

Reactive flash sintering of powders of four constituents into a single phase of a complex oxide in a few seconds below 700°C

Viviana Avila  | Rishi Raj 

Materials Science and Engineering Program, Department of Mechanical Engineering, University of Colorado Boulder, Boulder, Colorado

Correspondence

Rishi Raj, Materials Science and Engineering Program, Department of Mechanical Engineering, University of Colorado Boulder, Boulder, CO.
Email: rishi.raj@colorado.edu

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Abstract

Recent work on reactive flash sintering of powders of two oxides, bismuth and iron oxide, into pure single phase bismuth ferrite, which was accomplished in a few seconds at low furnace temperatures, is expanded to four constituents, alumina, lithia, zirconia, and lanthana, to produce reasonably dense polycrystals of a predominantly single phase, cubic LLZO(Al). Transformation and sintering occur concurrently at a furnace temperature near 700°C, in ambient atmosphere, in just a few seconds. The process may simplify the preparation of complex ceramics with new chemistries and dopants, which are predicted from *ab initio* calculations to have special attributes, not only because the powders sinter quickly at low temperatures, but also because the need for stoichiometric powders as starting materials is obviated.

KEYWORDS

complex oxides, elemental oxides, reactive flash sintering, sintering, solid state lithium ion batteries

1 | INTRODUCTION

Conventional sintering starts with a powder, of stoichiometric composition, which is mechanically pressed into specimens and then heated to high temperatures. Solid-state diffusion transports mass from grain boundaries to fill the adjacent pores, producing dense, and strong structures. Mass transport requires chemical diffusion, that is, the elements must be transported stoichiometrically. Sintering time and temperature are, therefore, determined by the migration rate of the slowest diffusing species. If the composition contains low melting, fast diffusing, or volatile species then it becomes difficult to maintain compositional and phase fidelity since the sintering temperatures can be too high and the sintering duration too long.

Sintering of bismuth ferrite is one such example. Low melting bismuth, and myriad phases that form below the sintering temperature makes it difficult to obtain phase pure ceramic with good electrical properties.¹ Flash sintering has been shown to be an enabling method for making phase pure bismuth ferrite in a few seconds at low furnace temperatures, in ambient air.² Furthermore it has been shown that mixtures

of elemental powders of bismuth oxide and iron oxide can be transformed into dense single phase polycrystals, also in a few seconds, which we call *reactive* flash sintering (RFS).³ Similarly mixtures of alumina and magnesia have been shown to form single phase spinel⁴; in situ experiments have shown that in this case, phase transformation is completed a little sooner than sintering.⁵

In the present work, reactive flash sintering is expanded to LLZO(Al) which is constituted from oxides of Li, La, Zr, and Al. The elemental oxides are shown to transform, and sinter, into the cubic phase with a reasonable value of Li⁺ conductivity at room temperature. This compound is projected to be used as solid state electrolytes, with Li-metal as the anode, with the promise of safe, long lasting, and high energy density lithium ion batteries.^{6,7}

Conventional sintering of LLZO(Al) is controlled by the diffusion of La or Zr which are slow diffusing species requiring time and temperature where Li can diffuse outwards, oxidize and volatilize. More complex processes such as hot-pressing⁸ and spark plasma sintering⁹ are necessary to prevent the loss of Li. Flash sintering with short processing time at low temperatures may help to overcome such issues.

The main topic of this article, reactive flash sintering (RFS), is shown to further simplify the processing of single phase complex ceramics, such as LLZO(Al), as illustrated in Figure 1. Conventional sintering of complex ceramics is a two-step process. First powders of the target composition are made by a combination of solid-state reactions, chemical synthesis, and calcination processes.¹⁰ Next, these powders are sintered at high temperatures typically for several hours, sometimes using hot-pressing and spark plasma sintering. In RFS powders of the constituent oxides can be directly sintered and transformed into the stoichiometric single phase of the complex chemistry in mere seconds at low furnace temperatures. Phase transformation and sintering occur concurrently.

As a precursor to the present work, we experimented and were successful with RFS of undoped tetragonal LLZO. The tetragonal phase has a lower ionic conductivity than the alumina doped cubic phase; therefore, this work was not pursued further. These results are available on request.

2 | EXPERIMENTAL METHODS AND RESULTS

2.1 | Materials

Commercially available powders of oxides were used. Lithium oxide, Li_2O (97%) and zirconium oxide, ZrO_2 (99%), were purchased from Sigma Aldrich, and lanthanum oxide, La_2O_3 (99.9%) from Alfa Aesar. Manufacturer prescribed particle sizes were 250 μm , 5 μm , and 10 μm , respectively. Aluminum oxide, Al_2O_3 (99.99%), was purchased from Sumitomo Chemical; it had a particle size of 0.2 μm . However, as shown

later on, the actual particle size, as seen in SEM micrographs were smaller; especially for Li_2O , which was heavily agglomerated. It appears that the values given by the vendors referred to these agglomerates. The structure of the powders was checked by X-ray diffraction. In this way, we confirmed that the starting powder was lithium-oxide and not lithium-carbonate.

Powders of lithia, alumina, lanthana, and zirconia were then mixed to according to the composition $\text{Li}_{5.95}\text{Al}_{0.35}\text{La}_3\text{Zr}_2\text{O}_{12}$. The powders were mixed by hand in a glove-box, sealed under Ar in a plastic bottle with yttrium-stabilized zirconia balls, and taken to a low-energy vibrator machine for one hour to ensure uniform mixing. The particle size distribution of this mixture as seen in an SEM is shown by micrographs later in this article.

The mixture of oxides was then taken out of the Ar atmosphere to be pressed into dog-bone shapes for flash sintering, as described below.

2.2 | Reactive flash sintering

The flash phenomenon is initiated by applying an electric field at elevated temperature. A specific combination of these two parameters instigates the flash which is signaled by an abrupt rise in electrical conductivity.¹¹ In order to prevent thermal runaway from Joule heating, the power supply connected to the specimen is switched to current control.¹² The specimens can be held under current control in an active state of flash. Thus, the process occurs in three stages, the first is the incubation stage just before the onset of the flash, the second is the transition from voltage to current control, and Stage III is steady state of flash held under current control. Sintering and phase transformation occur during Stage II in just a few seconds.¹³ Interestingly, while the onset of flash depends on the combination of electric field and temperature, the extent of densification (and apparently phase transformation) is related to the current density limit placed at the power supply.¹³ At low current density only partial densification is achieved (surprisingly, further densification does not continue during Stage III even though the specimen remains in a state of flash¹³). The fundamental mechanism for this behavior is not understood. Nevertheless, the phenomenological evidence is supported by work on several ceramics.¹⁴ In this way, the phenomenology provides guidance for the application of electrical field and current at the power supply for optimum outcomes.

Since the extent of sintering is related to the current density, the uniformity of sintered microstructure is closely related to the uniformity of current flow. The localization of current is therefore of concern in the practice of flash sintering. The tendency for current localization varies from one material to another. Therefore, at the basic level, we use dog-bone specimens for our experiments. The metal electrodes are attached to the ears with a metal paste, usually platinum or silver. The shape of the specimen helps to

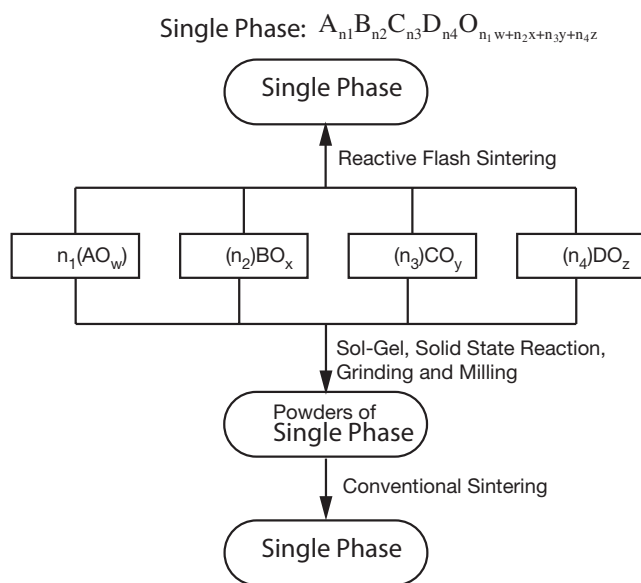


FIGURE 1 The difference between Flash Sintering and conventional sintering. This distinction is of significance in the manufacturing of ceramics with complex chemistries

channel the current uniformly through the gage section.¹⁵ The gage section in the present experiments was 15 mm long, with a width of 3.5 mm, and a thickness of ~1 mm. The powder is pressed into a die of these dimensions. The thickness can vary somewhat depending on the amount of powder placed into the die.

In the present experiment, the dog-bone specimens were made from the mixed powders as described previously. The powder was then taken out of the Ar atmosphere to be pressed into the dog-bone shapes within the die in ambient atmosphere. The specimens had a green density between 50% and 55%.

The flash experiments can be carried out in two ways: (a) where the field is applied and furnace is heated at a constant rate until the onset of flash,¹¹ and (b) where the furnace is held at a constant temperature and the voltage is applied as a step function.¹³ Usually the constant heating rate experiments are useful to identify the parametric combination of field and temperature for the onset of flash.

The reactive flash was performed in a vertical tubular furnace. The specimens were hung into the furnace with two platinum wires. Since platinum was discovered to react with lithium, a second pair of thin nickel wires were attached to the platinum wires and then to the specimen. The nickel wire was wrapped around the ears of the dog-bone specimens, and silver paste was applied to achieve good electrical contact. The electrical field and/or current to the specimen was applied using a 3000W DC power supply (Glassman High Voltage, Inc., Whitehouse Station, NJ) and the current recorded with a Keithley multimeter model 2000 (Keithley Instruments, Cleveland, OH).

In the present work, the materials made by the isothermal experiments did not yield single phase specimens. The constant heating rate ($10^{\circ}\text{C min}^{-1}$) experiments were attempted with applied fields of 30 V cm^{-1} , 40 V cm^{-1} , and 50 V cm^{-1} . The cleanest X-ray diffraction indicating nearly pure cubic phase was obtained with 50 V cm^{-1} . The furnace was heated at $10^{\circ}\text{C min}^{-1}$, and the flash occurred at 682°C . The specimen was held in the state of flash for 10 seconds when the power to the specimen and to the furnace was turned off.

Next, the experiments were carried out at different current density limits: 160 mA mm^{-2} , 180 mA mm^{-2} , and 200 mA mm^{-2} . The highest density was obtained with 200 mA mm^{-2} . The absolute density of this Al-LLZO specimen was 4.4 g cm^{-3} and its relative density was 86%. At lower current limits the relative density values were 76% and 82%, respectively. The field and current density profiles for this experiment as a function of the rising furnace temperature are given in Figure 2.

2.3 | Characterization

The sinter density of the specimens was 86%, which was determined from the physical dimensions and the weight of the

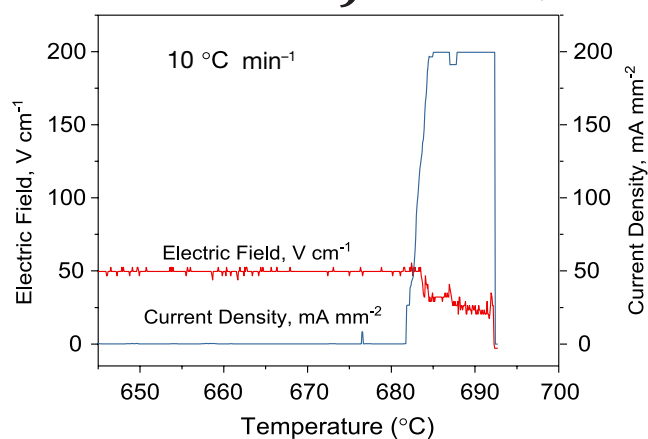


FIGURE 2 Current Density and Electric Field behavior in a constant heating rate experiment for reactive flash sintering of Li, Al, La, Zr, oxide powders into Al-LLZO. The onset of flash is signaled by the abrupt increase in conductivity [Color figure can be viewed at wileyonlinelibrary.com]

specimen. The microstructure of the specimen was examined in a scanning electron microscope (Hitachi SU3500). The specimen was fractured, and the surfaces were coated with 5 nm of gold to prepare for imaging.

Figure 3 shows the various SEM micrographs starting with pictures of the original four elemental powders, 3(A), then a picture of the powder mixture after milling, 3(B), next the micrograph of the flash sintered dense LLAO(Al), 3(C), and then the EDS mapping of the surface from the flash sintered specimen in Figure 3D.

The microstructure in Figure 3C shows a uniform microstructure with low porosity. The fracture surface is predominantly transgranular. EDS mapping of the elements, in 3(D), concludes that the Zr, La, and Al species are distributed uniformly. The specimens were translucent, presumably because of low density, with a yellowing color. High density LLZO is known to have transparency.¹⁶ The change from the morphology of the milled powder, which has a very wide particle size distribution into a fairly uniform grain structure after RFS is rather remarkable in view of the very short time span, just a few seconds, that it took for the process of complete. The kinetics of inter-diffusion and the formation of the single phase from particles of the constituent oxides is an important question for the future. However, the very rapid nature of the process would require new experimental techniques, such as ultrafast X-ray scans, which are in our plans.

Flash sintering process is prone to localization of current within the gage section of the dog-bone. Often it depends on the current density limit, with the higher current density causing the current to “channel” thereby producing higher densification in a streak across the gage length. Since the final density also depends on the current density, trial and error experiments are needed to find the optimum electrical parameters and the furnace temperature. The location of such

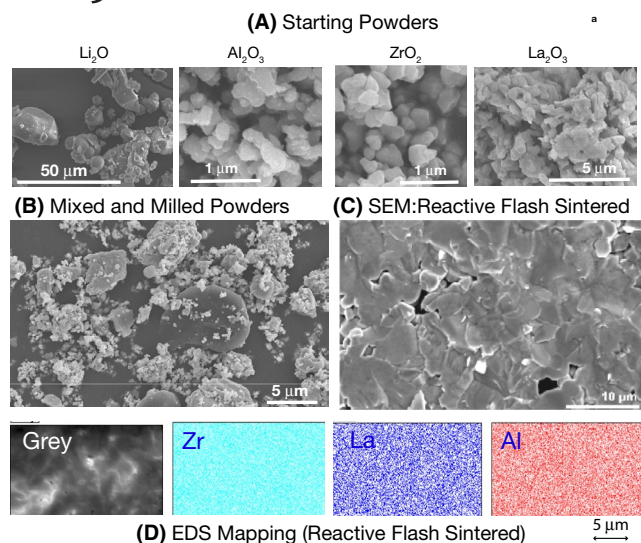


FIGURE 3 (A) SEM micrographs of as-receive powders of the four oxides, (B) SEM micrograph of mixed and milled powder. (C) Microstructure of single phase polycrystal of LLZO(Al) made by reactive flash sintering. (D) EDS mapping of the elements of the microstructure seen in figure (C) [Color figure can be viewed at wileyonlinelibrary.com]

a channel is unpredictable, sometimes it runs through the middle of the gage length but more often near one of the surfaces of the specimen. In the present experiments there was evidence of a “different” microstructure near either of the surfaces, which could have resulted from the loss of lithium. These surface layers were polished away before the electrochemical measurements. The micrograph seen in Figure 2A was from the central core of the specimen.

The crystal structure and the single phase nature of the specimens were characterized by X-ray diffraction in a Bruker-D2 Phaser X-ray machine. The specimens were then polished to remove unevenness of the surface and directly taken to the X-Ray machine. The XRD pattern was obtained in steps of 0.05° , which unfortunately is not a high enough resolution for Rietveld analysis that requires a minimum resolution of 0.02° . Nevertheless, when the diffraction pattern is matched to handbook peaks for cubic LLZO, a fairly convincing match for a single phase structure is obtained, as shown in Figure 4. There are small stray peaks marked by “star” and “+” shaped symbols; they were identified to be consistent with diffraction from carbonates of lithium, Li_2CO_3 and lanthanum, $\text{La}_2\text{O}_2\text{CO}_3$, respectively.¹⁷

2.4 | Electrochemical evaluation

Small specimens were cut from the flash sintered specimen and then diffusion bonded to lithium metal sheets to create half-cells of $\text{Li} \mid \text{LLZO(Al)} \mid \text{Li}$. The cell has a surface area of $4 \text{ mm} \times 3 \text{ mm}$ and a thickness of 0.82 mm . For diffusion bonding Li foil was rolled within the glove box to expose

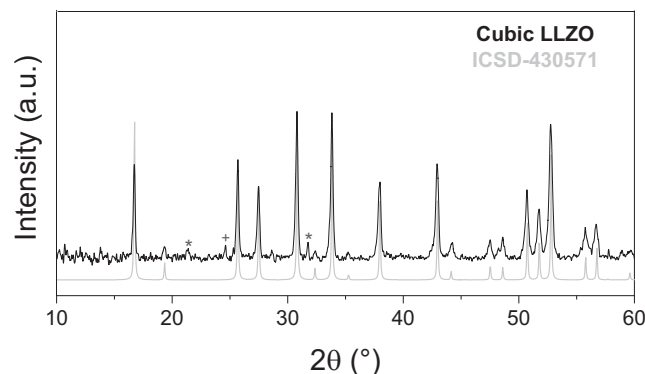


FIGURE 4 XRD pattern for the reactive flash sintered cubic-LLZO compared to the 430571-ICSD file. (*) indicates Li_2CO_3 and (+) $\text{La}_2\text{O}_2\text{CO}_3$ impurity peaks

fresh surface; the electrolyte was sandwiched between two Li foils and the assembly was heated to 150°C while applying a pressure with 10 kg load for 30 minutes, inside the glove box. Excess Li at the edges was removed with a knife and nail polish was applied to the sides to prevent leakage of lithium from the surfaces. The ionic conductivity of the bulk material was measured by impedance spectroscopy, with a Hewlett Packard 4192A LF, by sweeping the frequency from 5 Hz to 13 MHz at 0.1 V . Ionic conductivity values were calculated from the complex impedance plots using ZView software for analysis. Figure 4 shows the Nyquist plot for the Al-LLZO cell. The semicircle at the high frequency gives the bulk ionic conductivity, with a resistance of 4500 Ohms , which translates into specific ionic conductivity of 0.15 mS cm^{-1} (Figure 5).

3 | DISCUSSION

Reactive flash sintering (RFS) is a recently discovered process. It is an extension of flash sintering where several classes of ceramics, ranging from ionic conductors,¹⁸ electronic conductors,¹⁹ semiconductors²⁰ to insulators,^{15,21,22} have been shown to sinter quickly at temperatures well below the nominal sintering temperatures. In RFS the starting powders can be simple oxides that are the constituents of the single phase ceramic of a complex chemistry. During the flash process these powders react and transform into the single phase while, at the same time sintering to fairly high densities. In this way, the tedious and often laborious step of making powders of the single phase material is side stepped, adding considerable efficiency and economy to the overall process.

In earlier work, RFS has been used to prepare binary compounds bismuth ferrite and magnesium aluminate spinel from their elemental oxides. In the present work we show that RFS can also be applied to ceramics of far greater complexity where they are constituted from four elemental oxides, lithium oxide, lanthanum oxide, zirconium oxide, and aluminum oxide. Predominantly single phase cubic LLZO(Al) was produced.

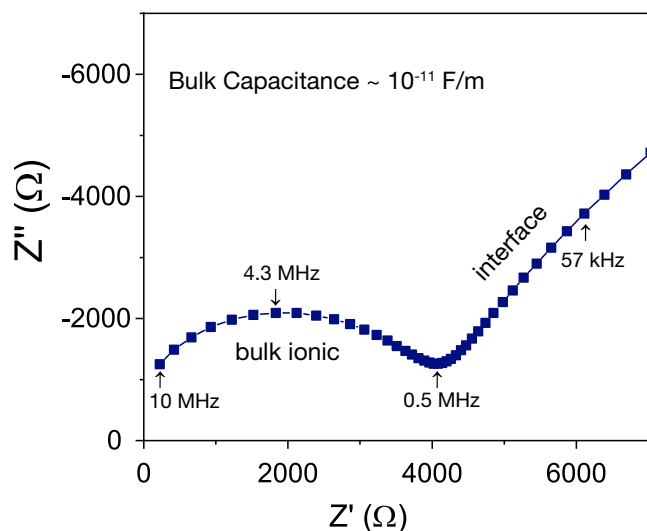


FIGURE 5 Nyquist plot for cubic-LLZO made by reactive flash sintering [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1111/jace.16625)]

Like flash sintering, RFS was carried out with a routine furnace in ambient air atmosphere. The principal sophistication in flash is programming of the power supply which provided electrical voltage and current to the specimen. Often platinum wires serve well, but in the present work Li reacted with Pt, and nickel wires were used instead with silver paste applied to the contact area between the metal and the dog-bone shaped ceramic sample. No special precautions were taken to prevent the loss of lithium during RFS, except to keep the furnace temperature low (we used $\sim 682^\circ\text{C}$). Some loss of lithium from the surface could have occurred. Therefore, the surface layer was removed by polishing the samples from their flash thickness of approximately 0.8 mm down to 0.45 mm. The lithium ion conductivity of these specimens was 0.15 mS cm^{-1} . Both higher and lower conductivities have been reported in the literature; they range from 0.001 mS cm^{-1} ,²³ to 0.16 mS cm^{-1} ,²⁴ to 0.99 mS cm^{-1} .¹⁶ The last result suggests a correlation between higher density and higher conductivity.

4 | CONCLUSIONS

The application of flash sintering (RFS) to a four component ceramic system has been demonstrated. Furthermore it has been applied to produce the cubic phase of alumina doped lithium lanthanum zirconate, of reasonable phase fidelity with ionic conductivity of lithium that lies within the range of values reported in the literature.

RFS has the following advantages over conventional sintering: (a) the furnace temperatures are low and the sintering time can be as short as a few seconds, (b) these processing conditions may prevent the significant loss of species that, in conventional sintering, can migrate towards the surface, (c) the sintering and phase transformation of elemental, primitive

oxides directly into single phase occurs in one step, which is a considerable simplification from the two-step conventional sintering process where first stoichiometric powders are made from the chemical route and then sintered in the usual way.

We foresee that RFS can be used in the discovery of new materials since a diversity of dopants can be incorporated into ceramic compounds and their properties evaluated quickly with a fast turnaround time.

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ORCID

Viviana Avila  <https://orcid.org/0000-0003-3476-1644>

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

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