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The dominant role of electrode-interfaces in flash induced electronic conductivity of rutile single crystals

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Abstract

The electronically conducting state of oxide single crystals in Stage III can be retained at room temperature by special experimental methods, thereby enabling investigations into the science of the flash phenomenon. For example, in-depth electron microscopy of cubic zirconia single crystals has revealed colossal colonies of oxygen vacancies that form their own crystal as seen in selected area electron diffraction; the defect-crystal was congruent with the parent crystal. Here, we present measurements of the electrode–ceramic interface and crystal matrix resistance in the rutile single crystal by the four-point method. Remarkably, the resistance is dominated by the interfaces; in comparison the matrix resistance is negligible. Furthermore, when the flash current is reversed the resistance at the anode switches between high and low values. The effect is reproduced over several cycles. This switching effect is explained by the segregation of cation defects to the anode and the formation of irreversible crystalline oxygen defect colonies at the cathode. The latter is consistent with "blackening" often seen at cathodes. The results highlight the role of segregation of charged defects into space charge layers at metal electrodes in the initiation and propagation of flash in oxides.

KEYWORDS
electronic conductivity, flash phenomenon, memristor, single crystals, titania

1 | Introduction

Flash sintering was discovered in 2010,[1] when yttria-stabilized zirconia was shown to sinter in mere seconds at low furnace temperature with the application of modest electrical fields. The experiment was carried out by applying an electric field and raising the furnace temperature at a constant rate. At a certain temperature, the sample flashes, sinters abruptly, and there is a sharp increase in conductivity (the transition temperature drops as the applied field is increased). Flash occurs not only in powder pressed samples but also in single crystals.[2,3] Indeed, in constant heating rate experiments, the single crystals exhibit the onset of flash at a lower temperature than powder-pressed samples as shown in Figure 1,[3] the reason being that, phenomenologically, flash onset occurs within a narrow band of the power density.[4] Power density is inversely proportional to the resistivity; therefore, single crystals having a lower resistance than powder compacts, reach the power density threshold at a lower temperature.

Interestingly, while the onset of flash sintering has drawn considerable interest in the community, the non-linear rise in conductivity at the onset of flash[1] has not received as much attention. The transition to high
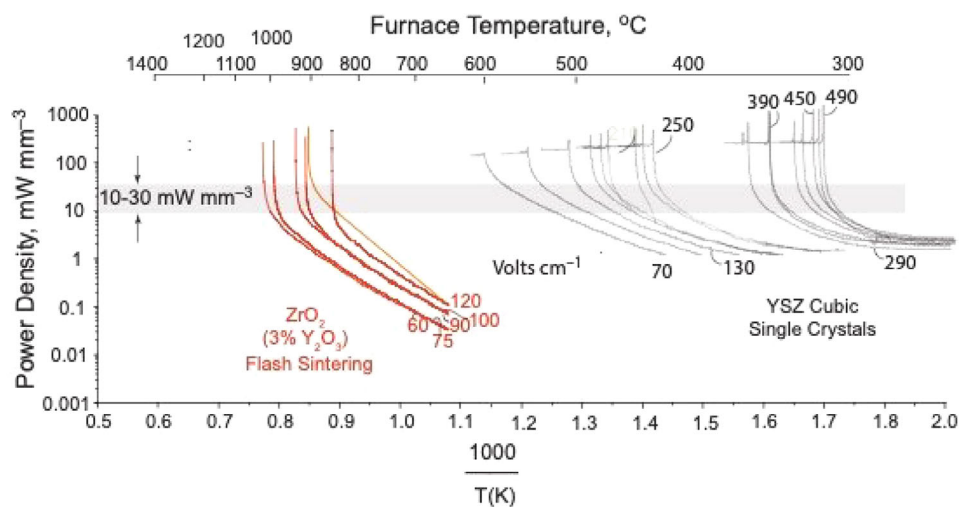
FIGURE 1 Flash transition during sintering of powder compacts, and in single crystals of yttria-stabilized zirconia. Both flash within a narrow range of power density. The single crystals having a lower resistivity therefore flash at a lower temperature.

conductivity is also a transition into electronic conductivity. This finding was first demonstrated by Maso and West,[5] and recently confirmed from in situ impedance spectroscopy measurement where the transition to electronic conductivity was identified by a change in the interface resistance at the metal electrode from blocking to non-blocking.[6] Mishra et al.[7] had identified electronic conductivity in Gd-doped ceria. The electronic conductivity was shown to be retained in zirconia by in-flash immersion and quench in liquid nitrogen.[8] More recently, it has been shown that flash in Ar atmosphere can lead to the retention of electronic conductivity in single crystals of cubic zirconia at room temperature.[9] These single crystal experiments can serve to provide insights into the overall flash process.

The work on single crystals has enabled detailed transmission electron microscopy (TEM) studies of the defect structure.[2] Recent measurements have investigated energy dispersive spectroscopu (EDS), electron emergy loss spectroscopy (EELS), and small area electron diffraction (SAED). They show colonies of colossal oxygen-vacancy concentrations (which form into a crystal of their own), pointing toward defect generation as the underlying cause of the flash effect. This conclusion is further substantiated by in situ calorimetric measurements of endothermic reactions during current rate flash which are attributed to the enthalpic generation of defects.[10,11] The defect concentrations so measured have a one-to-one relationship to the current density.[12] It is likely that the electronic structure of these defect colonies is the reason for flash induced electronic conductivity.[13]

Another method for retaining electronic conductivity has been to flash the single crystals at high electrical fields, which then retain their electronic conductivity as shown in Figure 2.[14] The experiment was carried out on single
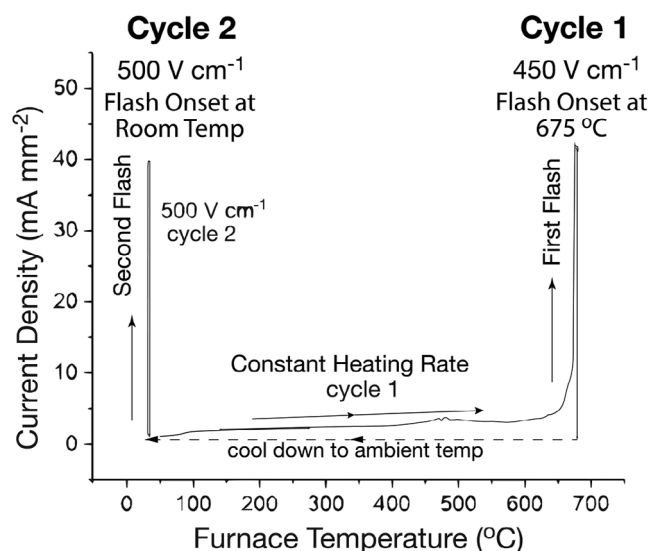

FIGURE 2 A titania single crystal initially flashed at high temperature at a field of 450°C, when cooled down and flash again, flashed at room temperature. The flashed crystal remains electronically conducting at room temperature.

crystals of titania by applying a field of 450 V cm^{-1} and then increasing the furnace temperature until the crystal flashed at 675°C. The onset of flash was marked by an abrupt increase in conductivity and electroluminescence. Remarkably, when the specimen was cooled down and the flash experiment repeated a second time by applying a field of 500 V cm^{-1} it flashed at room temperature. Furthermore, the crystal after the first flash became electronically conducting at room temperature having a conductivity of 9 S/m.

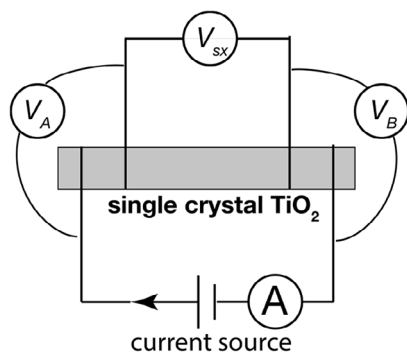Importantly, the effect was seen only when the first flash was carried out at an applied field above 450 V cm^{-1}. We

FIGURE 3 Schematic of the current and voltage measurements in the four-point method with a 5 mm long crystal of TiO_2. The voltage across the inner electrodes measures the crystal matrix resistance, while the outer and inner electrodes measure the interface resistances. The contacts were made by wrapping a thin platinum wire around the crystal.

argue that high fields are needed to form oxygen vacancies in high enough concentrations that they precipitate a new defect-phase (as seen in the TEM work).[2] Once this phase is formed it cannot be undone during cool down since that would involve a phase transformation. The phase becomes kinetically frozen and therefore enables electronic conductivity to be retained at room temperature.

2 | Four-Point Measurements of Resistance

The method of the four-point measurement is sketched in Figure 3. The outer electrodes are connected to a current source. The resistance of the crystal matrix is equal to the voltage across the inner electrodes divided by the current. The interface resistance at these electrodes is side stepped because the voltmeter, ideally having infinite resistance, does not draw any current. The measurements were carried out at room temperature.

The voltage between the outer electrode and the nearest inner electrode, when divided by the current gives the resistance of that electrode–ceramic interface. Often charged defects will gather next to the metal electrode, as a space charge, which will resist the transport of electrons from the ceramic into the metal. One can speculate that Frenkel pairs produced by flash can form dipoles rendering the ceramic to become like a ferroelectric which can give rise to complex electronic structure at the interface including diode like behavior[15]; something to keep in mind for the future.

The nature of the space charge is predominantly established when the device is initially flashed with a DC field of 450 V cm^{-1} at a 675°C, as shown in Figure 2. Therefore, the positive electrode and the negative electrodes of this DC field remain as the key reference. We refer to the positive electrode as A and the negative electrode as B.

Three types of voltages are measured, V_A, V_B, and V_{SX}. The first and the second are values between the metal electrodes A and B, and the nearest inner electrode in the ceramic. V_{SX} is measured across the two inner electrodes. When divided by the current they yield values for the interface resistance at the electrodes and the true resistance of the crystal matrix. We call them R_A and R_B, and R_{SX}. The total resistance of the device is then given by $R_{tot} = R_{SX} + R_A + R_B$.

Further experiments were carried out by re-flashing with a current of 40 mA mm^{-2} and cycling between forward (positive) and reverse (negative) currents. The results are shown in Figure 4. The resistances (R_A, R_B, and R_{SX}) were measured during the "dead" period, after the flash current was turned off. The influence of the direction of the current was determined over several cycles to check for reproducibility. Note that R_A changes from a high value for the forward (positive) cycle to a low value for the reverse cycle. The change is huge, nearly three orders of magnitude. However, R_B remains unchanged. The change in the total resistance is tempered by the relatively large value of R_B. The high/low ratio of the total resistance is plotted against the flash current in Figure 4c. As shown in Figure 4B the effect of the change in resistance is seen only when the current (40 mA mm^{-2}) is large enough to induce a flash.[16,17]

To summarize the key results from Figure 4A:

(i) $(R_A + R_B) \gg R_{SX}$, that is, the resistance of the crystal matrix is negligible in comparison to interface resistance. In other words, the total resistance of the device is approximately equal to the sum of the resistance at the interfaces.

(ii) The interface resistance measured at the A electrode depends on the direction of the flash current. It switches from a high value when the flash current is in the forward direction and low for the case of the reverse current.
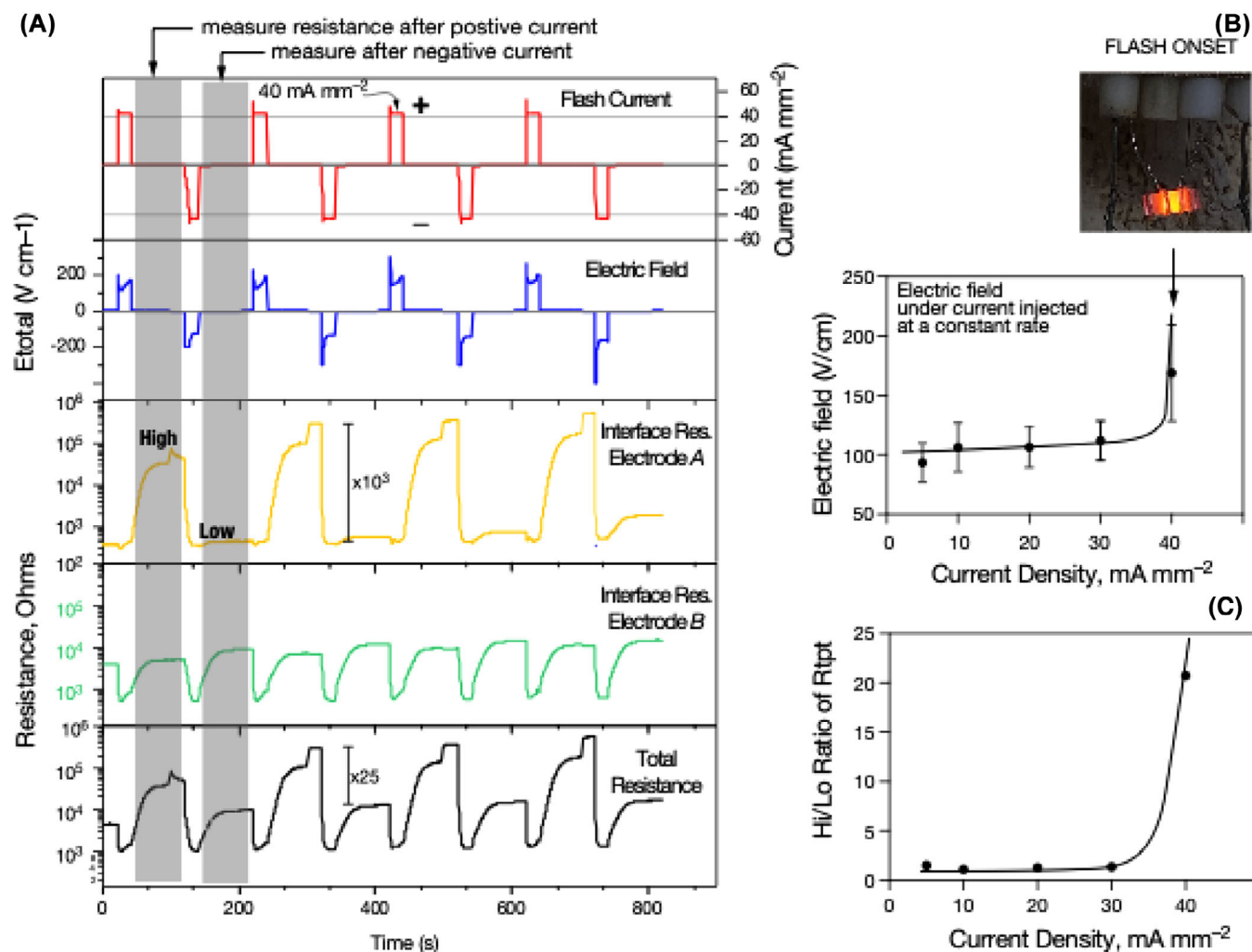
FIGURE 4 (A) The variation in the anode resistance with positive and negative injection of 40 mA mm^{-2}. (B) When current is increased at a constant rate (at room temperature) the flash onset is indicated by a "peak" in the voltage. (C) The ratio of the high to low resistance of the device as a function of the injection current. The results on the left are given for an ON/OFF injection current of 40 mA mm^{-2}.

(iii) The spikes in the electric field confirm that the interface space charge acts like a capacitor; it charges and discharges with a time constant equal to the product of its effective capacitance and resistance.[18]

Our understanding of the defect chemistry under flash is not sufficient to explain the rather unusual results described just above. The complexity arises from the four different kinds of defects that may be introduced in flash. They are vacancies and interstitials of both cations and anions. Since the resistance of the device is controlled by interfaces, it is reasonable to assume that the changes arise from the space charge constituted from these defects segregated against the metal–ceramic interface. Recent results on surface plasmas on titania induced by flash may also reflect an interface effect.[19]

3 | Discussion

It is now quite certain that colossal-concentrations of defects are generated during flash. The energy of the endothermic reactions, measured, in real time, from the difference between the input electrical energy and the energy lost to radiation, convection and specific heat, when divided by the energy of formation of Frenkel pairs, has repeatedly shown that colossal concentrations of Frenkels, as high as 0.25 mole fraction, are produced in ceramics[10] as well as in metals.[11,20,21] We take note that sintering requires chemical diffusion (i.e., stoichiometric mass transport). In titania, the transport of two oxygens must be accompanied by one titanium. Therefore, it is inferred that flash produces vacancies as well as interstitials of both oxygen and titanium.

It is likely that the formation of a "defect-crystal" phase, reported in reference,[2] plays a role in the present results. We note in Figure 2, that flash at room temperature requires that the crystal first be flashed above 450 V cm^{-1} at 675°C. The high field and temperature are necessary to produce vacancy concentrations that are large enough to precipitate into a second phase,[2] which can be kinetically preserved to render the crystal to be electronically conducting, and thereby, enabling flash at room temperature as in Figure 2. This crystal of oxygen vacancies which would have a positive charge would segregate at electrode *B*. The absence of the a change in the interface resistance at this electrode is ascribed to the kinetic stability of this phase. Blackening at the cathode during flash, reported in the literature[22,23] is consistent with this view.

Now, let us consider the possibilities for explaining the change in the interface resistance at electrode *A* in response to forward and reverse flash current as seen in Figure 4A, where the resistance R_A is high for the forward current and low for the reverse current. For the case of the forward current electrode *A* is held at a positive potential which would draw defects with a negative charge; in this instance, the interface repels electrons which would increase the interface resistance. For the reverse current, the electrode will be at negative potential drawing defects with a positive charge which will favor the transfer of electrons across the interface, causing the interface resistance to be low.

Various defects can form during flash. They are interstitials of titanium (positively charged), titanium vacancies (negative charge), interstitials of oxygen (negative charge), and oxygen vacancies (positively charged). Therefore, titanium vacancies and oxygen interstitials are the candidates for building up the space charge at electrode *A* for the case of the forward flash current.

Mobility of the negatively charged titanium vacancies and oxygen interstitials may not be an issue in the build-up of the space charge since the diffusion rate is extremely high in the flash plasma.[24] Thus, it is likely the positive potential at *A* will spontaneously draw these negative species toward itself and sequester them within a space charge. When the flash current is turned off, and since the experiment is carried out at room temperature, the space charge would remain in place. Negatively charged space charge will increase the interface resistance while positively charged charge will yield a low interface resistance.

4 | Summary

(i) Single crystals of oxides can be flashed at temperatures and electric fields that are lower than flash in polycrystals and powder pressed samples. The higher conductivity of the crystal makes it easier for them to reach the threshold condition of power density.[4]

(ii) The colossal concentration of oxygen vacancies formed in Stage III form into a new phase that is congruent with the crystal within which it grows. It appears that this phase remains intact because of the free energy barrier for it to disperse into randomly distributed species.

(iii) The presence of this "defect" phase imparts special properties to the single crystal. It enables flash at room temperature. It also enables resistive switching behavior, where the dormant device resistivity is different for current injected in opposite directions.

(iv) We speculate that the resistive behavior may have implications in memristor science.[25] If so then this work provides some insights: that the device resistance is controlled by the nanoscale resistance of interfaces, meaning that the switching behavior is independent of the thickness of the device. Further, we find that the switching behavior can be efficiently and reproducibly pulsed by forward and reverse current (rather than with the electric field).

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