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Correlations between conductivity, electroluminescence and flash sintering

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ABSTRACT

Flash experiments with single phase $SrTiO_3$, and two-phase composites of $SrTiO_3$ containing 2.5–20 vol% of $KNbO_3$, reveal remarkably different outcomes. While all compositions show the classical signature of the flash, that is, a sudden increase in conductivity, and electroluminescence, only the pure $SrTiO_3$ specimen sinters fully. The composites show only some densification. The results are interpreted in terms of the nature of the interphase grain boundaries, which are expected to be "metallic". They further lead to an understanding of whether flash sintering originates primarily at grain boundaries or within the grain matrix.

Flash sintering was discovered in a quest to understand the role of electric fields in spark-plasma-sintering [1]. Simple experiments were devised: the electric field was applied directly to the specimen with a pair of electrodes, which was placed within a conventional furnace. The current flowing through the specimen, and the voltage expressed across it, were measured. Experiments with yttria stabilized zirconia revealed that although sintering was significantly enhanced at low applied fields, it occurred abruptly, as if in a flash, when the field was increased above a threshold value [1].

These first experiments were carried out at constant heating rate. In the present work the furnace was held at a constant temperature and the field applied as a step function. After an incubation time the current rises abruptly indicating the onset of the flash [2]. The current flow through the specimen is then limited by switching the power supply from voltage to current control.

The flash is accompanied by electroluminescence in the visible range. These spectra are not consistent with black body radiation [3].

One key question in flash sintering is whether the flash effect is exclusively a "grain boundary effect" [4], or whether it is a grain matrix effect. The present work was motivated by reports in the literature that interfaces between a non-polar ceramic, like $SrTiO_3$ (ST), and a polar ceramic, like $KNbO_3$ (KN), have metallic character [5,6]. Thus, flash experiments with these composites, where the grain boundaries are expected to have metal-like behavior were expected to provide insights into the role of interfaces in the flash effect.

Experiments were carried out with powders of $SrTiO_3$ (99.99% purity), and $KNbO_3$ (99.99% purity) obtained from Alfa Aesar. The ST powders had a particle size of 50–150 nm. The KN-ST composites were made by ball milling the powder mixtures in ethanol using zirconia balls, for 1 h. The powder-slurry was strained and dried overnight at 80 °C. A binder (Duramax B-1000) — 3 vol.% in ethanol, was mixed in with powder, and dried overnight at 80 °C. The dried powder was pulverized with mortar and pestle. Micrographs of the powder of KN-ST prepared in this way, and the as received powder of for ST are shown in Fig. 1. Note that the ST powder is agglomerated. The ST powder was cold pressed into specimens without using the binder.

The physical details of the experimental setup are described in [7]. Dog bone specimens with a gage length of 20 mm and a cross-section of ~1 mm × 3.2 mm were pressed under a pressure of ~200 MPa. The relative green density of the specimens was measured geometrically. The values were 55% for ST, 56% for ST-2.5 vol% KN, 57% for ST-5 vol% KN, 57% for ST-10 vol% KN, and 58% for ST-20 vol% KN.

The specimens were suspended into a furnace, held at 800 °C, with platinum wires. The voltage was applied as a step function. The DC electric field was 600 V cm^{-1}, and the current limit was set at 12 mA mm^{-2}. Flash was signaled by a non-linear rise in conductivity that was followed by a constant state of flash under current control. The shrinkage along the length, and across the width of the specimen, was measured from photographs taken sequentially in time, as described in earlier papers [1,7].

Results from five compositions are reported. They are single phase ST, and four mixed compositions: ST-2.5 vol% KN, ST-5 vol% KN, ST-10 vol% KN, and ST-20 vol% KN. The plots for power dissipation from

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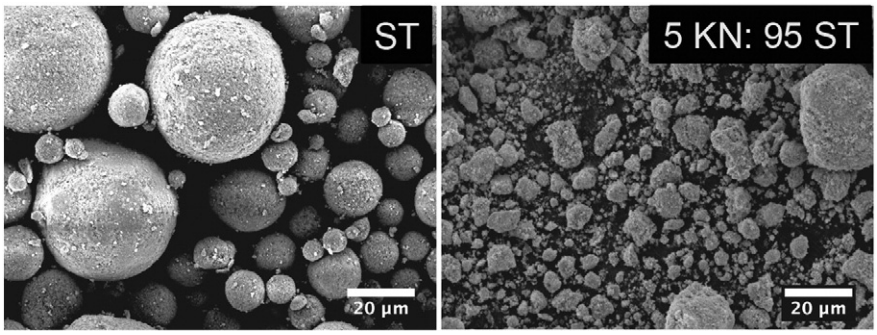

Fig. 1. SEM micrographs of powders of ST (agglomerated) and 5 vol% KN in ST, after milling for 1 h. The powder was used as shown to press dog-bones for sintering experiments.

the start to the end of the test are shown in Fig. 2. Plots of longitudinal and transverse shrinkage are shown in Fig. 3.

The power dissipation plots, in Fig. 2, show the classical behavior where the onset of the flash is signaled by a steep rise in the conductivity after an incubation time [2,8]. Note that the flash initiates more easily in the composites, with a much shorter incubation time than for pure ST. Remarkably the incubation times for all composites are the same even though the compositions range widely from ST-2.5 vol% KN to ST-20 vol% KN.

The peak in the power density in Fig. 2, which separates voltage control from current control, is necessarily equal to the product of the field and the current limit, since $P_W = EJ$ where E is the field and J is the current density. Under voltage control the specific conductivity, σ, is related to the power density by $\sigma = P_W/E^2$. Thus the curves for P_W before the power peak, when the applied field is constant, also represent the change in conductivity. Under current control $\sigma = J^2/P_W$; the values of conductivity determined from this equation by inserting the measured values of P_W are given in Table 1. Why the conductivity should have these particular values during the steady state of flash remains an open question.

During the steady state, P_W can be translated into fairly reliable values for the specimen temperature from a black body radiation model [9]. The model, setting the emissivity equal to 0.9, gives estimates of the specimen temperature which are quoted in Table 1. The temperature estimate varies by ± 50 °C. Note that the sample finds its own equilibrium temperature under current control (if the temperature were to increase then the resistance would decrease and so would power dissipation causing the specimen to cool; if the temperature cools too far then the resistance would increase and so would the power dissipation which would restore the steady state temperature).

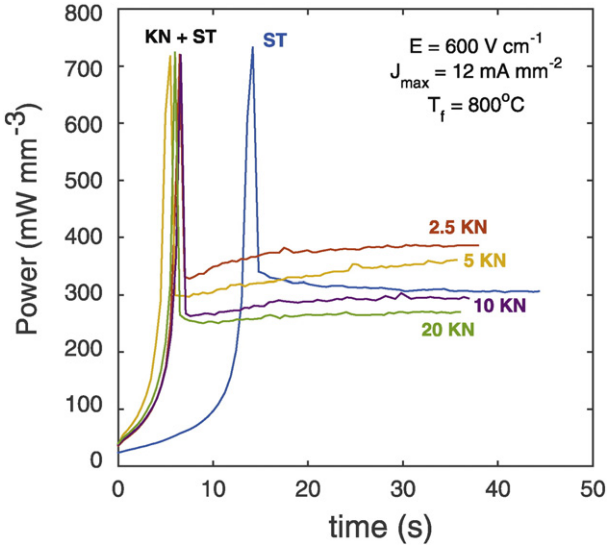

Fig. 2. Power density curves for the five specimens. Even small additions of KN to ST, just 2.5 vol%, has a significant influence on the incubation time, which then remain constant for high volume fractions of KN.

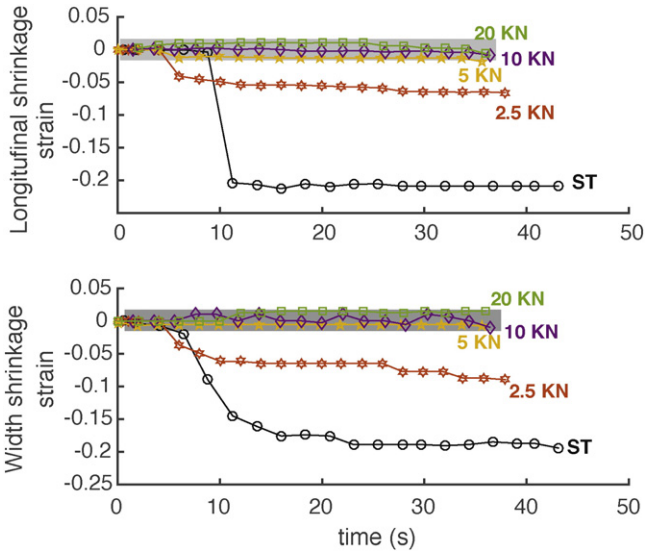

Fig. 3. Shrinkage in longitudinal and transverse directions during of ST and the KN-ST composites. While ST sinters to full density, only the 2.5 vol% KN specimen sinters to some extent, and high volume fractions not at all. Compared with the power density curves in Fig. 2 to note the sintering occurs close to the power peak during the transition from voltage to current control.

It is well recognized that nearly all sintering occurs during the transition from voltage to current control, that is near the peak in the power density [2]. Still, as shown in Fig. 3, despite the power density peak being similar for all five compositions the extent of densification achieved during the flash varies. While ST sinters to nearly full density, the 5-KN to 20-KN specimens show little sintering, while the 2.5-KN sample sinters half way. Interestingly these differences are similarly reflected in the intensity of the electroluminescence spectra, shown in Fig. 4. The higher KN compositions have low intensities, while ST, which sinters fully, emits high intensity electroluminescence. The 2.5-KN sample, which sinters partly, emits with intermediate intensities. (All data were obtained with the spectrometer placed at the same distance from the sample so the data give the relative intensities of the intrinsic emissions.)

The starting point in this work was to explore whether metallic interfaces can instigate the flash effect. The premise was that composites made of polar and non-polar oxides, which are known to develop metallic interfaces, would flash more readily.[1] The results presented in Fig. 2 are consistent with this hypothesis.

[1] We have published a model for the incubation time for flash sintering where embryos with a polar character nucleate within a non-polar matrix. The model assumes that the metallic interfaces that would form between the embryo and the matrix were expected to nucleate the flash [8].

Table 1
Summary of flash behavior of the five samples.

600 V cm^{-1}, 12 mA mm^{-2} and furnace temperature, 800 °C				
KN: ST (by vol)	Incubation time (s)	Sample temperature (°C)	Stage III power ($mW\ mm^{-3}$)	Specific conductivity $(Ohm\ cm)^{-1}$
0: 100	11.245	1126	313	4.6E−03
2.5: 97.5	4.0549	1175	372	3.9E−03
5: 95	2.9459	1133	333	4.3E−03
10: 90	4.0795	1114	287	5.0E−03
20: 80	3.5186	1098	263	5.5E−03

The surprising result is that although the KN-ST composites flashed more easily they showed less densification than $SrTiO_3$, implying that the local effect at grain boundaries generated fewer defects, overall, than were produced in single phase ST.

The interpretation of the role of metallic interfaces on flash behavior rests partly on whether or not they form a contiguous network thereby creating a continuous path for the current to flow through the polycrystal. It is difficult to imagine how 2.5 vol% of KN could have produced a contiguous network of metallic interfaces.

The mechanism by which the metallic interfaces instigate the flash must therefore consider isolated slivers of two-dimensional metal sheets distributed here and there in the polycrystal. In this instance the metal sheets form equipotentials (they do not have current flowing through them), with a sharp change in the electrical field due to the dielectric singularity at the edge of the metal sheets. Perhaps these fields are large enough to ionize charged vacancies and interstitials into charge neutral point defects and electron and holes, by the Poole-Frenkel mechanism [10]. The vacancies and interstitials, which are now charge neutral, may now travel independently, the vacancy being drawn to grain boundaries and the interstitials into the pores, driven by sintering pressure, effectively transporting mass from the grain boundaries into the pores to produce densification [11]. Meanwhile the electron–hole pairs can recombine and emit photons.

There remains the question of why metallic interfaces, which induce the flash, fail to produce as much densification as in the case of single phase ST. One possible explanation is that the intensity of defect generation in the composites, which is confined to interfaces, is not enough to produce significant sintering. On the other hand in ST, which does not have such interfaces, the overall defect concentration is higher because they are generated within the entire volume of the polycrystal. A similar inference was reached in the study of constrained sintering under electric fields [12]. Constrained sintering occurs during co-sintering of two different ceramic materials where one sinters at a much slower rate than the other. The constraint gives rise to shear stresses, and sintering may proceed only if this incompatibility can be relaxed by shear deformation. In conventional sintering mass is transported from the grain boundary to the pore, while shear or diffusional creep requires transport between grain boundaries. The latter entails twice the diffusion distance required in sintering, which gives rise to the constrained sintering effect. In flash sintering, if the defects are generated within the matrix [11], then the diffusion distance for sintering and shear deformation becomes the same, and constrained sintering becomes moot.

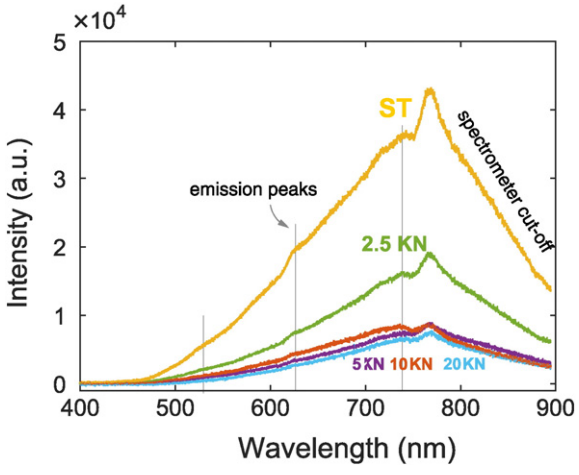

Fig. 4. Electroluminescence spectra in the visible regime. Note the correlation between sintering (Fig. 3) and the intensity of the luminescence.

The review of this manuscript has suggested that 2D metal layers at interfaces are suppressing defect generation since the KN-ST ceramics sinter less than single phase ST. It is important to recognize that the incidence of the flash, and sintering, are not necessarily correlated. This letter addresses two separate issues: the question of whether metallic interfaces can indeed instigate the flash, and next whether or not this mode of flash affects the sintering behavior.

To the first point, the data in Fig. 2 shows that the non-linearity occurs with much shorter incubation time in all composites, even when the volume fraction of the KN phase is merely 2.5%. The first premise of this study, that metallic interfaces promote the onset of the flash, is therefore validated. Furthermore, all specimens are accompanied by electroluminescence, Fig. 4, even though the intensity depends on the composition. Any expression of electroluminescence means that defects are being generated.

A comparison of Fig. 2 and Fig. 3 shows that the onset of flash is not necessarily accompanied by full sintering. The disconnect between flash and sintering is open to discussion. The present explanation is based upon our earlier work on constrained sintering, which was successfully explained by defect generation being a grain matrix effect [12]. Thus, we hypothesize that defect generation, which, in the present experiments is pre-empted by metallic interfaces, is not copious enough to produce massive sintering, since the fraction of the material volume associated with the boundaries is only a small fraction of the total volume of the specimen.

We return to ask how metallic interfaces can promote the flash. In the case of 2.5 vol% KN, it is almost certain that the interphase grain boundaries are isolated from one another. Floating two-dimensional metal-slivers become regions of equipotential, that is, they themselves cannot have current flowing through them. These 2D metal patches, however, will experience a dielectric singularity at their edges, thereby creating very a high concentration of the electric field, which may indeed be large enough to separate charged defects into electrons and holes and charge neutral point defects [10]. We are anticipating more information about defect generation from *in-situ* experiments at synchrotrons in the coming future.

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