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RPPR Final Report
as of 02-Jun-2022

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Agreement Number: W911NF-18-1-0361

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STEM Degrees: 3
STEM Participants: 5

Major Goals: (Goal #1) to develop synthetic and processing techniques capable of producing ceramic parts with grain sizes in the nanoscale regime (targeting sizes below 10nm);
(Goal #2) utilize the obtained products to explore mechanical properties of nanoceramics, enabling development of fundamental understanding on size induced effects on, particularly, hardness and toughness;
(Goal #3) based on the developed knowledge, understand and propose mechanisms to increase toughness and hardness of nanocrystalline ceramics.
(Goal #4) Train graduate and undergraduate students on contemporary issues of nanoceramic processing, testing and microstructural characterization.

Accomplishments: The project has achieved the proposed scientific and training goals, and as expected, the scientific results have opened new research perspectives for future projects.

One of the main products was the education of a new generation of PhD with expertise in advanced ceramic processing. Three graduate students have graduated from this project, Arseniy Bokov (Ph.D., graduated 2018), Chenguang Yang (M.Sc. graduated 2018), and Brian Rogers (M.Sc. graduated 2019). Additionally, one Ph.D. student will graduate in the Summer of 2022, Luis Sotelo Martin and another Ph.D. student, Isabella Costa, will graduate in 2023 (will be funded by other sources since the project is now concluded). In the summer of 2021, one undergrad student participated in the Summer Internship program sponsored by ARO - AEOP, Taha Hussain.

The project was performed during the period of the COVID pandemic. This impacted the proposed activities due to lab closures and limited lab access in 2020 and 2021. During the gap, we have developed partnership with Prof. Jeremy Mason at UC Davis and Dr. Blas Uberuaga in the Los Alamos National Laboratory, for a collaboration on modelling of the systems using atomistic simulation. Both current grad students, Luis Martin and Isabella Costa, were co-mentored during the period and has developed significant data that adds up well to the theories and concepts developed on the experimental part.

During this project, the group has published 14 articles, all in peer reviewed and respected journals in the field. There are other four manuscripts submitted or under preparation with expected publication time still in 2022. We produced three thesis under this project, one PhD and two Masters, and have two others lined up, one for 2022 and one in 2023.

More details about the scientific accomplishments can be found in the attached document.

Training Opportunities: The project trained graduate and undergraduate students on modern techniques of manufacturing, characterization and testing of nanoceramics. It allowed the students to be educated not only through course work at UC Davis, but also with hands-on research activities in the laboratory and with the modelling add-ons.

Students were trained in manufacturing via conventional sintering and spark plasma sintering, being now capable of development manufacturing protocols, including detailing materials and designing of dies, temperature and heating profiles, and pressure parameters to achieve controlled microstructures.

Synthesis of nanocrystalline powders, being able to adapt processes to complex chemistries for homogeneous and 'clean' nanopowders.

They have been trained in sophisticated characterization techniques, including:
- (Scanning) Transmission Electron Microscopy and its diverse set of combined techniques, such as EDS, EELS and electron diffraction, as well as protocols of sample preparation and Experience in analyzing data.
- Scanning Electron Microscopy, including EDS, microprobe, Focus Ion Beam, and details of sample preparation. Experience in analyzing data.
- X-ray diffraction, covering equipment calibration, maintaining, fixing, and running powder and pellet samples. Running fitting programs to extract information from the diffraction patterns. Experience in analyzing data.
- Calorimetric techniques, including Differential Scanning Calorimetry and Water Adsorption Microcalorimetry. Data analysis and interpretation of complex heat signals.
- Other microstructural tests: Density measurements, BET surface area measurements, infrared spectroscopy, UV-Vis spectroscopy.
- Mechanical tests, such as hardness measurements and flexural strength with 3-point bending. Including sample preparation and data interpretation with statistics.

Results Dissemination: The results produced in this project were disseminated by different modes: articles published in peer reviewed journals, talks presented in scientific/engineering conferences, seminars at different schools and within UC Davis.

Talks by the PI presenting project's results (since 2021):
-Invited Talk: Engineering the Nano-Revolution in Energy Solutions. LNNano – Brazilian National Laboratory of Nanotechnology.
- Invited Talk: Enhancing Strength in Nanocrystalline Transparent Ceramics. MS&T'21 - Materials Science and Technology 2021, Columbus, OH, USA.
- Invited Talk: Controlling Synthesis of Nanostructures with Nanoscale Phase Diagrams. MS&T'21 - Materials Science and Technology 2021, Columbus, OH, USA.

Talks by Students:
Costa, I, Castro RHR. Dopant designed to increase toughness in nanocrystalline spinel. ICACC'22 - International Conference and Exposition on Advanced Ceramics and Composites, Virtual Presentation, January 27, 2022. (Talk)

Costa, I, Castro RHR. Effect of sodium on the Processability and Mechanical Properties of Nanocrystalline Magnesium Aluminate. MS&T'21 - Materials Science & Technology Technical Meeting and Exhibition, Virtual Presentation, October 19, 2021. (Talk)

Sotelo Martin LE, Castro RHR. Enhanced hardness from modified stoichiometry in nanocrystalline zinc aluminate. ICACC'22 - International Conference and Exposition on Advanced Ceramics and Composites, Virtual Presentation, January 27, 2022. (Talk)

Sotelo Martin LE, Castro RHR. Hall-Petch behavior in stoichiometric and Al-rich nanocrystalline ZnAl2O4. MS&T'21 - Materials Science & Technology Technical Meeting and Exhibition, Virtual Presentation, October 19, 2021. (Talk)

Sotelo Martin LE, Castro RHR. Interface stability of nanocrystalline ZnAl2O4 doped with rare earths (RE). American Ceramic Society, ICACC'21 - International Conference and Exposition on Advanced Ceramics and Composites, Virtual Presentation, February 8, 2021. (Talk)

Publications:
[1] C. Yang, A. Thron, R.H.R. Castro, Grain boundary strengthening in nanocrystalline zinc aluminate, J. Am. Ceram. Soc. 102 (2019) 6904–6912. https://doi.org/10.1111/jace.16512.
[2] L.E. Sotelo Martin, R.H.R. Castro, Al excess extends Hall-Petch relation in nanocrystalline zinc aluminate, J. Am. Ceram. Soc. 105 (2022) 1417–1427. https://doi.org/https://doi.org/10.1111/jace.18176.
[3] A. Bokov, J.B. Rodrigues Neto, F. Lin, R.H.R. Castro, Size-induced grain boundary energy increase may cause softening of nanocrystalline yttria-stabilized zirconia, J. Am. Ceram. Soc. 103 (2020) 2001–2011. https://doi.org/10.1111/jace.16886.
[4] A. Bokov, J.A. Aguiar, M.L. Gong, A. Nikonov, R.H.R. Castro, A Strategy to Mitigate Grain Boundary Blocking in Nanocrystalline Zirconia, J. Phys. Chem. C. 122 (2018) 26344–26352. https://doi.org/10.1021/acs.jpcc.8b08877.
[5] B.M. Rogers, I.L.M. Costa, W. Zhu, S. Sen, R.H.R. Castro, Sintering, hardness and cation inversion of nanocrystalline Beryllium – Magnesium aluminate ceramics, Ceram. Int. 48 (2022) 15116–15123. https://doi.org/https://doi.org/10.1016/j.ceramint.2022.02.041.
[6] R.L. Grosso, K.S.N. Vikrant, L. Feng, E.N.S. Muccillo, D.N.F. Muche, G.S. Jawaharram, C.M. Barr, A.M. Monterrosa, R.H.R. Castro, R.E. García, K. Hattar, S.J. Dillon, Ultrahigh temperature in situ transmission electron microscopy based bicrystal coble creep in Zirconia II: Interfacial thermodynamics and transport mechanisms, Acta Mater. 200 (2020) 1008–1021. https://doi.org/https://doi.org/10.1016/j.actamat.2020.08.070.
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[9] A.G. Sheinerman, R.H.R. Castro, M.Y. Gutkin, A model for direct and inverse Hall-Petch relation for nanocrystalline ceramics, Mater. Lett. 260 (2020) 126886. https://doi.org/10.1016/j.matlet.2019.126886.
[10] R.L. Grosso, E.N.S. Muccillo, D.N.F. Muche, G.S. Jawaharram, C.M. Barr, A.M. Monterrosa, R.H.R. Castro, K. Hattar, S.J. Dillon, In Situ Transmission Electron Microscopy for Ultrahigh Temperature Mechanical Testing of

ZrO2, Nano Lett. 20 (2020) 1041–1046. https://doi.org/10.1021/acs.nanolett.9b04205.
[11] B.M. Rogers, R.H.R. Castro, Experimental phase diagram for beryllium-magnesium aluminate nanoparticles, Ceram. Int. 46 (2020) 2703–2708.
[12] R.L. Grosso, D.N.F. Muche, T. Yonamine, E.N.S. Muccillo, S.J. Dillon, R.H.R. Castro, Sintering of translucent and single-phase nanostructured scandia-stabilized zirconia, Mater. Lett. 253 (2019) 246–249. https://doi.org/https://doi.org/10.1016/j.matlet.2019.06.076.
[13] L. Feng, A. Bokov, S.J. Dillon, R.H.R. Castro, Size-induced room temperature softening of nanocrystalline yttria stabilized zirconia, J. Eur. Ceram. Soc. 40 (2020) 2050–2055. https://doi.org/https://doi.org/10.1016/j.jeurceramsoc.2020.01.046.
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Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Ricardo H. R. Castro
Person Months Worked: 1.00 **Funding Support:**
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Participant Type: Graduate Student (research assistant)
Participant: Luis Sotelo Martin
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Isabella Costa
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: High School Student
Participant: Taha Hussain
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Chenguag Yang
Person Months Worked: 3.00 **Funding Support:**
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National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Brian Rogers
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Article Title: A Strategy to Mitigate Grain Boundary Blocking in Nanocrystalline Zirconia
Authors: Arseniy Bokov, Jeffery A. Aguiar, Matthew L. Gong, Alexey Nikonov, Ricardo H. R. Castro
Keywords: grain boundary, dopants, ionic conductivity
Abstract: A major challenge in the application of nanostructured electrolytes in solid oxide electrochemical cells is grain boundary blocking originated from unsatisfied atomic bonding and coordination. The resulting increase in grain boundary resistivity works against the expected benefits from the enhanced ion exchange rates enabled by the extensive interfacial network in nanocrystalline materials. This study addresses this challenge by demonstrating that a reduction in the grain boundary excess energies increases the net ionic conductivity as directly measured by impedance electrical spectroscopy in nanocrystalline yttria-stabilized zirconia. The reduced grain boundary energy was designed by doping the system with lanthanum, leading to local excess energy reduction due to segregation of La to boundaries as observed by scanning transmission electron microscopy-based energy-dispersive spectroscopy. The results suggest rare-earth ions with favorable grain boundary segregation enthalpy can smooth
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Article Title: Site Inversion Induces Thermodynamic Stability against Coarsening in Zinc Aluminate Spinel
Authors: Chenguang Yang, Weidi Zhu, Sabyasachi Sen, Ricardo H. R. Castro
Keywords: Zinc aluminate, inversion, structure, interfacial energy
Abstract: Experimental thermodynamic and structural informations on surfaces and grain boundaries are of prime relevance for an in-depth understanding and control of microstructural evolution, including the stability of catalytic supports exposed to elevated temperatures. In this work, interfacial energies of quasi-stoichiometric ZnAl2O4 and Al-rich ZnAl2O4 nanoparticles were directly measured by using differential scanning microcalorimetry. The surface and grain boundary energies for ZnAl2O4 were measured to be 1.77 and 0.47 J/m2, respectively, whereas for Al-rich ZnAl2O4, these energies are 1.88 and 0.70 J/m2, respectively. The remarkable increase in grain boundary energy in the Al-rich spinel is observed to improve thermodynamic stability of the nanoparticles, allowing zinc aluminate to resist coarsening even after annealing at 1300 °C, potentially extending lifetime of ZnAl2O4-based catalysts. The 27Al NMR spectra were consistent with the calorimetric results and indicate that compared to th
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Article Title: Sintering of translucent and single-phase nanostructured scandia-stabilized zirconia
Authors: Robson L. Grosso, Dereck N.F. Muche, Taeko Yonamine, Eliana N.S. Muccillo, Shen J. Dillon, Ricardo
Keywords: CeramicsMicrostructureNanocrystalline materialsSinteringPhase stabilization
Abstract: Fully-dense and single-phase nanostructured scandia-stabilized zirconia specimens were produced by high-pressure spark plasma sintering technique. Nanocrystalline powders were prepared by the coprecipitation method. Green pellets were sintered at temperatures varying from 700 to 900?°C and pressures from 1.4 to 2? GPa, resulting in dense microstructures with single-phase fluorite-type cubic structure within a wide range of Sc2O3 content (6–15?mol%). The average grain size of sintered specimens ranged from 8 to 20?nm. Transmittance spectra confirm translucence in sintered specimens, which is consistent with full density. The results reported here reveal that the polymorphism challenge in the zirconia-scandia system can be successfully suppressed by this consolidation technique, which allows for controlling the grain size of bulk specimens.
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Article Title: Grain boundary strengthening in nanocrystalline zinc aluminate
Authors: Chenguang Yang, Andrew Thron, Ricardo H. R. Castro
Keywords: zinc aluminate, nanoceramics, harness, Hall-Petch
Abstract: Fully dense transparent zinc aluminate ceramics with nanoscaled grain sizes were fabricated by Deformable Punch Spark Plasma Sintering (DP?SPS). Optical transmission spectra showed high transparency, with up to 70% transmitted light in the visible spectrum. Vickers hardness was measured and grain boundary strengthening observed, showing hardness increase from 18.2 GPa up to 22.5 GPa as the grain sizes decreased from 60.3 to 10.1 nm. The trend followed the Hall?Petch relationship, with hardness linearly proportional to the inverse of square root of grain size. A low grain size limit reported in previous literature below which hardness decreases, known as inverse Hall?Petch relationship, was not observed within the studied grain size range. Cross?sections of the hardness tests' indentations were prepared by focused ion beam and observed by electron microscopy and showed radically different crack patterns underneath the indentation imprint when contrasting samples with dissimilar grain si
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Article Title: Size-induced room temperature softening of nanocrystalline yttria stabilized zirconia
Authors: Lin Feng, Arseniy Bokov, Shen Dillon, Ricardo Castro,
Keywords: zirconia, hardness, inverse Hall-Petch, nanoceramics
Abstract: Functional nanocrystalline oxides show significant interface-mediated effects on mechanical performance and reliability. When fully dense, such as in solid electrolytes, nanocrystalline oxides exhibit exceptional resistance to plastic deformation, manifesting increase in strength and hardness with reducing grain dimension that follows the so-called Hall-Petch relationships. However, below a critical grain size, softening has been observed to occur, in the so-called inverse Hall-Petch regime. The mechanisms underlying these phenomena are still not well understood in oxides. Here we observe using nanopillar compression that while the yield strength increases with decreasing grain size for yttria-stabilized zirconia ceramics produced by high-pressure spark plasma sintering, a hardening-softening transition occurs at very high interfacial areas, with grain sizes below ?21 nm. The experiments indicate that this transition depends on strain rate, and the onset of the decrease in yield streng
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Article Title: Size-induced grain boundary energy increase may cause softening of nanocrystalline Yttrium Stabilized Zirconia
Authors: Arseniy Bokov, Joao B. Rodrigues Neto, Feng Lin, Ricardo Castro
Keywords: zirconia, grain boundary energy, Hall-Petch relationship
Abstract: An increase in hardness with reducing grain sizes is commonly observed in oxide ceramics in particular for grain sizes below 100 nm. The inverse behavior, meaning a decrease in hardness below a critically small grain size, may also exist consistently with observations in metal alloys, but the causing mechanisms in ceramics are still under debate. Here we report direct thermodynamic data on grain boundary energies as a function of grain size that suggest that the inverse relation is intimately related to a size-induced increase in the excess energies. Microcalorimetry combined with nano and microstructural analyses reveal an increase in grain boundary excess energy in yttria-stabilized zirconia (10YSZ) when grain sizes are below 36 nm. The onset of the energy increase coincides with the observed decrease in Vickers indentation hardness. Since grain boundary energy is an excess energy related to boundary strength/stability, the results suggest that softening is driven by the activation o
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Article Title: Atomistic modeling of La
Authors: Shenli Zhang, Haoyan Sha, Ricardo H. R. Castro, Roland Faller
Keywords: GRAIN-BOUNDARY SEGREGATION; SOLID OXIDE ELECTROLYTES; MINIMUM ENERGY PATHS; ELASTIC BAND METHOD; MOLECULAR-DYNAMICS; OXYGEN DIFFUSION; SADDLE-POINTS; SIMULATIONS; ZRO2; YSZ
Abstract: The effect of La3+ doping on the structure and ionic conductivity change in nanocrystalline yttria-stabilized zirconia (YSZ) was studied using a combination of Monte Carlo and molecular dynamics simulations. The simulation revealed the segregation of La3+ at eight tilt grain boundary (GB) structures and predicted an average grain boundary (GB) energy decrease of 0.25 J m(-2), which is close to the experimental values reported in the literature. Cation stabilization was found to be the main reason for the GB energy decrease, and energy fluctuations near the grain boundary are smoothed out with La3+ segregation. Both dynamic and energetic analysis on the sigma 13(510)/[001] GB structure revealed La3+ doping hinders O2- diffusion in the GB region, where the diffusion coefficient monotonically decreases with increasing La3+ doping concentration. The effect was attributed to the increase in the site-dependent migration barriers for O2- hopping caused by segregated La3+, which also leads to
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Article Title: In Situ Transmission Electron Microscopy for Ultrahigh Temperature Mechanical Testing of ZrO
Authors: Robson L. Grosso, Eliana N. S. Muccillo, Dereck N. F. Muche, Gowtham S. Jawaharram, Christopher M
Keywords: In situ; Transmission electron microscopy; Ultrahigh temperature; Nanomechanical testing; Nanocrystalline; Grain boundary
Abstract: This work demonstrates a novel approach to ultrahigh-temperature mechanical testing using a combination of in situ nanomechanical testing and localized laser heating. The methodology is applied to characterizing and testing initially nanograined 10 mol % Sc2O3-stabilized ZrO2 up to its melting temperature. The results suggest that the low-temperature strength of nanograined, d < 50 nm, oxides is not influenced by creep. Tensile fracture of ZrO2 bicrystals produce a weak-temperature dependence suggesting that grain boundary energy dominates brittle fracture of grain boundaries even at high homologous temperatures; for example, T = 2050 degrees C or T approximate to 77% T-melt. The maximum temperature for mechanical testing in this work is primarily limited by the instability of the sample, due to evaporation or melting, enabling a host of new opportunities for testing materials in the ultrahigh-temperature regime.
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Article Title: Experimental phase diagram for beryllium-magnesium aluminate nanoparticles
Authors: Brian M. Rogers, Ricardo H.R. Castro
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Abstract: An experimental phase diagram for nanoscale dimensions was constructed for BeAl2O4-MgAl2O4 solid solutions in which polymorphs can be identified as a function of crystallite size (or temperature) and composition. Spinel and chrysoberyl are the main phases present in the diagram. Because nanoscale phase diagrams account for the energetic contribution of the surface of particles, the results enabled the calculation of the surface energies for spinel and chrysoberyl nanoparticles at various compositions, which showed a decrease in the average surface energy of spinel particles as the Be2+ content increased while the average surface energy of chrysoberyl slightly increased. The energetic data suggest spinel particles incorporate Be2+ into the structure until it reaches a saturation concentration, after which, additional Be2+ ions segregate to the surface. Chrysoberyl particles do not readily incorporate Mg2+, as evident by the minimal change in surface energies and the formation of spinel
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Article Title: A model for direct and inverse Hall-Petch relation for nanocrystalline ceramics
Authors: Alexander G. Sheinerman, Ricardo H.R. Castro, Mikhail Yu. Gutkin
Keywords: Ceramics; Hardness; Hall-Petch effect; Micromechanical modeling
Abstract: A model describing both direct and inverse Hall-Petch dependences observed in nanocrystalline ceramic MgAl2O4 spinel is proposed. Within the model, plastic deformation in nanocrystalline ceramics (NCCs) is realized via lattice dislocation slip combined with thermally activated grain boundary (GB) sliding. The model strongly suggests that the controlling parameter determining the type (direct or inverse) of the Hall-Petch dependence is the GB sliding activation energy. It is assumed that this quantity can be affected by the temperature regime of NCC synthesis and therefore rationalize conflicting data reported in the literature concerning the onset of the inverse Hall-Petch behavior in this system.
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Article Title: Ultrahigh temperature in situ transmission electron microscopy based bicrystal coble creep in Zirconia II: Interfacial thermodynamics and transport mechanisms
Authors: Robson L. Grosso, K.S.N. Vikrant, Lin Feng, Eliana N.S. Muccillo, Dereck N.F. Muche, Gowtham S. Jaw
Keywords: grain boundary kinetics, strain rate, zirconia, deformation, model
Abstract: This work uses a combination of stress dependent single grain boundary Coble creep and zero-creep experiments to measure interfacial energies, along with grain boundary point defect formation and migration volumes in cubic ZrO2. These data, along with interfacial diffusivities measured in a companion paper are then applied to analyzing two-particle sintering. The analysis presented indicates that the large activation volume, v(*) = v(f) + v(m) primarily derives from a large migration volume and suggests that the grain boundary rate limiting defects are delocalized, possibly due to electrostatic interactions between charge compensating defects. The discrete nature of the sintering and creep process observed in the small-scale experiments supports the hypothesis that grain boundary dislocations serve as sources and sinks for grain boundary point defects and facilitate strain during sintering and Coble creep. Model two-particle sintering experiments demonstrate that initial-stage densific
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Article Title: Ultrahigh temperature in situ transmission electron microscopy based bicrystal coble creep in zirconia I: Nanowire growth and interfacial diffusivity
Authors: K.S.N. Vikrant, Robson L. Grosso, Lin Feng, Eliana N.S. Muccillo, Dereck N.F. Muche, Gowtham S. Jaw
Keywords: in situ Electron microscopy, Creep, ZrO2, nanoceramics
Abstract: This work demonstrates novel in situ transmission electron microscopy-based microscale single grain boundary Coble creep experiments used to grow nanowires through a solid-state process in cu bic ZrO2 between approximate to 1200 degrees C and approximate to 2100 degrees C. Experiments indicate Coble creep drives the for mation of nanowires from asperity contacts during tensile displacement, which is confirmed by phase field simulations. The experiments also facilitate efficient measurement of grain boundary diffusivity and surface diffusivity. 10 mol% Sc2O3 doped ZrO2 is found to have a cation grain boundary diffusivity of D-gb = (0.056 +/- 0.05)exp(-380,000 +/- 41,000/RT)m(2) s(-1), s and surface diffusivity of D-s = (0.10 +/- 0.27)exp(-380,000 +/- 28,000/RT)m(2) s(-1).
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Article Title: Interfacial energies in nanocrystalline complex oxides
Authors: Ricardo H.R. Castro
Keywords: nanoceramics, synthesis, processing, thermodynamics
Abstract: This paper presents a brief description of the role of interfacial energies in the understanding and control of nanocrystalline complex oxides in both particulate and bulk forms. Interfacial energies are fundamental parameters in microstructural evolution processes such as phase transformation, grain growth, and sintering. Although generally considered constant driving forces, experimental evidences confirm the possibility of intentional modification of both surface and grain boundary energies in oxide systems via ionic doping. This opened the perspective for a systematic understanding of their roles as refining parameters in microstructural control during processing and in operation. In this work, the theoretical framework in the context of Gibbs adsorption isotherm and the formation of dopant excess (i.e. interfacial solute segregation) is introduced in a similar manner as formalized for liquid systems. A collection of data demonstrating interfacial energy control in oxides is presen
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Date Submitted: 5/19/22 12:00AM Date Published: 10/21/21 7:00AM
Publication Location:
Article Title: Al excess extends Hall-Petch relation in nanocrystalline zinc aluminate
Authors: Luis E. Sotelo Martin, Ricardo H. R. Castro
Keywords: nanoceramics, mechanics, hardness, zinc alumiante
Abstract: Increasing hardness with decreasing grain size is a well-known effect observed in ceramics and metals referred to as the Hall-Petch relationship. In ceramics, there has been controversy surrounding the existence of a low size limit below which size-induced hardening no longer occurs and softening is observed instead. In the present study, this so-called inverse-Hall-Petch relationship is observed in quasi-stoichiometric dense nanocrystalline zinc aluminate, but an extension of the normal Hall-Petch behavior is demonstrated in Al-rich zinc aluminate nanoceramics. Vickers hardness increased with grain refining for quasi-stoichiometric samples prepared by High Pressure Spark Plasma Sintering, exhibiting a maximum of 18.6 GPa at a grain size of 21.4 nm. Conversely, Al-rich zinc aluminate produced by the same technique strengthened up to 19.2 GPa at 12.6 nm grain sizes. Cross-sections of Vickers indentation imprints showed that while quasi-stoichiometric zinc aluminate presented changes in
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Article Title: Sintering, hardness and cation inversion of nanocrystalline beryllium – magnesium aluminate ceramics
Authors: Brian M. Rogers, Isabella L.M. Costa, Weidi Zhu, Sabyasachi Sen, Ricardo H. R. Castro
Keywords: nanoceramics, mechanics, hardness, beryllium magnesium aluminate
Abstract: Beryllium-magnesium aluminate (Be0.1Mg0.9Al2O4 and Be0.2Mg0.8Al2O4) nanoparticles are synthesized by a coprecipitation method and sintered using Spark Plasma Sintering (SPS) to achieve near full density ceramics with grain sizes at the nanoscale. The sintered nanoceramics display grain sizes ranging from 14 to 33nm, which are analyzed for optical transmission, Vickers hardness, and cation site inversion. When compared to Be-free MgAl2O4 nanoceramics, both Be0.1Mg0.9Al2O4 and Be0.2Mg0.8Al2O4¬ show transmissions ~30% lower at wavelength in the infrared range. The samples show a Vickers hardness of ~19. 2GPa with no apparent dependence on grain size. These values are consistently lower to those reported for beryllium-free MgAl2O4 spinel with similar grain size. 27Al and 9Be Nuclear Magnetic Resonance (NMR) spectroscopy reveals that beryllium does not have a significant effect on cationic site inversion in the spinel and, similar to beryllium-free MgAl2O4, inversion remains solely a functi
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Journal: Materials Letters
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Article Title: Sodium as densification aid in $MgAl_2O_4$ nanoceramics
Authors: Isabella Costa, Joice Miagava, Ricardo Castro
Keywords: $MgAl_2O_4$, magnesium aluminate, hardness, SPS, sintering
Abstract: Magnesium aluminate nanoceramics show superior hardness due to an extension of the Hall-Petch relationship down to grain sizes below 10 nm. However, the manufacturing of nanoceramics with such exceedingly small grains constitutes a significant challenge. This work proposes sodium as an effective dopant to reduce the processing requirements to achieve full densification with inhibited coarsening. Using Spark Plasma Sintering, we produced fully dense transparent Na doped $MgAl_2O_4$ under 400 MPa at 1000°C with grain sizes below 15 nm. Na-doped samples achieved toughness (K_{1C}) as high as 5.23 MPa/m1/2, surpassing values characteristic of undoped $MgAl_2O_4$ with a similar grain size, 3.57 MPa/m1/2 . The role of Na^+ as a sintering aid is briefly discussed.
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Date Received: 07-May-2020
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Description: Highlight on ARO funded research by the American Ceramic Society

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Partners

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I certify that the information in the report is complete and accurate:
Signature: Ricardo Castro
Signature Date: 5/31/22 11:45AM

Title: Metastable Grain Boundary Configurations for Ultrahigh Strength Nanoceramics

PI: Ricardo H. R. Castro

Final Report - W911NF1810361

Summary: This document describes the activities performed by the PI's group towards the achievement of the goals of the project, which are: (Goal #1) to develop synthetic and processing techniques capable of producing ceramic parts with grain sizes in the nanoscale regime (targeting sizes below 10nm); (Goal #2) utilize the obtained products to explore mechanical properties of nanoceramics, enabling development of fundamental understanding on size induced effects on, particularly, hardness and toughness; (Goal #3) based on the developed knowledge, understand and propose mechanisms to increase toughness and hardness of nanocrystalline ceramics.

One of the main products was the education of a new generation of PhD with expertise in advanced ceramic processing. Three graduate students have graduated from this project, Arseniy Bokov (Ph.D., graduated 2018), Chenguang Yang (M.Sc. graduated 2018), and Brian Rogers (M.Sc. graduated 2019). Additionally, one Ph.D. student will graduate in the Summer of 2022, Luis Sotelo Martin and another Ph.D. student, Isabella Costa, will graduate in 2023 (will be funded by other sources since the project is now concluded). In the summer of 2021, one undergrad student participated in the Summer Internship program sponsored by ARO - AEOP, Taha Hussain.

The project was performed during the period of the COVID pandemic. This impacted the proposed activities due to lab closures and limited lab access in 2020 and 2021. During the gap, we have developed partnership with Prof. Jeremy Mason at UC Davis and Dr. Blas Uberuaga, for a collaboration on modelling of the systems using atomistic simulation. Two of the grad students, Luis Martin and Isabella Costa, were co-mentored during the period and has developed significant data that adds up well to the theories and concepts developed on the experimental part.

During this project, the group has published 14 articles, all in peer reviewed and respected journals in the field. There are other four manuscripts submitted or under preparation with expected publication time still in 2022. We produced three thesis under this project, one PhD and two Masters, and have two others lined up, one for 2022 and one in 2023.

Below we present the summary of discoveries of this project divided by the specific goals:

Goal #1: Developing processing capabilities for dense nanoceramics

The project has developed and consolidated methodologies for the processing of nanocrystalline ceramics with grain sizes below 20nm. **Figure 1** presents a step-by-step protocol for the achievement of fully dense nanoceramics.

The protocol includes the synthesis of nanoparticles with grain sizes below 10nm. Although simple oxides have generally been produced as nanopowders in the past, complex oxides such as $MgAl_2O_4$ and $ZnAl_2O_4$, as well as systems containing dopants, require synthesis design. We focused most of our attention on coprecipitation methods within this projects, making usage of precipitation window software, such as MEDUSA, to find the conditions for combined precipitation of multiple ions. This allowed a refined control of the stoichiometry of the system, an important parameter impacting the mechanical properties of the final nanoceramic product. The second step constitutes the degassing of the powders. This is a critical stage to allow a surface clean of impurities such as water and CO2 molecules. These molecules are typically ignored during common ceramic sintering protocols. However they require temperature and time to be removed for the surface. If the sintering is pushed to occur without the proper elimination of these molecules, those can get trapped and affect the integrity of the final dense nanoceramics. On the other hand, if sintering is carried out slowly to allow for the molecules to desorb, the process will induce coarsening, compromising the nanocrystallinity of the product. In this project we introduced the degassing stage as a key element for successful manufacturing. The powders are subjected to mild temperatures, 400 °C, under vacuum using a Micromeritics SmartVac degassing station, causing the molecules to desorb. The degassed powder is then transferred to a N_2 filled glove box, in which it is assembled in a SiC-Diamond die. This die is designed to withstand high pressures under high temperatures.

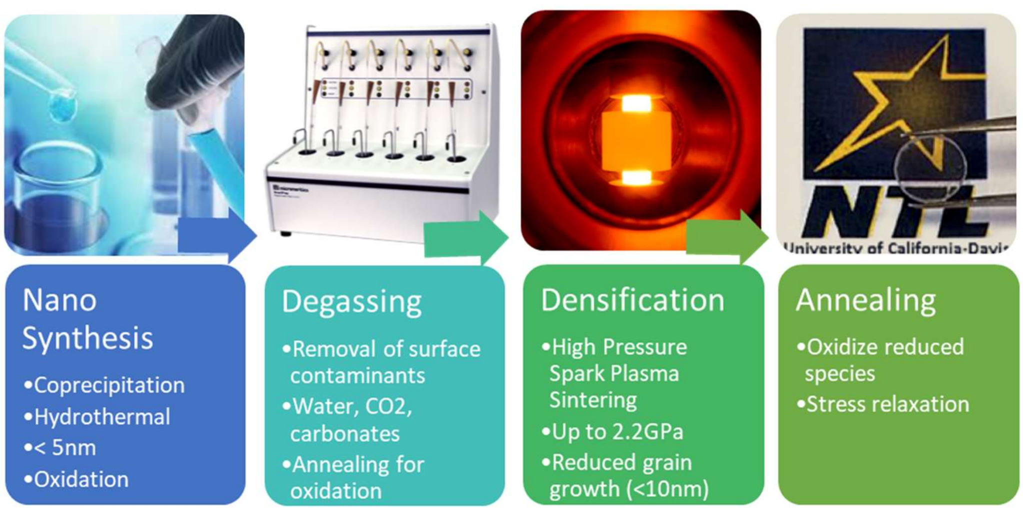


Figure 1. Schematics of the processing steps to fabricate nanocrystalline dense ceramics. Highlights for this project are the development of the high pressure die (SiC/Diamond composite) and the degassing step.

As a subsequent step, the loaded die is transferred to the SPS, in which high pressures and high heating rates are applied to cause densification. Pressures up to 2.2PGa are needed, with temperatures ranging from 700 to 1200 °C. The sintering time is no longer than 15 minutes, resulting in fully dense materials. Fine conditions for densification are defined after preliminary tests and design of experimental grids. The final product needs to be carefully handled. This is because the pellets are generally fragile because of the intense reduction happening during sintering in an oxygen free chamber. The pellets need to be annealed under oxygen to regain mechanical strength.

The project started with the production of small samples in the shape of discs with 4mm in diameter. That dimension limits the characterization that can be performed in terms of mechanical tests. For instance, while hardness tests can be performed in such pellets after extensive polishing (**Figure 2**), toughness can only be calculated by the edge cracks representing K1C. This is known to be only an indirect measure of toughness due to the high complexity of the cracking formed underneath the indentation. Therefore, it is desirable to develop more complex shapes.

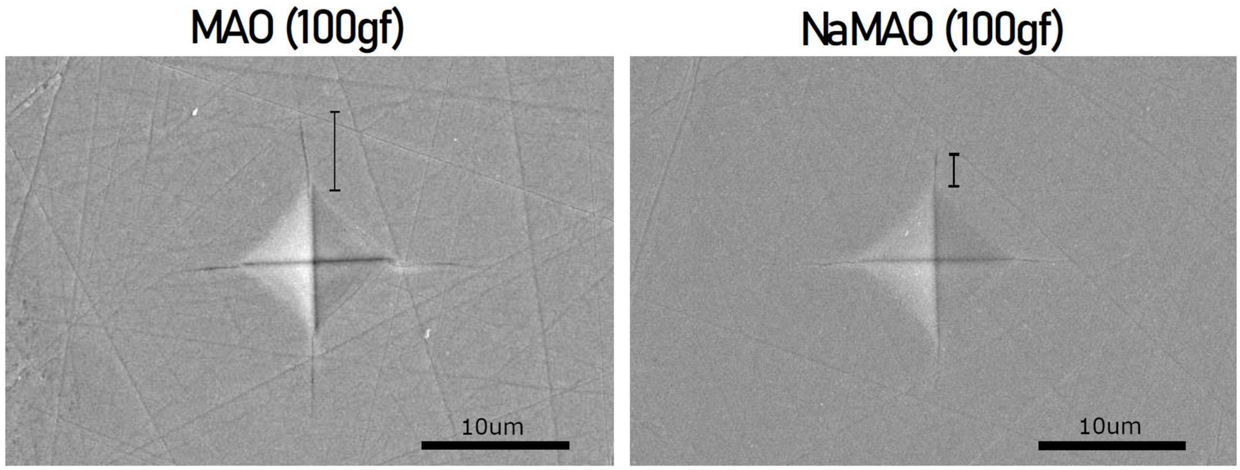
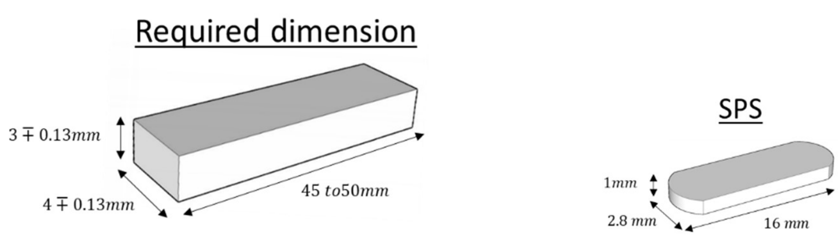


Figure 2. $MgAl_2O_4$ (MAO) and Na-doped $MgAl_2O_4$ (NaMAO) indicating distinct edge cracks supporting Na doped samples show increased toughness. K1C is 3.57 for MAO and 4.45 for NaMAO.

This constitute a non-trivial problem because of the high pressures used in the sintering process. Targeting samples of proper dimension for flexural strength tests, we designed a bar-die setup. According to ASTM C1421-10 requirements, a sample for toughness/ flexural strength test is required to have at least 45mm in length. Based on the maximum forces available in our instrumentation (27kN), this dimension was not practicle as it would not be possible to input 2.1 GPa of pressure given the large sample area. Alternatively, as seen in **Figure 3**, we proposed a smaller bar-shaped die set, with round edges to minimize stress concentration and with 16mm in length and a proportional width adjustment.



	Flexural Strength (MPa)
This work	234 ± 20
Rowthu et. al	262

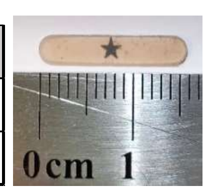


Figure 3. ASTM C1421-10 requirement of dimensions versus proposed SPS die designed for high pressure.

The newly designed die was effective in providing high density ceramics during sintering in bar-shape. To test how mechanical properties measured in these dimensions compare with the ASTM C1321-10, we ran micro-alumina bars to compare with the literature. As seen in **Figure 3**, the measured flexural strength of alumina in the small bar shape was very consistent with the data found in the literature by Rowthy et al (Ceram Int, 44, 2018). This reassured we could continue with the project for the flexural strength measurements using the sample with the reduced dimensions. This new SiC/Diamond die allowed high pressures and therefore the fabrication of highly transparent Na-$MgAl_2O_4$ free of cracks as seen in Figure 4.

The processing advancements are unique and have been reported in the literature in terms of manuscripts, as represented by these citations: [1–6]

More importantly, the development of the processing technique for ultra-fine nanoceramics enables a systematic study of the dependencies of hardness and toughness of nanoceramics on the chemistry of interfaces and microstructures for the develop a coherent predictive theory. This entails Goals #2 and #3.

Goal #2 and #3: Understanding nanomechanics

The high quality samples produced by the project enabled the systematic study concerning hardness and toughness of nanoceramics. The project made major advancements in hardness understanding, but the results for toughness are still limited and more studies are needed beyond this project.

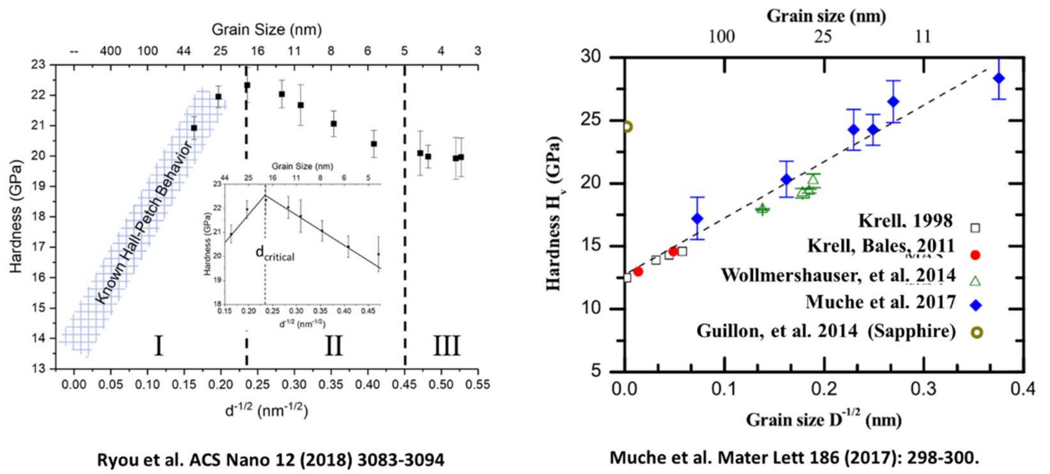
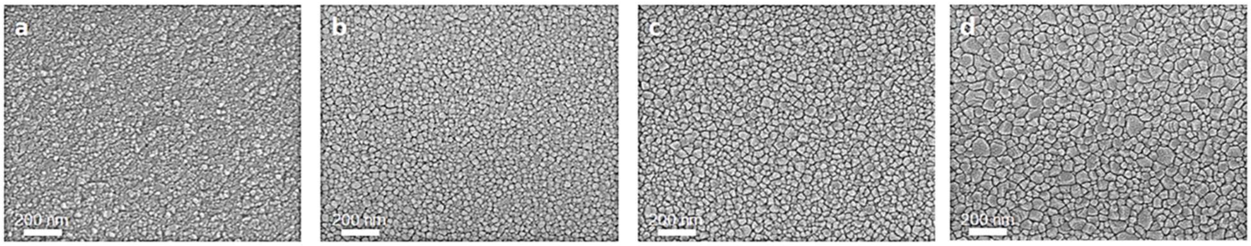


Figure 4. Hardness trends in $MgAl_2O_4$ nanoceramics as published by our group and from other literature.

As seen in **Figure 4**, there has been significant discussions regarding the hardness increase and potential decrease as grain sizes reach the nanoscale dimensions. While it is expected hardness should increase as a result of grain refinement following the known Hall-Petch relationship, some studies have reported an inverse behavior. This is consistent with the metals' literature although with likely very different mechanisms governing the process. In metals, grain boundary sliding was set as the main mechanism behind softening of nanocrystalline metals. However, it is not obvious that in ceramics there would exist such high mobility.

To test this hypothesis, YSZ was selected as a model system. Nanoceramics was produced as detailed in **Figure 5** showing SEM of the produced pellets as well as the processing conditions. Note that the samples are fully dense and grains very homogeneous in size.



10YSZ samples for mechanical testing

16.8 ± 0.9 nm	to 660°C in 7 min	to **925°C** in 11 min	120 MPa at 7 ½ min	430 MPa at 8 ½ min	870 MPa at 9 ½ min	1300 MPa at 10 ½ min	1600 MPa at 11 ½ min	1900 MPa at 12 ½ min	**2100 MPa** at 13 ½ min
19.1 ± 1.0 nm	to 700°C in 7 min	to **960°C** in 10 min	120 MPa at 8 min	430 MPa at 9 min	870 MPa at 10 min	1150 MPa at 11 min	1450 MPa at 11 ½ min	**1700 MPa** at 12 ½ min	
21.4 ± 1.2 nm	to 710°C in 7 min	to **970°C** in 10 min	120 MPa at 8 min	430 MPa at 9 min	870 MPa at 10 min	1150 MPa at 11 min	1450 MPa at 11 ½ min	**1700 MPa** at 12 min	
27.3 ± 1.6 nm	to 840°C in 8 min	to **1040°C** in 10 min	120 MPa at 9 min	430 MPa at 10 min	870 MPa at 11 min	1050 MPa at 11 ½ min	**1250 MPa** at 12 min		
36.3 ± 2.5 nm	to 900°C in 8 min	to **1090°C** in 9 min	120 MPa at 9 min	430 MPa at 10 min	870 MPa at 11 min	**1000 MPa** at 11 ½ min			
47.7 ± 3.2 nm	to 950°C in 9 min	to **1140°C** in 8 min	120 MPa at 9 ½ min	430 MPa at 10 ½ min	**800 MPa** at 11 ½ min				

Bold represents the final (maximum) temperature and pressure reached during the processing cycle.

Figure 5. YSZ nanoceramics produced by SPS. SEM images on the top and a table describing the sintering protocols developed after extensive experimental grid design.

Vickers hardness was measured as well as the grain boundary energy using calorimetric techniques. **Figure 6** plots the hardness as a function of grain size along with the energy data. It is noticeable that the hardness increases with grain size decrease but presents a softening behavior for grains below about 28nm. The softening onset coincides with the increase in grain boundary energy. In fact, grain boundary energy is related to the strength of individual grain boundary. A reduction of energy is therefore representing stronger grain boundaries.

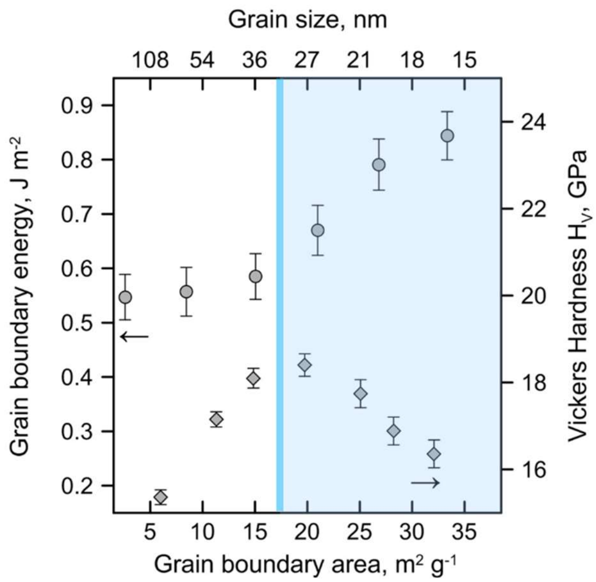


Figure 6. YSZ nanoceramics hardness and grain boundary energy measured using calorimetric techniques.

To further understand this connection, we used Focus Ion Beam to observe the deformation (or cracking behavior) found underneath the hardness indentation point. As seen in **Figure 7**, a sample identified before the breakdown point presents a single crack normal to the indentation. On the other hand, a sample with grain size smaller than the breakdown point shows a complex network of cracks. Both samples showed a limited unaffected zone, referred to as quasi-plastic behavior. It is unclear if these areas present shearing of grain boundaries but it is evident that crack formation is much more favorable at smaller grain sizes.

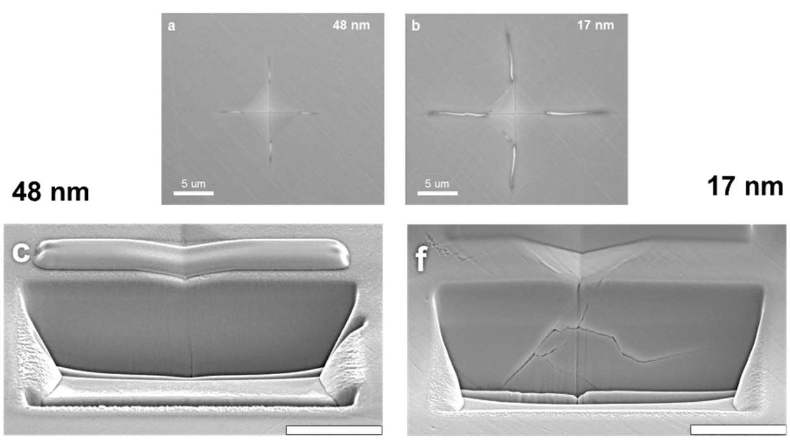


Figure 7. YSZ nanoceramics Vickers hardness indentations and cross section showing cracking pattern underneath.

The scenario implies that an increase in strength of the grain boundary, by reduction of grain boundary energy, could be a potential strategy to improve hardness. We selected La as a dopant on YSZ and demonstrated that the dopant indeed reduces grain boundary energies by using DSC techniques as seen in **Figure 8** for 0.5, 1 and 1.5 mol%La in 10YSZ. The energy scales with the K1C data, demonstrating the grain boundary reduction improves toughness. However, it was intriguing to observe that such a small reduction in GB energy can cause a significant macroscopic impression. This is because crack energy is typically of the order of 12J/m^2, and a change in energy of 0.5J/m^2 should not be meaningful. We later proposed studies correlating the energy distribution across multiple grain boundaries as more relevant than the absolute energy itself.

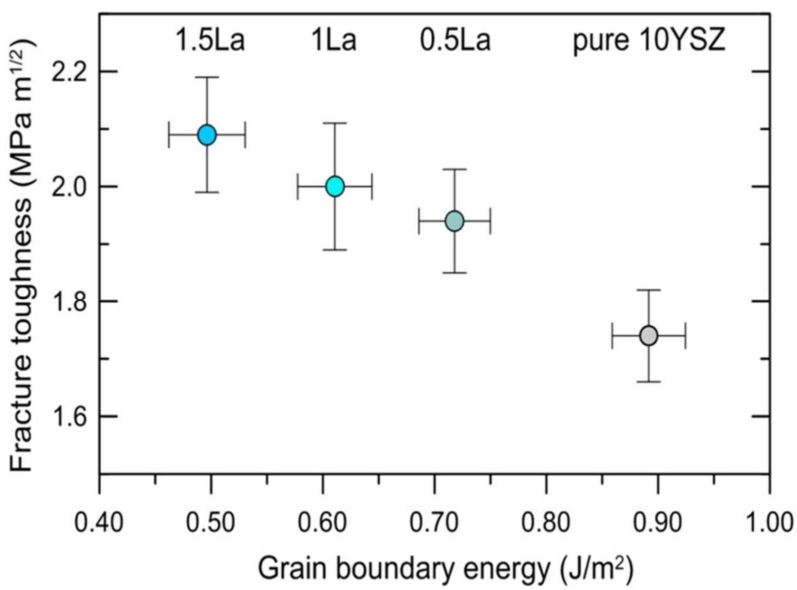


Figure 8. Grain boundary energy as measured by Differential Scanning Calorimetry plotted against K1C for YSZ nanoceramics.

The combined data provide better understanding on how and why the breakdown of the Hall-Petch relationship happens in some materials and not in others. Here we demonstrate that high grain boundary energies are responsible for it, and so, metastable low energy grain boundaries can provide an enhanced hardness in the material. The metastable configuration can be achieved by dopants segregated, such as La and Gd in YSZ. It is still not sure why and how these dopants act so that a more detailed and predictive dopant selection can be made, but **Figure 9** shows unpublished data on Gd doped YSZ nanoceramics showing improved hardness as compared to the undoped YSZ system.

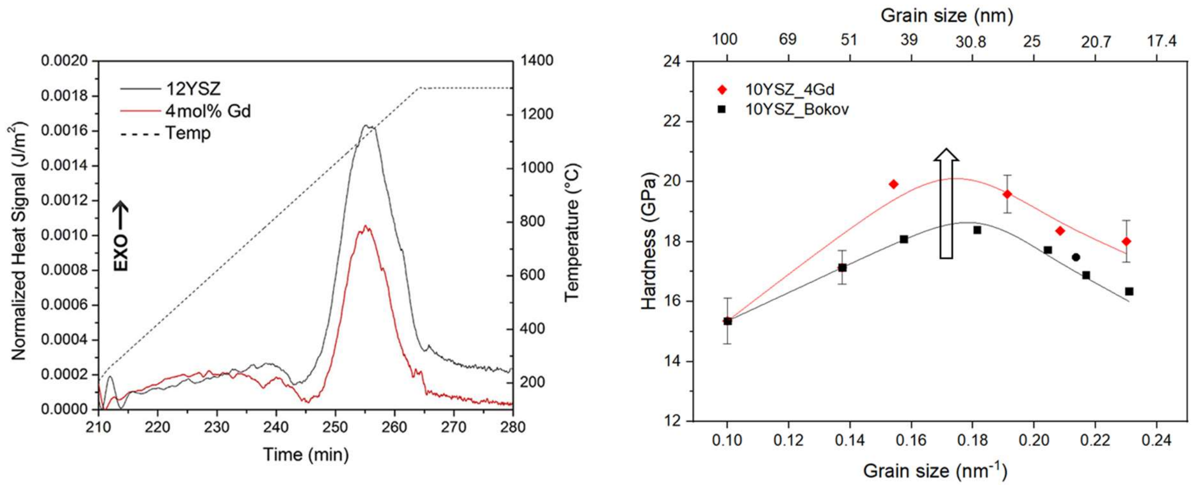


Figure 9. Left is the DSC run for undoped and doped YSZ nanoceramics showing how Gd as a dopant reduces the growth energy, and hence the grain boundary energy itself. The right image shows the increase in Vickers hardness for the doped YSZ, with hardness surpassing 20GPa.

While dopants are an attractive option for doping, we have also explored the possibility of using off-stoichiometry to manipulate the grain boundary chemistry in complex oxides. Taking the example of Zinc Aluminate, $ZnAl_2O_4$, we produced dense nanoceramics with two different Zn:Al ratio, stoichiometric (S-ZAO) and Al-rich (E-ZAO). As seen in **Figure 10**, the samples containing excess of Al presented significant postponement of the Hall Petch relationship down to grain sizes below 15nm, as compared to 20-25nm for the undoped aluminate. Cross-sections of Vickers indentations showed that while quasi-stoichiometric zinc aluminate presented changes in sub-surface cracking pattern from larger to smaller grain sizes (before and after the inverse Hall-Petch), the Al-rich samples had sub-surface cracking consistently similar to those found in large 9rain sizes in quasi-stoichiometric samples. **Figure 10** shows a schematic representation of the sub-surface cracking pattern and the respective hardness data as a function of grain size for stoichiometric (S) and Al-excess (E) zinc aluminate (ZAO).

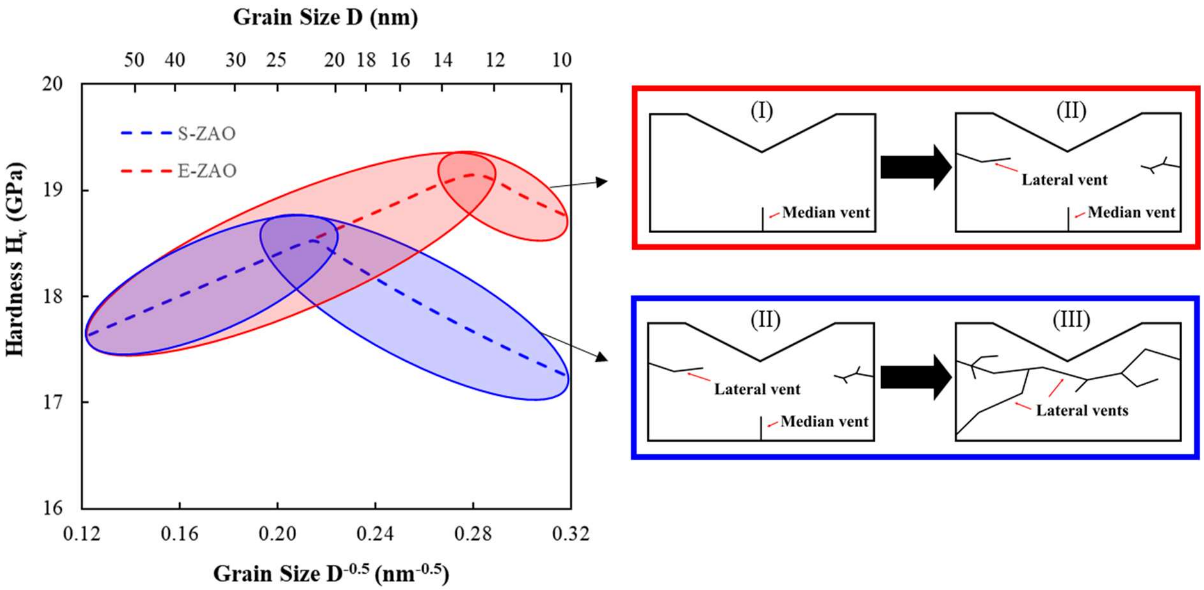


Figure 10. (I) Indentation cross-section exhibiting only a median vent found only in E-ZAO (II) cracking pattern featuring limited lateral vents, and a median vent which was found in large-grained S-ZAO and small-grained E-ZAO, and (III) pattern observed in small-grained S-ZAO with lateral vents extending through the entirety of the cross-section. S-ZAO transitions from mode II cracking to mode III with decreasing grain size while E-ZAO instead moves from mode I to mode II.

An analytical model developed also within this project was then used to better understand the data. In the model, the activation energy for grain sliding, or grain shearing, was set as the main parameter affecting the reduction of hardness. As seen in **Figure 11**, the data can be nicely fit with the model, and the activation energy calculated. It is clear that the Al-excess increased the activation energy for grain boundary shearing, leading to the postponement of the Hall-Petch relationship down to smaller grain sizes.

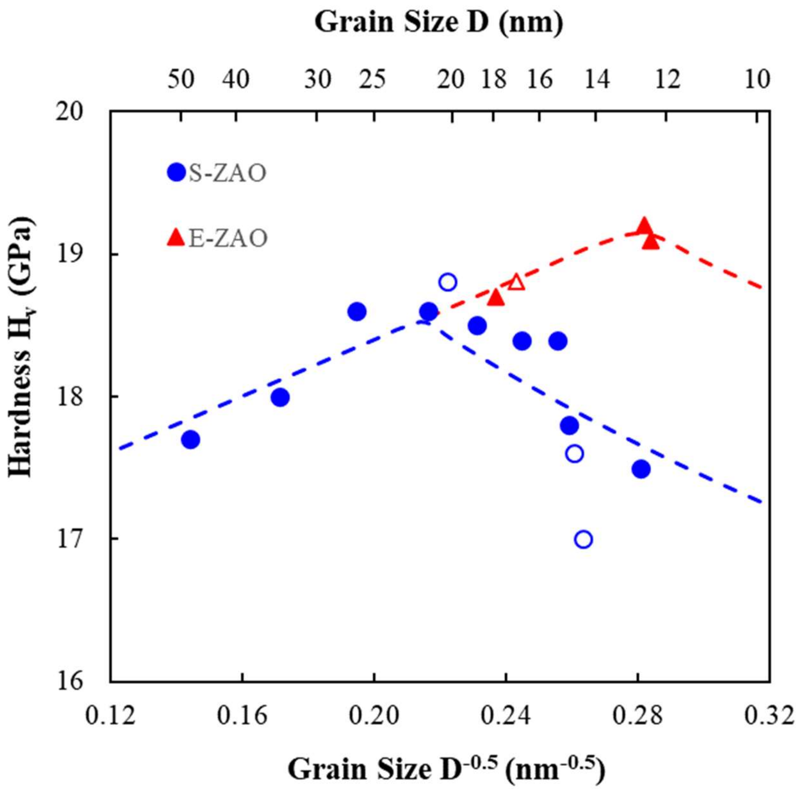


Figure 11. Vickers hardness plotted in Hall-Petch form for all S-ZAO (blue) and E-ZAO (red) samples along with their fits (dashed lines) according to the Sheinerman et al. model. Samples sintered using deformable-punch spark plasma sintering are denoted in hollow symbols. The model estimates a grain boundary sliding activation energy of 94.9 and 97.2 kJ/mol for S-ZAO and E-ZAO respectively.

This result constitutes the first published evidence the Hall-Petch behavior can be intentionally controlled in ceramics, and one can use grain boundary configurations (with Al-excess) to improve the mechanical properties of transparent ceramics. The demonstration of this hypothesis is one of the main goals of this project, and we now continue to refine the controlling strategies, particularly targeting the increase in toughness and flexural strength.

Atomistic Simulations

The pandemic created some obstacles for experimental research, particularly during the year of 2020. Therefore, we have connected with Dr. Jeremy Mason, a faculty in the Department of Materials Science and Engineering, and Dr. Blas Uberuaga at the Los Alamos National Laboratory, to pursue alternative research projects which could be done remotely and were still aligned with the goals of this proposal.

With Dr. Mason, we started a front targeting the Monte Carlo simulation of the energy of segregation of dopants to the interfaces (surface and grain boundary) of zinc aluminate. Based on the preliminary experimental data, it is apparent the grain boundary energy offers a concrete opportunity to control mechanical properties of nanoceramics. Grain boundary energy can be tuned with the change in local chemistry, which is associated with the segregation of ions to the interfacial region. The potential for segregation of a dopant ion can be assessed by Monte Carlo simulation as we have previously reported in our group for other systems. Dr. Mason educated the student Luis Martin on the techniques of coding the structure and simulating the energy of the system reliably. The results are now finalizing and show interesting trends on the surface energies as a function of dopant. For example, we have studied a sigma3 grain boundary for zinc aluminate, and computed the total energy system when Y was included in the system at different positions. As we moved the dopant from the bulk to the grain boundary region, it was clear the energy of the system decreased, representing a spontaneous heat of segregation of the dopant as seen in **Figure 12**. Four dopants were studied (Y, Sc, In, Nd) and the Y was the one with the highest energy of segregation for this particular grain boundary.

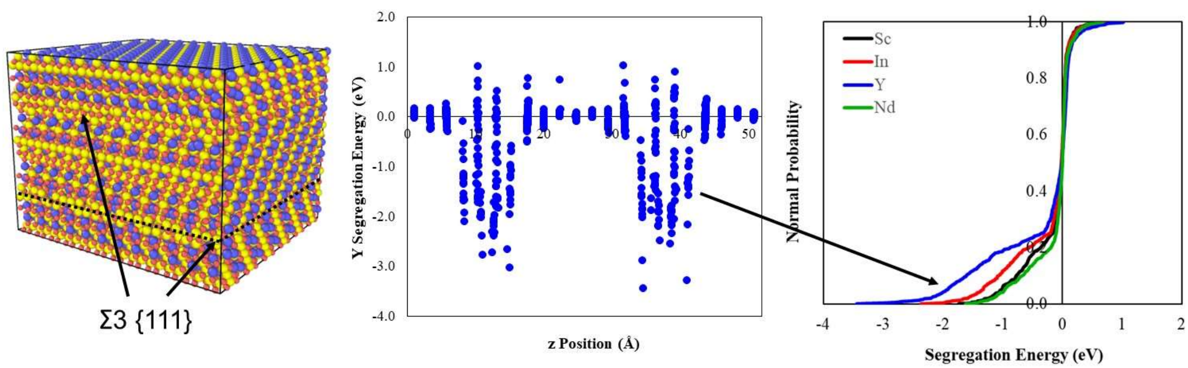


Figure 12. (left) Structured constructed for zinc aluminate with two grain boundaries. (center) Relative **p**otential energy of a zinc aluminate system doped with Y. The dopant was positioned at different locations of the system and the lowest energy positions represent the grain boundary regions created in the modelled system. (right) Four dopants were studied and the segregation energies are shown here.

The results from MC calculations are well aligned with the experiments but during this Summer the student is still working to finalize experiments and putting together an article on the topic.

With Dr. Uberuaga, we focused on Na as a potential dopant for $MgAl_2O_4$ nanoceramics to increase strength of the grain boundaries. A clear potential for segregation of Na to the interfaces of $MgAl_2O_4$ could be calculated as seen in **Figure 13**. The results suggest Na is an effective dopant to strengthen $MgAl_2O_4$ grain boundaries, possibly affecting its mechanical properties. In fact, we performed a simulation of the mechanical behavior of a system with two grain boundaries, as seen in **Figure 14**. The results indicate Na improves the toughness of the material.

The simulated results are consistent with experimental data on the flexural strength of Na-doped $MgAl_2O_4$. As seen in **Figure 15**, Na improved the performance in contrast to the undoped sample, but both 12 and 1.5mol% Na showed comparable improvement. The results for the $MgAl_2O_4$ nanoceramics were consistently superior to the single crystal in terms of elastic modulus.

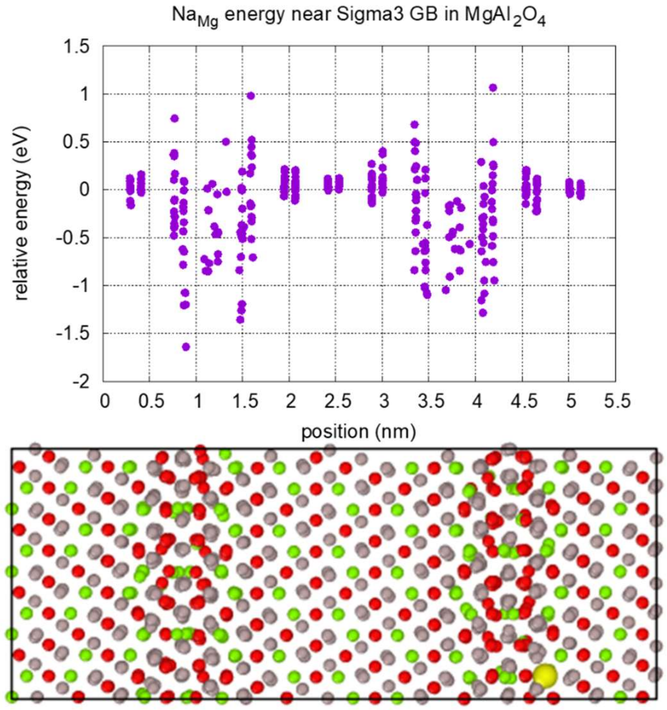


Figure 13. Relative energy of a $MgAl_2O_4$ system with two grain boundaries as a function of Na replacement at different locations. Segregation to interfaces, or more precisely to the first vicinity of the grain boundary, leads to reduced energies.

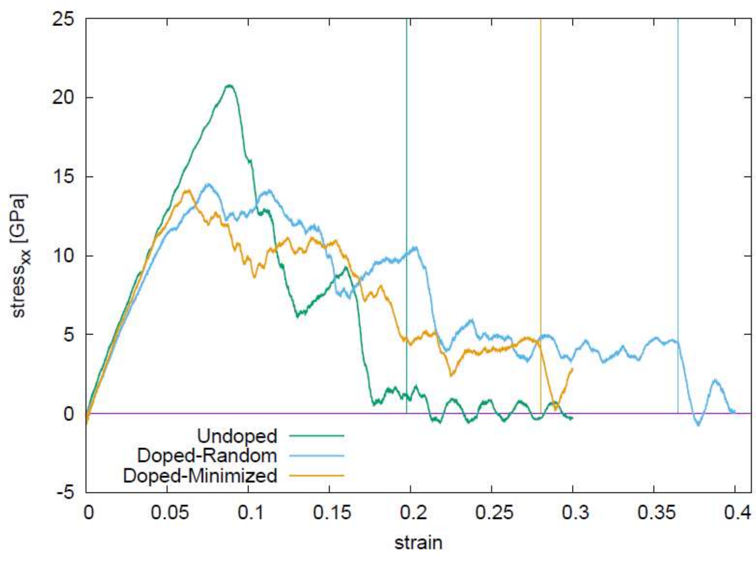


Figure 14. Simulated stress-strain curve demonstrating that although the undoped system has still higher strength, the dopant improves toughness.

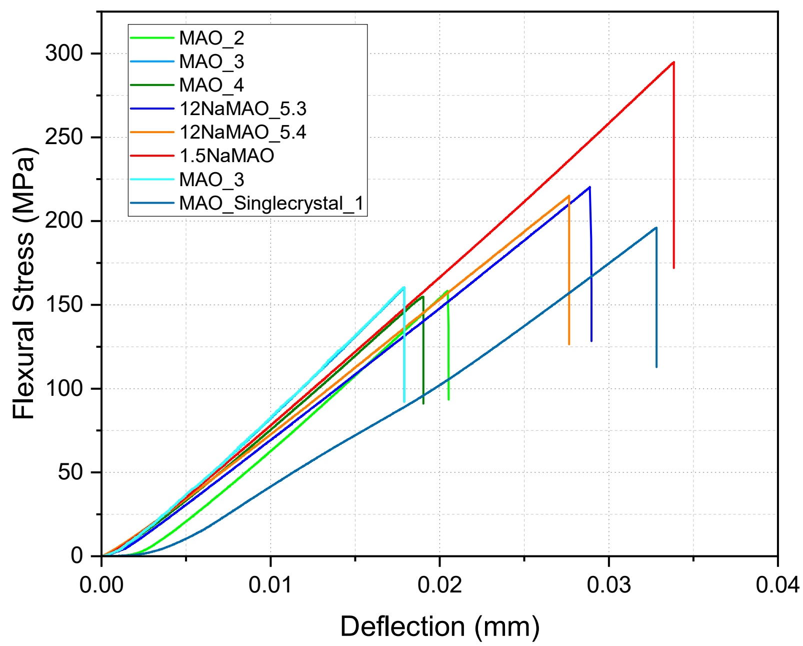


Figure 15. Experimental data on the flexural strength of $MgAl_2O_4$ nanoceramics bars with Na. Single crystal data is added for reference.

Although these results are still incomplete, it is clear that the design of grain boundaries with segregated dopants can improve the toughness of nanoceramics. Simulation techniques can apparently help to identify ions with potential for segregation even when considering the assumptions and oversimplifications of the models. This is encouraging as can serve as a potential tool to explore multiple dopants and minimize experimental efforts.

Publications

During this project, 14 papers have been published, representing a significant advancement to the scientific and engineering community concerned with nanocrystalline ceramic materials. (see references for extended list) [1-3, 6–16]

Talks by the PI presenting project's results (since 2021):

Invited Talk: Engineering the Nano-Revolution in Energy Solutions. LNNano – Brazilian National Laboratory of Nanotechnology.

Invited Talk: Enhancing Strength in Nanocrystalline Transparent Ceramics. MS&T'21 - Materials Science and Technology 2021, Columbus, OH, USA.

Invited Talk: Controlling Synthesis of Nanostructures with Nanoscale Phase Diagrams. MS&T'21 - Materials Science and Technology 2021, Columbus, OH, USA.

Talks by Students:

Costa, I, Castro RHR. Dopant designed to increase toughness in nanocrystalline spinel. ICACC'22 - International Conference and Exposition on Advanced Ceramics and Composites, Virtual Presentation, January 27, 2022. (Talk)

Costa, I, Castro RHR. Effect of sodium on the Processability and Mechanical Properties of Nanocrystalline Magnesium Aluminate. MS&T'21 - Materials Science & Technology Technical Meeting and Exhibition, Virtual Presentation, October 19, 2021. (Talk)

Sotelo Martin LE, Castro RHR. Enhanced hardness from modified stoichiometry in nanocrystalline zinc aluminate. ICACC'22 - International Conference and Exposition on Advanced Ceramics and Composites, Virtual Presentation, January 27, 2022. (Talk)

Sotelo Martin LE, Castro RHR. Hall-Petch behavior in stoichiometric and Al-rich nanocrystalline ZnAl2O4. MS&T'21 - Materials Science & Technology Technical Meeting and Exhibition, Virtual Presentation, October 19, 2021. (Talk)

Sotelo Martin LE, Castro RHR. Interface stability of nanocrystalline ZnAl2O4 doped with rare earths (RE). American Ceramic Society, ICACC'21 - International Conference and Exposition on Advanced Ceramics and Composites, Virtual Presentation, February 8, 2021. (Talk)

Student training

The project trained graduate and undergraduate students on modern techniques of manufacturing, characterization and testing of nanoceramics. It allowed the students to be educated not only through course work at UC Davis, but also with hands-on research activities in the laboratory and with the modelling add-ons.

Students were trained in manufacturing via conventional sintering and spark plasma sintering, being now capable of development manufacturing protocols, including detailing materials and designing of dies, temperature and heating profiles, and pressure parameters to achieve controlled microstructures.

Synthesis of nanocrystalline powders, being able to adapt processes to complex chemistries for homogeneous and 'clean' nanopowders.

Students have been trained in sophisticated characterization techniques, including:

- (Scanning) Transmission Electron Microscopy and its diverse set of combined techniques, such as EDS, EELS and electron diffraction, as well as protocols of sample preparation and Experience in analyzing data.

- Scanning Electron Microscopy, including EDS, microprobe, Focus Ion Beam, and details of sample preparation. Experience in analyzing data.

- X-ray diffraction, covering equipment calibration, maintaining, fixing, and running powder and pellet samples. Running fitting programs to extract information from the diffraction patterns. Experience in analyzing data.

- Calorimetric techniques, including Differential Scanning Calorimetry and Water Adsorption Microcalorimetry. Data analysis and interpretation of complex heat signals.

- Other microstructural tests: Density measurements, BET surface area measurements, infrared spectroscopy, UV-Vis spectroscopy.

- Mechanical tests, such as hardness measurements and flexural strength with 3-point bending. Including sample preparation and data interpretation with statistics.

Future Works

The present project has brought novel understanding of nanocrystalline ceramic processing and mechanical properties. While the processing of nanoceramics with grain sizes below 20nm in fully dense ceramics have been demonstrated, there are many questions still open concerning the mechanical behavior and how to design metastable interfaces.

1) While we have established a relationship between grain boundary energy and hardness in YSZ, we are still testing if a similar relationship exists in other materials.
2) It is apparent that a reduction of grain boundary energy can improve the hardness of nanoceramics by changing the cracking pattern underneath the indentation. We are using dopants to create metastable configurations of grain boundaries but the rational behind selection of dopants and how they act are still open for research.
3) Toughness and flexural strength of nanoceramics are also related to grain boundary energies and chemistry. The metastable configurations can provide improvement, but the dopant roles are still unclear. While we noticed that Gd/La increased hardness and toughness in YSZ, Na was able to more remarkably improve fracture toughness of $MgAl_2O_4$. More systematic works will be required to delineate the role of valences states, ionic radius, and grain boundary energies.
4) While we proposed a model for the inverse Hall Petch relationship addressing grain boundary strength as a key controlling parameter, the model is still very simplified and needs further development in terms of thermos-kinetic parameters to allow for design.
5) There are other questions concerning the segregation locations. That is, is anisotropy of segregation playing a major role in the mechanics of the system? We had one evidence that La (by simulations) was observed to change the energy landscape in YSZ nanoceramics. Is this a rule? How can we exploit this more quantitatively?
6) The project also opens the perspective for exploring dual doping in nanoceramics. Can different grain boundaries accommodate different dopants? Perhaps with the concept of making on grain boundary strong, but another more ductile?

These and other questions have emerged as potential developments of this project. The current results are already of great interest to the ARO as we enabled the fabrication, although in very small scale, of nanoceramics with novel properties. We hope to continue the partnership with ARO to further push the limits of nanoceramic materials for future Army technologies.

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