset of flash. Previous studies have reported, that a large surface-to-volume ratio of nanoscale particles can influence the phonon spectra since softer surface phonon modes may enhance the specific heat at lower temperatures [25,26]. Therefore, in the present work, for the sake of comparison, we

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consider the flash-onset behavior of both dense polycrystalline samples prepared by conventional sintering, and powder-pressed green samples that are directly flash sintered. The present study focuses on 10 mol% gadolinium-doped ceria (GDC10, $Gd_{0.10}Ce_{0.90}O_{1.95}$).

Additionally, the generality of the concept of Debye temperature is applied to three oxides. In addition to ceria doped with 10 mol% Gadolinium oxide (GDC10), 3 mol% yttria stabilized tetragonal zirconia (3YSZ) [18], 8 mol% yttria stabilized cubic zirconia (8YSZ) [18] and titania [18] are considered.

The experiments were carried out with commercial gadolinium-doped ceria (10 mol% Gd, $Gd_{0.10}Ce_{0.90}O_{1.95}$: GDC10, Fuelcellmaterials, USA) powders with an average particle size of $d_{50} = 0.13$ μm ($d_{10} = 0.07$ μm, $d_{90} = 1.97$ μm), measured with the particle size analyzer Horiba LA-950 V2 (Retsch Technology GmbH, Haan, Germany). The BET specific surface area of 10.5 m^2/g was measured with the Area Meter II (Ströhlein Instruments, Viersen, Germany).

Conventionally sintered dense specimens were prepared by uniaxially pressing the GDC10 powder into a pellet at 50 MPa. The pellets were 20 mm in diameter and 5 mm tall. The green pellet was then pressed again by cold isostatic pressing (CIP) at 300 MPa. The green density of these samples was 55%. The CIPed samples were free sintered in a high-temperature furnace (Nabertherm, Germany) at 1500 °C, 4 h dwell, heating and cooling rate 3 K min^{-1} in air to achieve full density. The relative density of the sintered samples, measured by the Archimedes method was 99%. Rectangular samples were cut from the dense pellets; they were 7 mm long, 1.6 mm wide and 1 mm thick.

For flash sintering expeirments, powder-pressed dog-bone shaped specimens were prepared from the GDC10 powder by uni-axial pressing, at 100 MPa, within a die. These specimens had a gauge-length of 15 mm, a width of 3.3 mm, and a thickness between 1.8 and 2.1 mm. The amount of powder used for these specimens was between 0.8 and 1 g. The green body samples were too fragile and difficult to connect to the electrodes. Therefore, the samples were pre-sintered at 1000 °C for 30 min with a heating and cooling ramp of 3 K min^{-1}. The relative densities of these pre-sintered samples, measured from their physical dimensions and weight, were approximately 62.5%.

The dense rectangular and the green dog-bone shaped samples were connected to the power source with a platinum wire. Platinum paste was applied between the sample and the platinum wire to ensure good electrical contact. The flash sintering experiments were carried out in a vertical tubular furnace, the experimental set-up is described in [7]. Electric field was applied from a Glassman 3 kW DC power source (Glassman High Voltage Inc., KL series, NJ, USA). This maximum voltage available from this power source was 2000 V. The current flowing through the sample was measured with a digital multimeter (Keithley 2000, Keithley Instruments, Cleveland, OH). Communication with, and the control of the power supplied to the sample were achieved by DAQ USB-6008 (National Instruments). The GPIB was used to communicate with the multimeter, the device that monitored the current. Data were acquired through a graphical user interface (GUI) developed in-house, running on the MATLAB platform.

The experiments were carried out by applying a constant electric field at room temperature and then heating the furnace at a constant rate of 10 K min^{-1}. The fields ranged from 100 V cm^{-1} to 2000 V cm^{-1}. After the flash event the experiment was switched from voltage control to current control, with the current limit set to 100 mA mm^{-2}. The specimen was held at this current for 120 s before the power was switched off.

The flash sintering process is classified into three different stages: Stage I (incubation), is the period from the application of electric field until the abrupt increase in electrical conductivity which indicates the onset of the flash. Stage II (transient) is the turnover of the power supply from voltage to current control. In Stage III the sample can be held in steady state at constant current [1]. The present work is concerned only with Stage I, *i.e.* with the onset of the flash.

Measurement of the sample temperature during the flash experiment remains a challenge, since the sample temperature can rise above the furnace temperature by Joule heating. The extent of Joule heating depends on the power density. For the present experiments the highest values of the power density, at the lowest field were ~100 mW mm^{-3}; it was much lower at high electric fields. Recently, Cao et al. [27] have measured the sample temperature for 10 mol% yttria doped ceria by applying a low electric field during Stage I. They used a cylindrical shaped sample with a diameter 8 mm and height 13 mm. The experiment was conducted on a custom made sinter forging device. The sample temperature was measured with the help of an insulating thermocouple. They found at 63 mW mm^{-3} power density, the sample temperature was only 22 °C higher than the furnace temperature. Therefore, it is assumed that the sample temperature is similar to the furnace temperature at the onset of flash.

The real time data for the power density, for the dense GDC10 specimens, carried out at a constant heating rate of 10 K min^{-1}, are shown in Fig. 1. Data for 15 experiments are included. The peak in the power density, which is the product of the electric field and the current density limit, increases with the field up to 500 V cm^{-1}. At higher fields the samples splintered before reaching the current limit. At very high electric fields, 3000, 4000 and 5000 V cm^{-1}, which are not included in this figure the samples splintered with only a few mA current flowing through them.

There are two possible explanations for the cracking of the samples: It may be related to the non-uniform lattice expansion from non-uniform defect generation [28]. The resulting gradient in lattice expansion could have produced elastic stresses which caused the fracture. Another possibility would be of course thermal shock [29]. The power surge happens quickly. At high fields and low furnace temperatures, the power surge can produce thermal gradients and thereby, heterogeneous stress distribution leading to mechanical failure. Specimen splintering during flash at high fields is a new finding. In our minds we favor the defect generation hypothesis, which needs to be followed up with further *in-*

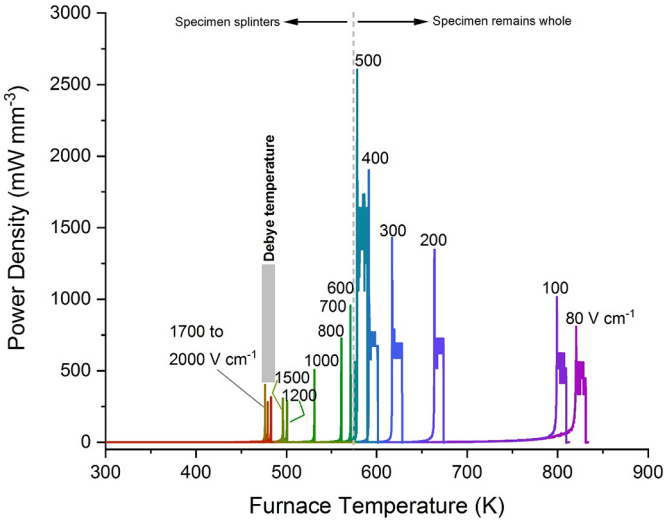

Fig. 1. The data for the change in power density with time (in this case temperature) in constant heating rate experiments, for 15 experiments carried out at increasing electric fields.

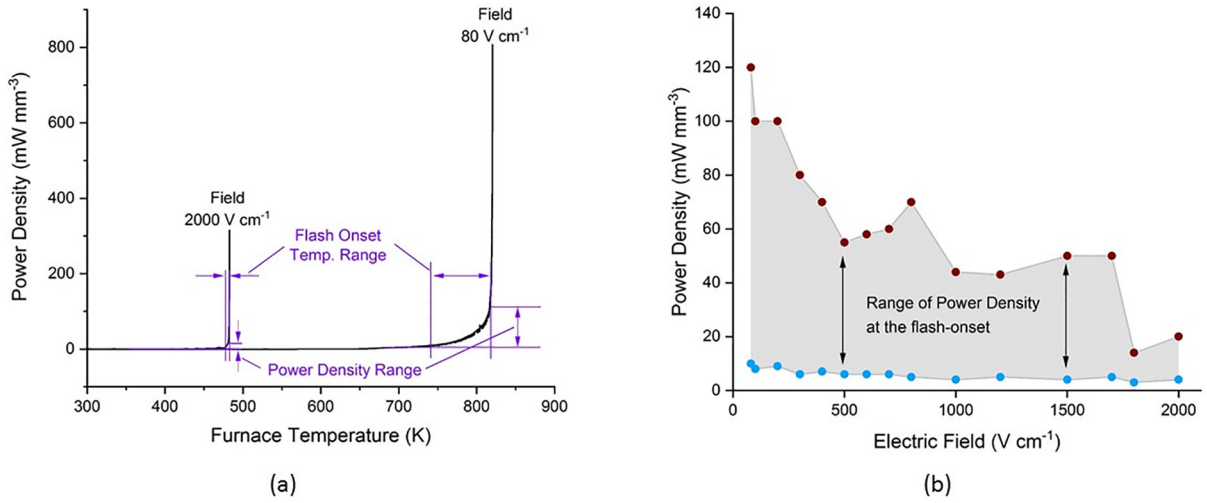

Fig. 2. (a) The method for measuring the range in temperature and power density at the flash-onset. The ranges become narrower at higher applied fields, (b) the range of the power density encompassing the onset of flash at 15 different electric fields. Generally speaking the range varied up to 40–60 mW mm^{-3}, although it is wider at the lowest fields and narrower at the very high fields.

situ experiments of X-ray diffracction and simulations. It may provide deeper and broader understanding of the flash phenomenon.

The flash-onset temperature was measured as a range from the power density profile as a function of furnace temperature. Tangents were drawn to the Stage I and Stage II period in the power density curve. Two examples of this method, one at low and the other at high electric field, are shown in Fig. 2(a). The data yield values for the range in temperature and the range in powder density for the onset of the flash at different electric fields.

The range of the power density for the flash-onset at different electric fields, measured by the method illustrated in Fig. 2(a), is shown in Fig. 2(b). Note that the lower limit of the range if the same because of the tangent method used above. The flash-onset is wide at low electric fields but narrows as the field is increased. The range of the flash onset temperature at different electric fields are summarized in the Table S1, included in Supplementary material, and plotted in Fig. 3.

The onset temperature of the porous GDC 10 and dense GDC 10 samples as a function of the electric fields are compared in the inset within Fig. 3. While both sets of data show similar trend the dense sample flash at a lower temperature as compared to the porous sample, at low electric fields. At higher electric fields the onset temperature for porous and dense samples are similar.

The main graph in Fig. 3 shows how the flash temperature declines with electric field, approaching a lower bound. Previous studies on flash sintering of GDC [30,31] have suggested that higher fields lower the temperature for the flash-onset. The present work seeks the limit to which the flash temperature can be lowered by applying higher and higher electric fields, and, then, to see if this lower bound in flash temperature is related to the Debye temperature. Direct measurements of the Debye temperature for GDC 10 have not been reported in literature. However, Hisashige et al. [32] report on the Debye temperature of rare earth-doped ceria. They found that the Debye temperature with different doping elements (10 mol%) changes by less than ±20 °C from the Debye temperature of pure Ceria, which is reported

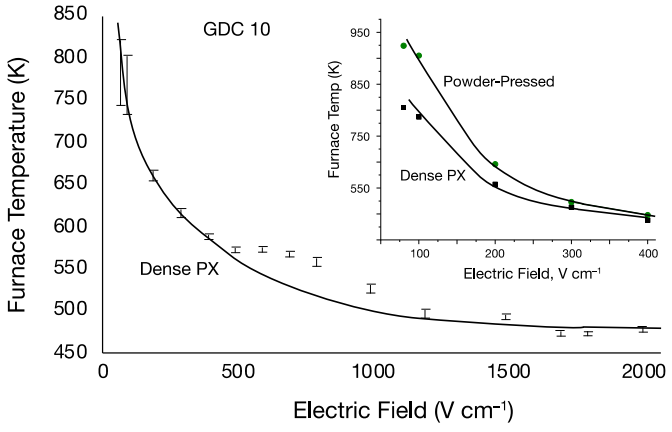

Fig. 3. Plots of the onset temperature of as a function of the electrical fields. The error bars were calculated from the procedure outlined in Fig. 2. The numerical data are included in Supplementary Material in Table S1. The inset compares the data from powder-pressed and dense polycrystalline samples. The main graph shows the temperature to approach an asymptotic values at high electric fields.

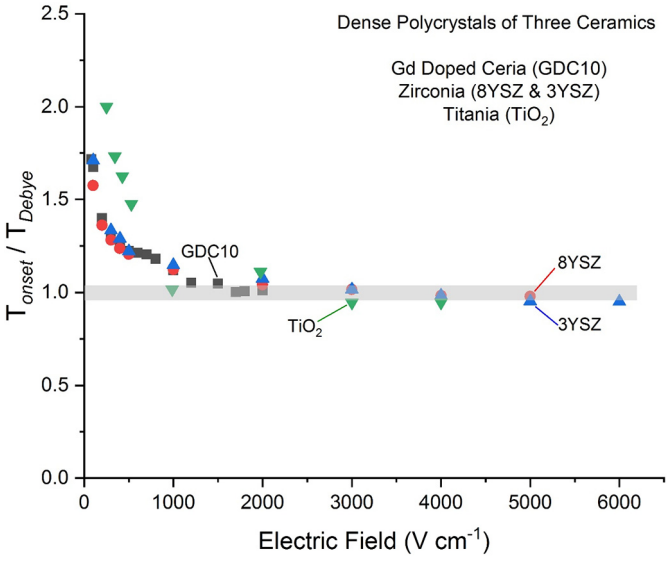

Fig. 4. Normalized plot of the flash onset temperature, with respect to the Debye temperature for three oxides, confirming the hypothesis that Debye can be the lower bound for flash. The numerical data are included in Supplementary material in Table S2.

to be about 480 K. Therefore the Debye temperature for the current experiments with GDC is taken as 480 ± 20 K, which is in agreement with the data in Fig. 4.

Data for the lower bound flash temperature from literature [18] for 3YSZ, 8YSZ and titania are gathered with the present results to prepare a universal plot where the flash onset temperature is normalized with respect to the Debye temperature. These data are summarized in the Table S2, included in Supplementary material, and plotted in Fig. 4. The plot conforms to the idea that the Debye temperature for several ceramics may indeed serve as the lower bound for the onset of the flash.

Although the flash sintering process is a relatively simple process that has been successfully applied to many ceramics, the underlying mechanism that leads to the nonlinear rise in conductivity and rapid densification coupled with electroluminescence is still not established. While the thermal runaway model shows a promising explanation for the initiation of the flash event [33], it cannot alone explain other factors such as electroluminescence and phase transition [14, 34]. Yadav and Raj hypothesize that nonlinear lattice vibrations could be the reason for initiation of the flash event, in which case Debye temperature is predicted to be the lower bound. The present study confirms previous findings (in YSZ and titania) and contributes additional evidence (GDC10) that that Debye temperature may indeed be the lower bound temperature to initiate flash. The relationship between defect generation, phonon proliferation and the Debye temperature has been confirmed by recent elegant molecular dynamics simulations by Jongmanns et al. [24].

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scriptamat.2019.05.030.

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