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Feasibility Investigation to the Interfacial Understanding of Dissolution, Supersaturation, and Crystallization
Enabling the Cold Sintering Process of Ceramics

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14. ABSTRACT

Apply the non-equilibrium process known as 'cold sintering' to a broad spectrum of material systems to explore and establish the maximum potential for future research interests to the Air Force, establishing the enabling critical basic science. Cold sintering is a new sintering technique that incites densification and grain growth in ceramic materials below 400C; having been demonstrated in several ceramic materials already. The dramatic reduction in sintering temperature (about an order of magnitude) of any polycrystalline ceramic is deserving of its own merit, but such low temperatures also present new opportunities for nanocomposites and grain boundary functionalization between ceramics and polymers/metals, hitherto unattainable due to the incompatibilities of the conventional sintering temperatures and the thermal stability of these such additives. The objectives of the research included the understanding of densifying conventional ceramic systems far from their equilibrium sintering temperature, designing new nanocomposites of ceramics with polymers/metals made possible by cold sintering, and probe the mechanisms of cold sintering for guidance on future research. In this report each of these aspects was successfully addressed.

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Nanocomposites and circumventing equilibria *via* Cold Sintering: Fundamental studies and broad applications

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Statement of Objectives/Goals: Apply the non-equilibrium process known as “cold sintering” to a broad spectrum of material systems to explore and establish the maximum potential for future research interests to the Air Force, establishing the enabling critical basic science. Cold sintering is a new sintering technique that incites densification and grain growth in ceramic materials below 400°C; having been demonstrated in several ceramic materials already. The dramatic reduction in sintering temperature (about an order of magnitude) of any polycrystalline ceramic is deserving of its own merit, but such low temperatures also present new opportunities for nanocomposites and grain boundary functionalization between ceramics and polymers/metals, hitherto unattainable due to the incompatibilities of the conventional sintering temperatures and the thermal stability of these such additives. The objectives of the research included the understanding of **densifying conventional ceramic systems far from their equilibrium sintering temperature, designing new nanocomposites of ceramics with polymers/metals made possible by cold sintering, and probe the mechanisms of cold sintering for guidance on future research. In this report each of these aspects was successfully addressed.**

1. Cold Sintering Background

Previously funded cold sintering programs by the AFSOR have explored the following topics

- **Gain fundamental insight into the mechanisms underpinning Cold Sintering**
- **Identify characterization methods to aid processing science**
- **Explore composite designs with new approaches**

From those earlier studies an intriguing opportunity has been noted, which is the design of a new family of nanocomposite materials. Previously, we never had the ability to process polymer intergranular phases to modify properties of composites in high volume fractions of ceramics. Similarly, we can now integrate 2-D nanomaterials into the grain boundaries of a dense ceramic. The program was exploratory and enabled cold sintering to be developed sufficiently to permit a working understanding of the cold sintering process, as shown in figure 1 and 2. Below we summarize some of the insights gained in the cold sintering study, and to now consider the next steps for making and understanding the novel nanocomposites *via* the cold sintering process. **These high-performance nanocomposites could be utilized in aerospace, aeronautics, submarine devices, car, sensor and flexible electronic devices in future applications.**

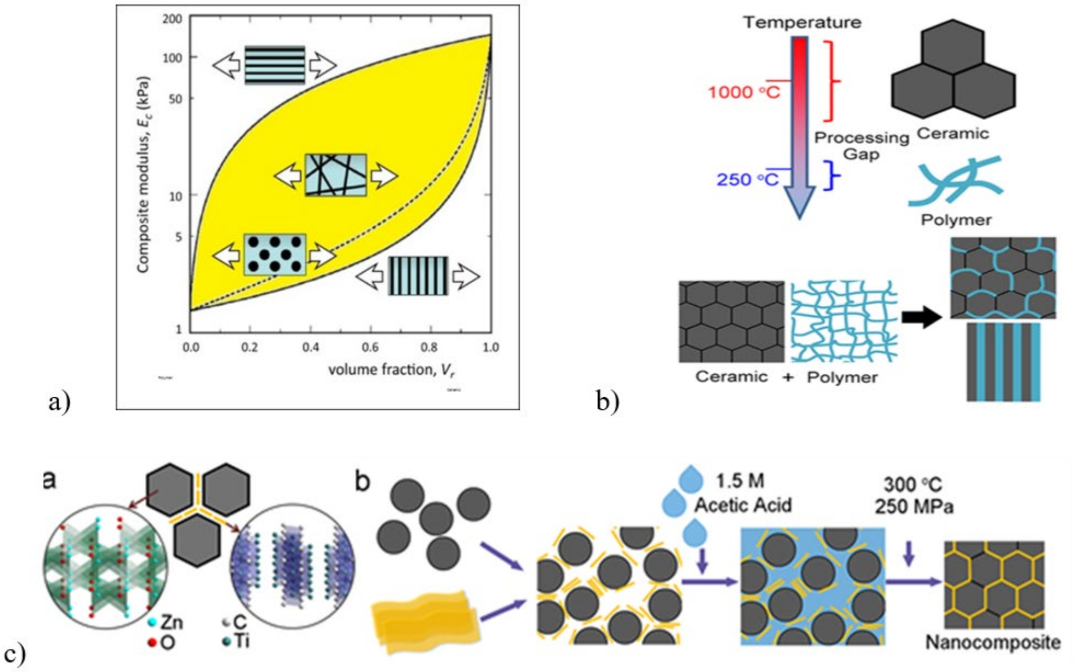

Figure 1 Schematic of a) typical variation of a disphaic composite mixing in a hard material into a softer matrix, b) schematic of the cold sintering process opportunity for nanocomposite with an intergranular polymer phase, or co-sintered laminated composite, c) intergration in to the grain boundary of 2-D nanomaterials.

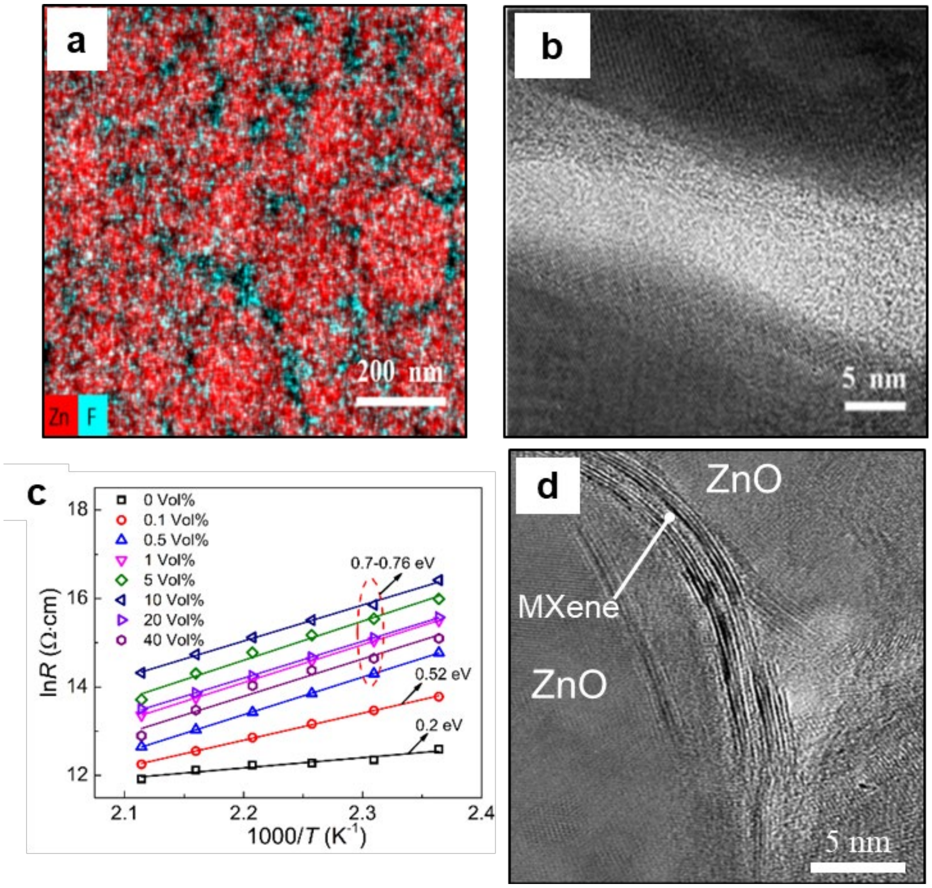

Figure 2 Composites fabricated by the cold sintering process. (A) Energy dispersive mapping evidence of PTFE (blue) distributed along the grain boundaries of ZnO (red) (B) High resolution TEM image of PTFE intergranular boundary (C) Tunable activation energies of electrical conduction in ZnO-PTFE nanocomposites and (d) demonstration of 2-D Mxene distributed at the grain boundaries of ZnO.

2. Goal: Exploratory Investigations to establish maximum potential of cold sintering

What materials can be cold sintered? Early publications of cold sintering[1] reported a broad spectrum of materials from elemental metals to quinary compounds which could be cold sintered to some degree. In the simplest case, a powder of composition *A* can be cold sintered with a small volume fraction of aqueous solvent resulting in a dense pellet of composition *A*; such is the case for ZnO and V_2O_5. In some cases (e.g. $BaTiO_3$) a subsequent annealing process is necessary to complete the recrystallization. However, there are many potential barriers to such a process, such as incongruent dissolution of certain elements into the solvent, surface passivation arresting densification, and slow kinetics of one or more steps of the cold sintering process. Current work has successfully addressed some of these barriers and in doing so broadens the scope of potential cold sintering investigations.

Fe_2O_3 and $ZnFe_2O_4$ are examples of two materials which cannot be easily densified by simply applying heat and pressure to a powder of the same chemistry. However, we have shown that a new path termed “Reactive Cold Sintering” is able to produce high density ceramic samples of these chemistries. Reactive cold sintering operates by utilizing a precursors (e.g. FeOOH or $Zn(OH)_2$ + FeOOH) reacting with a molten non-aqueous solvent (e.g. $FeCl_3\ or\ hydroxides$) to form the desired compound *during* the cold sintering process, thus concurrent with densification. The reactive nature of this approach introduces in some cases complexities such as secondary phase generation, but promising ongoing work shows that this can be ameliorated by tailoring processing parameters (Figure 3a).

Cold sintering has also addressed materials which have historically been difficult, if not impossible (for phase transformation or thermally stimulated decomposition reasons), to sinter by conventional means, examples including $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP), TiO_2, $BaTiO_3$, and $Na_3Zr_2Si_2PO_{12}$. The latter of these materials, the sodium ion conducting electrolyte $Na_3Zr_2Si_2PO_{12}$ (NZSP), conventionally required nominal sintering temperatures of 1250°C with a 6-hour dwell time, causing extensive Na and P volatilization and precluding its combination with any metal or polymer additive. By utilizing one of the most aggressive solvents available for cold sintering, a molten hydroxide compound at 375°C, cold sintered NZSP reaches relative densities of 94% and the highest of ionic conductivities of any material processed below 800°C (figure 3b-c). This approach has been successfully applied to other strongly bonded material systems, bringing even the most robust ceramic systems into the reach of cold sintering.

At the AFOSR review in 2019, there was discussions on the applicability of cold sintering to covalent high temperature materials such as nitrides and carbides. There is a chemist funded in the program that offers a new transient chemistry that could enable the densification of TiC. A collaboration will be conducted on this opportunity to show proof-of-concept in the fall of 2019.

Cold sintering may also be used to fabricate devices in a single step. Building on previous experience in the processing of multilayer ceramic capacitors (MLCC), cold sintering has also been applied to such layered metal-ceramic devices with great success (figure 3d). In these devices, the alternating micrometric layers of metal (Cu) and ceramic (ZnO) are co-processed by cold sintering to fabricate MLCC's at low temperatures and high interfacial fidelity. Such a demonstration is a step towards future large-scale implementation of cold sintering. By employing cold sintering in the co-firing of disparate material systems, each with their own potential pitfalls (e.g. metallic oxidation), one avoids such processing concerns and opens the door for a multitude of functional devices fabricated by the cold sintering process. In developing the knowledge base for cold sintering layered devices *via* tape casting and then sintering, a confluence of cold sintering for many applications may be possible; for example, cold sintering of an all-solid-state-battery, roll-to-roll cold sintering, MLCC's with a desired complex architecture. While it may be some time before cold sintering matures to tackle these problems at a commercially scale, it bears noting that such preliminary results strongly indicate that feasibility.

3. Goal: Design of new, functional, grain boundary interfaces

Parallel to the extensive progress made on functional ceramic systems and elementally segregated devices detailed above, cold sintering also has made significant advances in the field of ceramic dominated nanocomposite design and fabrication. As mentioned in the background of cold sintering section, placement of functional non-ceramic materials at the grain boundaries of polycrystalline matrices has always challenged ceramicists due to the discrepancy in processing windows of ceramics and most other materials of interest, and thus this thrust comprises a sizable fraction of the efforts expended on cold sintering. Recent studies have described two new polymer-ceramic nanocomposite materials made possible by the cold sintering process; (1) a V_2O_5 negative temperature coefficient (NTC) material[2] and (2) a polydimethylsiloxane (PDMS)-ZnO composite where the PDMS polymer was crosslinked *during* the cold sintering process[3].

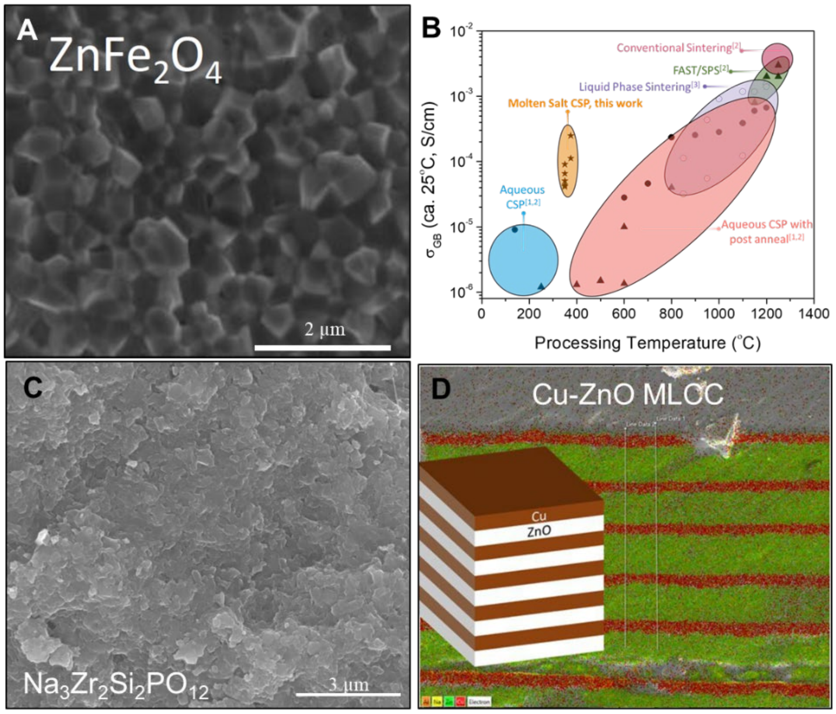

Figure 3 Pushing the boundaries of cold sintering. (A) ZnFe$_2$O$_4$ microstructure showing the promise of reactive cold sintering. (B) Literature comparison of NZSP fabricated by different sintering techniques[4]. (C) a microstructure of NZSP fabricated by molten salt cold sintering (unpublished). (D) Scanning electron microscopy with electron dispersive elemental mapping image of a Cu-ZnO MLCC device co-fired completely by cold sintering[5].

NTC materials are often used in thermistor applications in a broad swathe of commercial and domestic applications and would benefit greatly from both low temperature processing and a nanocomposite architecture which might impart flexibility or toughness from the inclusion of a polymer additive at the grain boundaries of a conventional NTC ceramic oxide. Zhao et al.[2] applied the cold sintering process to a (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)-V$_2$O$_5$ tape-casted nanocomposite and measured NTC values comparable to commercially available NTC devices. The tape casted PEDOT:PSS-V$_2$O$_5$ films (ca. 3 vol% PEDOT:PSS) could be cold sintered to > 90% of the theoretical density utilizing water as a transient solvent at the reduced temperature of 140°C in a little as 45 minutes. The resulting composites are shown to have a low activation energy of 0.18 eV while retaining the polaron hopping conduction of conventionally sintered samples. The figure of merit (*n*) is plotted for a 3 vol% PEDOT:PSS-V$_2$O$_5$ composite and pure V$_2$O$_5$ in figure 4a, along with a TEM micrograph illustrating the 5-10 nm layer of PEDOT:PSS grain boundary distributed at the grain boundary of the ceramic.

The opportunity for polymer-ceramic composites is further exemplified from recent studies showing of *in-situ* cross linkage of a PDMS polymer inside a ZnO ceramic matrix during the cold sintering process. Polymeric science, especially synthesis, has progressed greatly in recent decades but have largely remained insulated from the broader materials science community given the processing limits on organic based materials. Cold sintering bridges the gap between the processing advances being made in the soft matter community with that of ceramic processing and thus enables such composites to be synthesized. Noting that thermally stimulated cross-linking reactions share a temperature regime with the cold

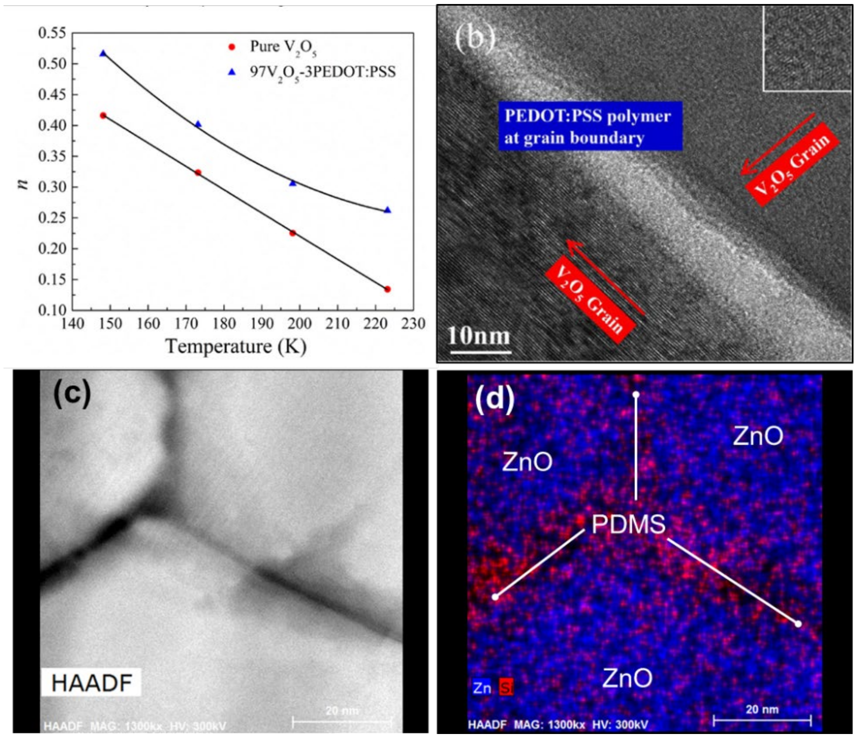

Figure 4 Nanocomposites enabled by cold sintering (A) Fractional exponent (n) plotted as a function of temperature illustrating similarities in electrical response between cold sintered PEDOT:PSS-V_2O_5 nanocomposites and pure V_2O_5 (B) TEM image of the same nanocomposite with polymerically functionalized grain boundaries (C) TEM image of a cold sintered ZnO-PDMS composite and (D) elemental mapping of said composite with indicators of phase distribution.

sintering process (ca. 100 to 300°C), we combined the two processes for the first demonstration of concomitant crosslinking and sintering[3]. TEM micrographs confirm this and are reproduced in figure 4B-D. In addition to the proof of this concept, the study also elucidated the role that polymers can play in aiding initial rearrangement process and presenting a diffusive barrier during the cold sintering process. Furthermore, impedance characterization of the samples with different volume fractions of PDMS showed that the electrical response of these nanocomposites is complex and dominated by PDMS-ZnO interfacial effects generated by cold sintering. These results foreshadow a multitude of potential combinatory polymeric/ceramic processing, where advances made in the polymer processing regime can be directly translated to the ceramic community.

4. Fundamental Insights

By making use of new semi-automated uniaxial press custom-designed and built at Penn State[4] (figure 1b), the kinetics of the cold sintering process can be rigorously studied and compared with other sintering processes for the first time. These kinetics and mechanistic studies, while still preliminary, have already advanced the scientific understanding that frames how cold sintering is to be viewed. Coupled with measurements of the decrease in surface after cold sintering, it is now possible to correlate the microstructures and properties of the cold sintered ceramics directly with the known densification path recorded by the instrument.

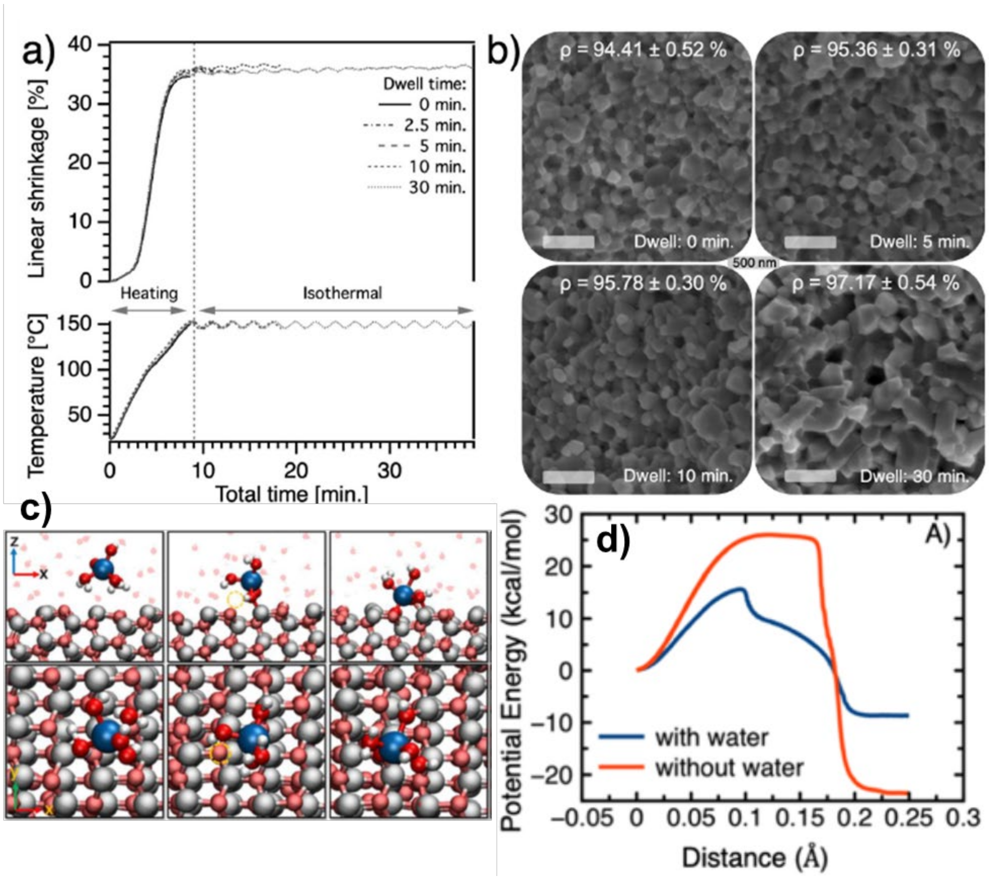

Figure 5 Fundamental insights into cold sintering. (a) linear shrinkage of a pellet during cold sintering, illustrating the 3 distinct regions densification over the course of sintering (b) SEM micrographs corresponding to the different dwell times presented in (a) (c) computational modeling of water interaction with a ZnO surface, serving to calculate the energy needed to solvate Zn^{2+} ions (d) the potential energy to liberate Zn-O atoms in the presence of a solvent and without.[6]

Present fundamental efforts are largely focused on the ZnO-acetic acid system, building on the large amount of previous studies employing a ZnO-based system. Figure 5A shows an example of data obtained of the linear shrinkage (i.e. densification) as a function of increasing dwell times during the cold sintering process. Figure 5B shows representative micrographs (and respective densities) corresponding the different dwell times, illustrating the clear correlation between the stages of densification and the resulting microstructure. Current analysis indicates that the initial stage of densification ($t < 3$ min) corresponds to a particle rearrangement process, a second stage ($3 \text{ min} < t < 10\text{min}$) scales similar to published models of liquid phase sintering, and the final stage ($t > 10$ min) likely corresponds to a final, pore-closing, stage of densification. These findings are corroborated with measurements of the free surface area of the bulk cold sintered samples. With these quantitative descriptions of the cold sintering process in hand, we are now working to compare the cold sintering process to known models from both ceramic processing literature and the geologic pressure solution creep theories. Even during the writing of this report, we see that these studies are guiding us to reduce the pressures, in ZnO to below 50 MPa, and still produce translucent ZnO ceramics at 140 °C.

Collaboration at the convergence of materials science and the geologic sciences may also extend to making use of the extensive body of literature regarding the kinetics and mechanisms of dissolution and precipitation at liquid-solid interfaces. With the realization of high-resolution liquid-solid interface structure observation instruments only recently becoming widely accessible, cold sintering may benefit, or even contribute, to the general scientific communities understanding of how minerals or oxide materials interact with liquid under pressure, and how one might exploit such processes for bulk commercial processing. Indeed, ongoing molecular dynamic computational studies of the cold sintering process of the same ZnO-acetic acid system described above have yielded great insight into the possible mechanisms of cold sintering. Through observations of interface development under cold sintering conditions, we have found that the barrier to diffusion of ZnO along a densifying path is greatly when the acidic aqueous medium is added (Figure 5C-D). These results are congruent with experimental kinetic studies of cold sintering of ZnO-acetic acid which report certain optimal temperatures, pressures, and solvent *pH* values which greatly reduce the activation barrier to densification.

5. Conclusions

Cold sintering continues to progress towards a mature and broadly accepted sintering technique, capturing the attention of those within the ceramic processing community, as well that of researchers in neighboring fields such as polymer science and geology. Progress of late has realized many of the early predictions portended by early workers; namely the direct application of cold sintering to nanocomposites for functional electronic devices and electroceramic materials such as $BaTiO_3$ and $Na_3Zr_2Si_2PO_{12}$, whose processing has challenged the ceramics community for decades. In parallel, cold sintering has been successfully applied to numerous novel polymer-ceramic nanocomposites, whose formulations have only recently been postulated with the advent of cold sintering, forging a path for promising future work. Fundamental studies of the mechanisms responsible for cold sintering are also under intense investigation, serving to both inform and be informed by applied cold sintering studies. These results, coupled with computational studies of the interfacial development and reactions during cold sintering, point to enhanced surface dissolution and diffusion under cold sintering conditions. While this result was expected based on all prior experimental studies of cold sintering, the precise operating mechanisms provide clear links to the literature regarding current work in the field of surface weathering and pressure solution creep in geology and thus open new opportunities for potential collaboration. In light of these numerous advances and we also see rapid adoption in laboratories around the world, cold sintering promises to continue to foster international and interdisciplinary collaboration to help meet the material processing needs of tomorrow. The work funded under this initial AFOSR program aids this effort and helps us to not only lead the discovery pathway but also aid in transitioning and protecting the intellectual property.

6. Profession Development and Communication

Zane Grady (graduate student 100% on project):

- Presentation at EMA 2019 Conference, Orlando, Florida, Jan. 23-25, 2019, "Low temperature processing of sodium ion battery electrodes and electrolytes via the Cold Sintering Process".
- Publication: *Arnaud Ndayishimiye, Zane A. Grady, Kosuke Tsuji, Ke Wang, Sun Hwi Bang, Clive A. Randall, Thermosetting polymers in cold sintering: The fabrication of ZnO - Polydimethylsiloxane composites, Submitted in Journal of the American Ceramic Society*
- Publication: NZSP in preparation

Clive Randal (PI):

- Invited presentation, 16th European Inter-Regional Conference on Ceramics, Torino, Italy, September 9-12, 2018, "State of Play in the Developing Story of Cold Sintering, and a Tribute to Paolo Nanni's Contribution to Ferroelectrics".
- Invited presentation, Japanese Ceramic Society Electroceramics conference, November 15-16, 2018, " State of Play in the Developing Story of Cold Sintering".
- Invited presentation, 43rd International Conference and Exposition on Advanced Ceramics and Composites (ICACC2019), Fulrath Session II, Daytona Beach, Florida, January 27-30, 2019, "State of Play in the Developing Story of Cold Sintering".
- Invited Presentation, German Ceramic Society meeting, Jena, Germany, March 28-29, 2019, "From Relaxors to Cold Sintering: A Wild Ride Dedicated to Eberhard Hennig".
- Plenary lecture, 11th International Conference on High-Performance Ceramics (CICC-11), Kunming, China, May 25-29, 2019, "Cold Sintering: Systems, Mechanisms, Applications, Opportunities, and Challenges".
- Invited presentation, European Ceramic Society Meeting, Torino, Italy, June 16-20, 2019, "Cold Sintering of Electroceramic Materials, Devices and Novel Nanocomposites".
- Invited presentation, 10th International Conference on Materials for Advanced Technologies (ICMAT), Marina Bay Sands, Singapore, June 23-28, 2019, "Cold Sintering of Electroceramic Materials, Devices and Novel Nanocomposites".
- Invited presentations, F2Cp2 Joint Conference 2019, Lausanne, Switzerland, July 14-19, 2019, "Electroceramic Materials, Devices, and Novel Nanocomposites via Cold Sintering", and "Sodium Based Perovskites: Chemical Design, Processing and Properties".

- **Awards Under this Program:**
- Honorary Fellow of the European Ceramic Society (July 2019).
- Distinguished Lecturer of the IEEE Ultrasonics, Ferroelectrics, and Frequency Control Society (2019).

7. Other Personnel:

(Partial coverage):

  - Sun Hwi Bang (graduate student, working on densification and quantification)
  - Sinan Dursun (postdoctoral scholar, tape casting)
  - Jing Guo (postdoctoral scholar, 2-D MAX phases; left Penn State for a faculty position)
  - Arnaud Ndayishimiye (postdoctoral scholar, PDMS – dispersion)

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3. Arnaud Ndayishimiye, Zane A. Grady, Kosuke Tsuji, Ke Wang, Sun Hwi Bang, Clive A. Randall, “Thermosetting polymers in cold sintering: The fabrication of ZnO - PDMS composites,” Submitted to Journal of the American Ceramic Society.
4. Zane Grady et al., unpublished work
5. Jing Guo, Richard Floyd, Sarah Lowum, Jon-Paul Maria, Thomas Herisson de Beauvoir, Joo-Hwan Seo, and Clive A. Randall, “Cold Sintering: Progress, Challenges, and Future Opportunities,” Annual Rev. of Mats. Res. 49, 275-296 (2019).
6. Mert Y. Sengul, Jing Guo, Clive A. Randall, and Adri C.T. van Duin, “Water-Mediated Surface Diffusion Mechanism Enables the Cold Sintering Process: A Combined Computational and Experimental Study,” Angewandte Chemie 131, 1-6 (2019).