Received: 12 June 2022 | Revised: 5 September 2022 | Accepted: 14 September 2022

DOI: 10.1111/jace.18798

Journal of the American Ceramic Society

RAPID COMMUNICATION

Room temperature flash of single crystal titania: Electronic and optical properties

Devinder Yadav[1] | **Yakun Yuan**[2] | **Venkatraman Gopalan**[2] | **Rishi Raj**[3] | **Seohyeon Jo**[3]

[1]Department of Metallurgical and Materials Engineering, Indian Institute of Technology Patna, Patna, Bihar, India

[2]Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania, USA

[3]Department of Mechanical Engineering, University of Colorado Boulder, Boulder, Colorado, USA

Correspondence
Rishi Raj, Department of Mechanical Engineering, University of Colorado Boulder, Boulder, CO 80309, USA.
Email: rishi.raj@colorado.edu

Present address
Yakun Yuan, Zhangjiang Institute for Advanced Study, Shanghai Jiao Tong University, Shanghai 200240, China.

2nd Revision (JACERS-49669.R2)

Submitted as a Communication to the Journal of American Ceramic Society.

Funding information
Office of Naval Research, Grant/Award Number: N00014-18-1-2270; National Science Foundation, Grant/Award Numbers: DMR 14020620, DMR 2011839

Abstract

A single-crystal specimen of rutile (titania) was flashed repetitively, while increasing the electric field after each cycle. As expected, the flash onset temperature continued to drop modestly at higher fields. However, when the field was increased from 400 to 450 V cm^{-1}, the flashed onset fell dramatically down to room temperature. We have investigated the electrical and optical properties of this room temperature flashed specimen (called SZ). The specimen was electronically conducting. Optical absorption spectroscopy revealed a narrow band of new energy levels that were generated just below the conduction band. The gap between the conduction band and this flash-induced energy level agreed with the peak in the electroluminescence spectrum. Optical second harmonic generation (SHG) is reported. The flash-on condition significantly lowered the SHG, which rebounded when the flash was turned off. This result suggests that the structure becomes more centrosymmetric in the state of flash, which may represent a disordered state of defects. The possibility of studying flash behavior at room temperature, without a furnace (as in SZ type specimens), opens a considerable simplification for in-situ characterization of flash behavior. For example, a possible relationship between memristor physics and the flash phenomenon can be studied.

KEYWORDS
flash sintering, memristors, room temperature, rutile, single crystals

1 | INTRODUCTION

The physics of flash sintering continues to be of significant interest. The phenomenon was first reported in 2010.[1] There have been several excellent reviews of the phenomenology, the mechanisms, and the application of flash to various materials. To our knowledge, the first review was by Dancer in 2016,[2] followed by a very comprehensive review by Yu et al.[3] in 2017, and then another in 2019 by Biesuz and Sglavo.[4] Moreover, Todd[5] has written about a possible relationship between the influence of high-heating-rate-sintering and flash-sintering. Just recently, the time line of the developments in this fledging field was published by Gil-González et al.[6] A recent edition of the MRS Bulletin has been dedicated to field-assisted sintering.[7]

Flash sintering is a young field. Explanations of the underlying mechanisms of flash continue to be overtaken by a steady stream of new results. For example, the simulations of the power density profiles in voltage-to-current experiments based upon thermal runaway brought about by a negative temperature coefficient of resistivity,

published in 2015,[8] are contraindicated by experiments of flash in electronic conductors such as carbon[9] and brand new results on tungsten carbide.[10] Local heating at particle–particle interfaces,[11] and even melting at grain boundaries,[12] is not consistent with experiments with single crystals.[13] Flash sintering in a few seconds usually coincides with a spike in the power density; argument has been made that such transients can produce very high temperatures that can induce rapid sintering. However, current–rate experiments can stretch the sintering time from a few seconds to several minutes by changing the rate of increase of current, with a gradual increase in the specimen temperature[14]; in current–rate experiments, the onset of flash is indicated by a rather broad peak in the voltage, rather than by a spike in the power density.

More commonly, the experiments are carried out in a voltage-to-current mode where the onset of flash is induced by applying an electric field while increasing the furnace temperature at a constant rate. The onset of flash is signaled by an abrupt rise in conductivity, which is harnessed by switching the power supply from voltage-to-current control. The run-up to the flash onset is called Stage I, the transition-to-current control is Stage II, and the steady state of flash that is established under current control is Stage III.[15] Sintering occurs quickly during Stage II.[15] The steady-state nature of Stage III has enabled the characterization of some unique features of flash such as electroluminescence[16]; experiments at X-ray synchrotrons have confirmed the formation of far-from-equilibrium phases[17], and in-flash temperature has been measured against a platinum standard.[18] However, nearly always the structure of Stage III apparently collapses toward the pre-flash state, which makes it difficult to study the flash phenomenon from characterization of post-operandi specimens. Still, the likelihood that some memory of flash is retained remains an intriguing issue.

In this communication, we explore the issue of retained memory in titania single crystals, by repetitive flash of the same specimen at successively higher electric fields. Remarkably we find that when flashed at a high field, the retained structure is such that the specimen can now be flashed at room temperature. This specimen, post flash, is called SZ. It is shown to remain electronically conducting a room temperature. Measurements of optical absorption show the emergence of a band of energy levels just below the conduction band that corresponds to the peak in the electroluminescence spectrum.

We also report on second harmonic generation (SHG) when SZ is cycled between flash-off and flash-on states. We find that SHG, which is present in the flash-off condition, is *greatly diminished* in the flash-on state. SHG is related to the symmetry of the crystal structure. It is present only if the structure does not possess inversion symmetry. The results from this work suggest a fundamental change in the symmetry of the structure instilled by flash; in simple words, it is proposed that the structure becomes disordered upon flash. Our interpretation is that this disorder is related to the generation of defects.

2 | EXPERIMENTS AND RESULTS

2.1 | Flash cycling experiments

The experiments were conducted on single crystals of titania (rutile). Specimens with the (100) orientation were obtained from MSE Supplies (Tucson, AZ, USA). They were cut into rectangular shapes with a gage length of ~4 mm (between the electrodes), a width of 2 mm, and a thickness of about 0.7 mm. Electrical connections were made by wrapping platinum wires (diameter of 0.127 mm) around the rectangular cross section.

The flash experiments were carried out by applying a field and heating thfurnace at a constant rate. The power supply was switched to current control upon the onset of flash. The current limit was set at 40 mA mm^{-2}. Specimens were flashed repetitively over several cycles, starting with a field of 50 V cm^{-1}, and increasing the field in steps, up to 500 cm^{-1}. The results are summarized in Figure 1.

Figure 1A shows the abrupt rise in the power density at the onset of flash, caused by a surge in the current. At this point, the power supply was switched to current control; the high conductivity causes the voltage expressed across the sample to fall abruptly as shown in Figure 1B. These data show the transition temperature falling as the applied electric field is increased for cycles 1–8 up to a field of 400 V cm^{-1}. However, in cycle 9, when the field is increased to 450 V cm^{-1}, the specimen flashes at room temperature—this specimen is called SZ9. The specimen flashes again at room temperature if the experiment is repeated at 450 V cm^{-1}.

We were interested to know whether or not the full nine-cycle routine is necessary to create SZ specimens. Therefore, a fresh sample was flashed for just two cycles, the first below and the second above the threshold field. As shown in Figure 1C, this sample also flashed at room temperature at the higher field. This specimen is called SZ2.

The flash history of SZ9 and SZ2 specimens is shown in Figure 1D. In both instances, there is a dramatic drop to room temperature flash in the 450–500 V cm^{-1} range.

Although we use SZ9 and SZ2 nomenclature to distinguish between samples flashed for nine and two cycles, we have not seen any discernible difference in their

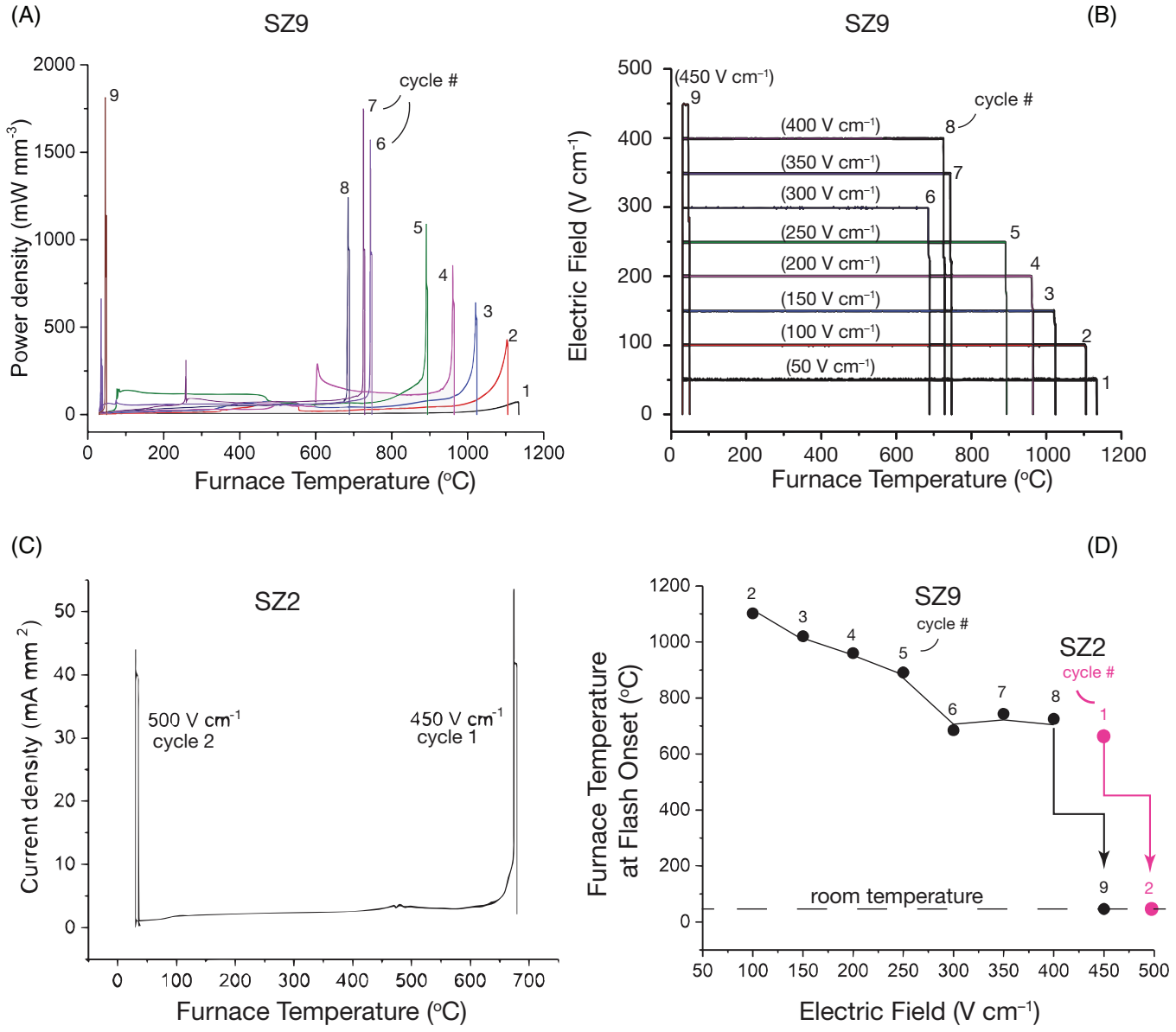

FIGURE 1 (A) and (B) Power density and electric field as a function of the furnace temperature in cycles 1–9; (C) results from two cycles showing the room temperature flash at 500 V cm^{-1}; (D) the change in the flash onset temperature with increasing electric field

properties; for example, both are electronically conducting at room temperature.

2.2 | Electrical conductivity (SZ9)

As shown in Figure 2, the conductivity was measured by the four-point method, where the current is injected through the outer electrodes, whereas the potential difference is measured in open-circuit configuration with the inner electrodes. The very high internal resistance of the voltmeter approximates an open-circuit measurement. As no current is drawn, the interface resistance does not contribute to the voltage measurement.

The DC electrical conductivity of the pristine sample was in the range of several MΩ, and therefore it is not reported. The *I–V* curve for SZ9, measured by the four-point method, at room temperature, shows a small intercept offset along the voltage axis. It is not clear whether this offset arises from interface polarization at the inner electrodes (unlikely in a view of the open-circuit measurement), or it is a consequence of an energy barrier for electron conduction within the bulk. In any event, thereafter, the data show a good linear *I–V* fit with an absolute resistance of 500 Ω and a specific conductivity of 9 S m^{-1}. This value is comparable to the in-flash immersion-and-quench experiment in liquid nitrogen from nominal flash experiments with yttria-stabilized zirconia.[7]

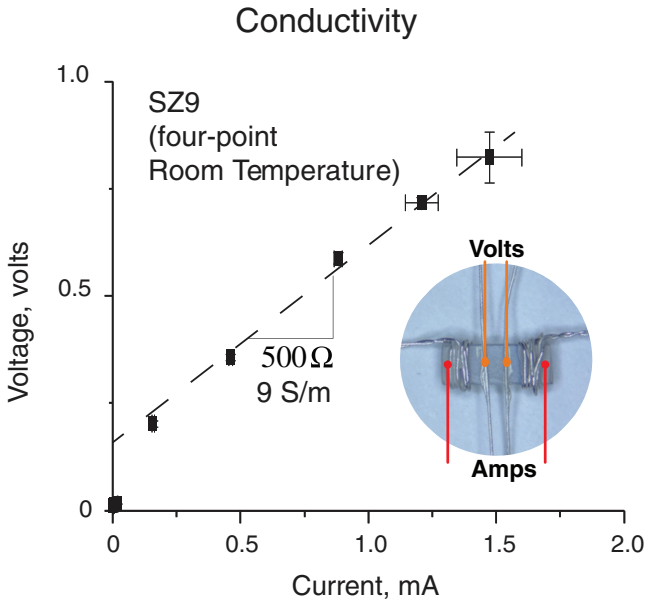

FIGURE 2 Four-point measurement of electrical conductivity in SZ9 shows the ohmic behavior. The slight offset near the origin remains unexplained.

2.3 | Optical properties (SZ2)

The opportunity to create a sample that can be flashed at room temperature (in open atmosphere without a furnace) facilitates the characterization of the flash event. Here we report two kinds of optical measurements: electroluminescence and the influence of flash on SHG. The experiments were carried out on SZ2 specimens.

The intensity of electroluminescence was measured with an Ocean Optics USB4000 fiber optic spectrometer (Dunedin, FL). The spectrometer was capable of measuring wavelengths in the range of 200–900 nm. The response time of the spectrometer was 10 μs. An integration time of 500 ms was used. The distance between the sample and the collimating lens was 140 mm. The area of the sample exposed to the spectrometer for electroluminescence measurement was 8 mm^2.

Flash was initiated at 450 V cm^{-1}, and the intensity was measured while the current density was increased in steps of 10 mA mm^{-2}, up to 140 mA mm^{-2}. At each step, the specimen was held at constant current for 10 s while the optical emission spectrum was recorded. The results in Figure 3A show the increase in the intensity of luminescence as the current injected into the specimen was increased. The optical spectrum shows a peak in the 750–850 nm region.

As the single-crystal specimens were visually transparent, they were used to measure the optical absorption spectrum. The difference between the absorption spectrum of the flashed-minus-the-pristine sample is given in Figure 3B. The peak in the absorption spectrum correlates well with the peak in the luminescence.

The simplicity of the room temperature flash experiment enabled us to measure the influence of flash on second harmonic generation (SHG). The process converts incoming photons at frequency ω into photons at frequency 2ω.[19] SHG in oxides arises fundamentally from broken inversion symmetry either within a unit cell or at interfaces and surfaces.[20,21] A polar order can break inversion symmetry, for example, in the bulk crystal structure of a ferroelectric. Similarly, electric fields, either applied or intrinsic, can break the inversion symmetry. Even without an electric field, some degree of polarization can remain, giving rise to weak SHG.[22] Therefore, most oxides exhibit some degree of SHG. In our case, rutile TiO_2 has a centrosymmetric point group of 4/*mmm*, and therefore, SHG is forbidden from the bulk structure; nonetheless, we do measure some SHG, which is likely due to defect dipoles formed by cation and anion vacancies and interstitials; this is not uncommon, for example, $SrTiO_3$ single crystal is centrosymmetric, but small amounts of oxygen vacancies can result in local polar order and an SHG signal.[23] Defect dipoles are also formed in the classic ferroelectrics.[24]

The SHG data were recorded in reflection mode with a wavelength of 800 nm. The 800 nm (~1.545 eV) wavelength output from a Ti:sapphire oscillator laser system (Spectra-Physics, Mai Tai, 80 MHz, 100 fs) was used as the fundamental beam. The reflection SHG setup was based on a modified WITec microscope system, where the fundamental beam was focused onto the sample by a 50× objective (N.A. ~0.75) under normal incidence geometry. The reflected SHG signal at 400 nm (3.09 eV) was collected by the same objective, then filtered by a 400 nm notch filter, and detected by a photomultiplier tube (Hamamatsu H7826). The electric signal from the photomultiplier tube was recorded using the Lock-in method (Stanford Research, SR830) with a mechanical chopping frequency of ~1.2 kHz on the fundamental 800 nm beam; this detection method was checked to ensure that there was no spurious signal at 400 nm purely from flashing in the absence of the incoming 800 nm laser.

Optical SHG measurements were carried out in situ on SZ2, which could be flashed at room temperature at a field of 500 V cm^{-1}, and with a very low current limit of 0.9 mA mm^{-2} in order to avoid spurious signal from electroluminescence (as seen in Figure 3A, the intensity of electroluminescence is negligible at this current limit).

Remarkably, as seen in Figure 4, the SHG signal is lower in the flash-on state; it rebounds when the flash is turned off. Two possible explanations are offered: (i) that the sample, when in flash, absorbs light more strongly at 400 (3.09 eV) and 800 nm (1.545 eV), and (ii) that the defects that give rise to SHG in the off-state become

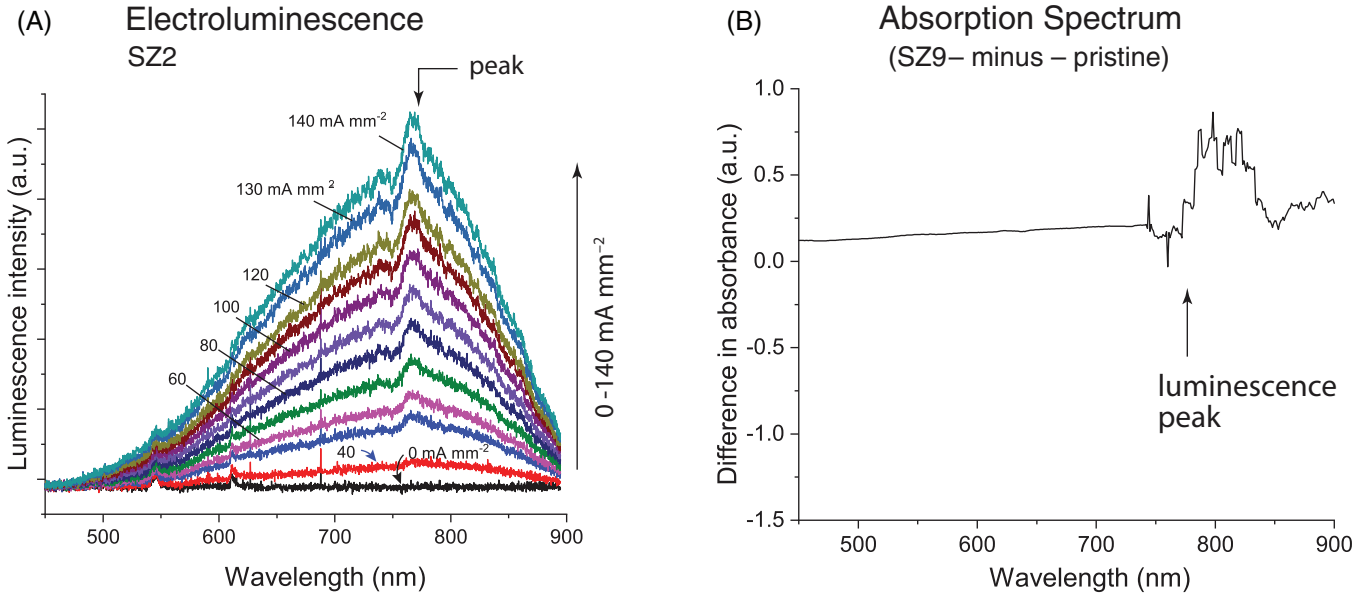

FIGURE 3 Results from reflash of SZ at room temperature with a field of 450 V cm^{-1}: (A) the intensity of luminescence increases when the current; (B) the absorption spectrum showing the new level in the 750–850 nm regime, which is consistent with the peak in the electroluminescence emission

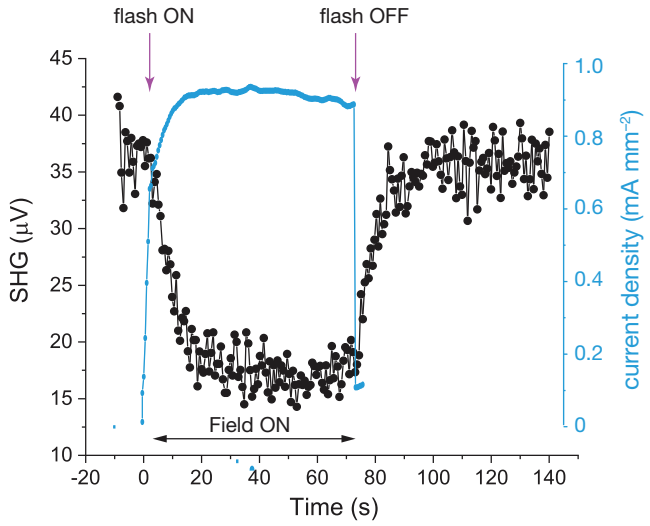

FIGURE 4 A rather unexpected result showing the loss of second harmonic generation (SHG) in SZ2 when the flash is turned off

disordered in the on-state causing the crystal to become increasingly centrosymmetric.

With regard to the suggestion (i), the absorption spectra showed that absorbance change is negligible at 3.09 eV but significant at near 1.5 eV. However, these measurements were taken at room temperature; hence, they correspond to the flash-off condition. Assuming that similar absorbance remains when the flash is turned on, then the first explanation does not satisfy. Furthermore, the SHG measurement was done in reflection, and thus, changes in absorbance should have a smaller effect on the SHG reflectivity.

The second explanation is related to the change in the defect configurations at the onset of flash. In the view of the low current limit, it can be stated that the flash-on condition did not include the vast generation of additional defects. Rather we would conclude the onset of flash (in the very low current limit) simply affects the ordering of the existing defects; the implication being that they become more disordered thereby reducing the SHG signal. However, more rigorous quantification of the absorbance is required in future studies to further clarify these explanations.

It is worthwhile to note that recent work on the induction of flash in free floating specimens, induced by the superposition of magnetic fields,[25] has suggested that the state of flash may be akin to a solid-state plasma, which can be expected to be centrosymmetric.

3 | SUMMARY

In nominal flash experiments, the structure that develops in the active state is usually lost when the flash is turned off. However, here we show that if the onset of flash is instigated by a high field, above a threshold, then the structure can be retained even when the flash is turned off. Thus, single crystals of rutile titania become electronically conducting after being flashed in this way. We report on the electrical and optical properties of the SZ specimen at

ambient temperature. These specimens now can be flashed at room temperature without a furnace. The changes in the SHG in on–off flash experiments with SZ are reported. The transition from the off- to the on-state lowers the SHG signal, which may be attributed to a change in the absorbance of the fundamental beam, or to a change in the symmetry of defects precipitated by the onset of flash.

In summary, the present results are a new development in the science of flash. The possible overlap with memristor physics is interesting. It has not escaped us that like flash,[28] a memristor function is obtained with many if not all oxides.[29,30]

The origin of electronic conductivity in flash experiments remains to be understood. It has been suggested that it is triggered at the cathode and then propagates through the specimen[26,27]; however, this is not consistent with general experience. For example, in our work, we have seen that flash can originate at either the cathode or the anode, and sometimes in the center of the specimen. As shown in this movie,[31] from early work in our laboratory by John Francis, flash is seen to form bright spots in the middle portion of the specimen.

ACKNOWLEDGMENTS

We are grateful to the Office of Naval Research for supporting this research under the grant no. N00014-18-1-2270. We thank Dr. Antti Makinen for his guidance and interest in this project. Y.Y. and V.G. acknowledge support from the National Science Foundation Grant nos. DMR 14020620 and DMR 2011839.

ORCID

Rishi Raj https://orcid.org/0000-0001-8556-9797

REFERENCES

1. Cologna M, Rashkova B, Raj R. Flash sintering of nanograin zirconia in <5 s at 850°C. J Am Ceram Soc. 2010;93(11):3556–9.
2. Dancer CEJ. Flash sintering of ceramic materials. Mater Res Express. 2016;3(10):102001. https://doi.org/10.1088/2053-1591/3/10/102001
3. 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. https://doi.org/10.1080/17436753.2016.1251051
4. Biesuz M, Sglavo VM. Flash sintering of ceramics. J Eur Ceram Soc. 2019;39(2):115–43. https://doi.org/10.1016/j.jeurceramsoc.2018.08.048
5. Todd RI. Flash sintering of ceramics: a short review. In: Lee B, Gadow R, Mitic V, editors. Proceedings of the IV advanced ceramics and applications conference. Paris: Atlantis Press; 2017. p. 1–12. https://doi.org/10.2991/978-94-6239-213-7_1
6. Gil-González E, Pérez-Maqueda LA, Sánchez-Jiménez PE, Perejón A. Flash sintering research perspective: a bibliometric analysis. Materials. 2022;15(2):416. https://doi.org/10.3390/ma15020416
7. 6 papers. Synthesis and processing under electric/electromagnetic fields. MRS Bull. 2021;46(1).
8. Todd RI, Zapata-Solvas E, Bonilla RS, Sneddon T, Wilshaw PR. Electrical characteristics of flash sintering: thermal runaway of Joule heating. J Eur Ceram Soc. 2015;35(6):1865–77. https://doi.org/10.1016/j.jeurceramsoc.2014.12.022
9. Ingraci Neto RR, Raj R. The flash effect in electronic conductors: the case of amorphous carbon fibers. Scr Mater. 2020;179:20–4. https://doi.org/10.1016/j.scriptamat.2020.01.003
10. Mazo I, Molinari A, Sglavo VM. Electrical resistance flash sintering of tungsten carbide. Mater Des. 2022;213:110330. https://doi.org/10.1016/j.matdes.2021.110330
11. Muccillo R, Muccillo ENS. An experimental setup for shrinkage evaluation during electric field-assisted flash sintering: application to yttria-stabilized zirconia. J Eur Ceram Soc. 2013;33(3):515–20. https://doi.org/10.1016/j.jeurceramsoc.2012.09.020
12. Chaim R. On the kinetics of liquid-assisted densification during flash sintering of ceramic nanoparticles. Scr Mater. 2019;158:88–90. https://doi.org/10.1016/j.scriptamat.2018.08.029
13. Yadav D, Raj R. The onset of the flash transition in single crystals of cubic zirconia as a function of electric field and temperature. Scr Mater. 2017;134:123–7. https://doi.org/10.1016/j.scriptamat.2017.02.015
14. Kumar MKP, Yadav D, Lebrun J-M, Raj R. Flash sintering with current rate: a different approach. J Am Ceram Soc. 2019;102(2):823–35. https://doi.org/10.1111/jace.16037
15. Francis JSC, Raj R. Influence of the field and the current limit on flash sintering at isothermal furnace temperatures. J Am Ceram Soc. 2013;96(9):2754–8. https://doi.org/10.1111/jace.12472
16. Lebrun J-M, Raj R. A first report of photoemission in experiments related to flash sintering. J Am Ceram Soc. 2014;97(8):2427–30. https://doi.org/10.1111/jace.13130
17. Lebrun J-M, Morrissey TG, Francis JS, Seymour KC, Kriven WM, Raj R. Emergence and extinction of a new phase during on–off experiments related to flash sintering of 3YSZ. J Am Ceram Soc. 2015;98(5):1493–7.
18. Terauds K, Lebrun J-M, Lee H-H, Jeon T-Y, Lee S-H, Je JH, et al. Electroluminescence and the measurement of temperature during Stage III of flash sintering experiments. J Eur Ceram Soc. 2015;35(11):3195–9. https://doi.org/10.1016/j.jeurceramsoc.2015.03.040
19. Denev SA, Lummen TTA, Barnes E, Kumar A, Gopalan V. Probing ferroelectrics using optical second harmonic generation. J Am Ceram Soc. 2011;94(9):2699–727. https://doi.org/10.1111/j.1551-2916.2011.04740.x
20. Pauling L. The chemical bond: a brief introduction to modern structural chemisty. Cornell University Press; 1967.
21. Bloembergen N, Chang RK, Jha SS, Lee CH. Optical second-harmonic generation in reflection from media with inversion symmetry. Phys Rev. 1968;174(3):813–22. https://doi.org/10.1103/PhysRev.174.813
22. Terhune RW, Maker PD, Savage CM. Optical harmonic generation in calcite. Phys Rev Lett. 1962;8(10):404–6. https://doi.org/10.1103/PhysRevLett.8.404
23. Jang HW, Kumar A, Demev S, Biegalski MD, Maksymovych P, Bark CW, et al. Ferroelectricity in strain-free $SrTiO_3$ thin films. Phys Rev Lett. 2010;104:197601.

24. Gopalan V, Dierolf V, Scrymgeour DA. Defect–domain wall interactions in trigonal ferroelectrics. Annu Rev Mater Res. 2007;37(1):449–89. https://doi.org/10.1146/annurev.matsci.37.052506.084247
25. Jalali SIA, Raj R. Touch-free flash sintering with magnetic induction within a reactor activated by the usual flash method. J Am Ceram Soc. in press. 2022;105:6517–22.
26. Mishra TP, Neto RRI, Speranza G, Quaranta A, Sglavo VM, Raj R, et al. Electronic conductivity in gadolinium doped ceria under direct current as a trigger for flash sintering. Scr Mater. 2020;179:55–60. https://doi.org/10.1016/j.scriptamat.2020.01.007
27. Biesuz M, Pinter L, Saunders T, Reece M, Binner J, Sglavo VM, et al. Investigation of electrochemical, optical and thermal effects during flash sintering of 8YSZ. Materials. 2018;11(7):1214. https://doi.org/10.3390/ma11071214
28. Dong Y, Chen I-W. Onset criterion for flash sintering. J Am Ceram Soc. 2015;98(12):3624–7. https://doi.org/10.1111/jace.13866
29. Jung S, Kong J, Song S, Lee K, Lee T, Hwang H, et al. Resistive switching characteristics of solution-processed transparent TiO_x for nonvolatile memory application. J Electrochem Soc. 2010;157(11):H1042. https://doi.org/10.1149/1.3489370
30. Raj R. Analysis of the power density at the onset of flash sintering. J Am Ceram Soc. 2016;99(10):3226–32. https://doi.org/10.1111/jace.14178
31. Francis JC. A small flash movie; https://www.youtube.com/watch?v=HvOfoyhu2aE

How to cite this article: Yadav D, Yuan Y, Gopalan V, Raj R, Jo S. Room temperature flash of single crystal titania: Electronic and optical properties. J Am Ceram Soc. 2023;106:46–52. https://doi.org/10.1111/jace.18798