FINAL Report DOE DE-SC0006637

a. DOE Grant Number: DE-SC0006637 - Recipient: University of California, Davis
b. Title of Award: "Energetics of Radiation Tolerant Nanoceramics" - PI: Ricardo H. R. Castro
c. Report Date: December 5, 2016 - Period of Report: May/2015 – July/2016 - FINAL

d. A brief description of accomplishments.

In this fifth year of project, the project achieved maturity and achieved the goals as for scientific objectives and career development of the PI, giving this is an Early Career Program Award. The project clearly established the role of energetics on the stability of nanocrystalline materials under irradiation, proposing solid theories, supported by experimental data, to the scientific community. The PI is highly regarded in the field at this point and will continue a fruitful career in nuclear materials for energy solutions thanks to this grant. For his contributions to the usage of calorimetry to solve nuclear materials problems, the PI has received the 2015 Stig Sunner Award at the Calorimetry Conference, another testimonial of his impact to the society.

More specifically, the project delivered 9 papers during this past year of review, being a total of 20 since the start of the project. There are still 2 manuscripts in preparation that were supported by this grant and will have proper acknowledgements. In addition, we have presented invited talks in many international conferences, e.g. MS&T20152, Calcon 2015, ICTAC 2016, had two papers published in **Chemistry of Materials** (impact factor 9.4) and one in **International Materials Reviews** (impact factor 11.4). The project also helped educate graduate students (Dereck Muche, Arseniy Bokov, Hui Li), undergraduate (David Loyola), and postdocs (Sanchita Dey).

According to the initial proposal, the general aim of this project was to consolidate a research group dedicated to using calorimetric methods to provide a comprehensive thermodynamic background for the development of novel nanocrystalline ceramics capable of withstanding intense radiation damage. Specifically, we proposed the experimental evaluation of what is the dependence of the phase-transition induced by radiation (e.g. crystalline to amorphous) in nanocrystalline materials on the grain boundary energy and area. We proposed the directly measurement of interface energies using calorimetry in series of nanomaterials with compositions of potential interest in radiation shielding: the aluminate based spinels (MAl_2O_4, M = Mg, Ni, or Zn), and zirconia based materials (ZrO_2 doped with Mg, Y, or Ca).

The activities planned for these years of the project (1^{st} to 5th year) included (1) the synthesis and characterization of spinels, (2) the synthesis and characterization of ZrO_2 based nanoparticles, (3) measurement of interfacial energies, (4) irradiation of samples at Los Alamos National Lab, (5) characterization of irradiated produced and (6) development of fundamental theories combining thermodynamics and defects. In summary, the project achieved its main goal as reported in two main publications by the group (and one more in preparation), that summarize the points [1]. Below are key conclusions from the project:

- In summary, we have discovered and proven that the radiation tolerance of nanomaterials is strongly dependent on their thermodynamics, in particular the balance between the interfacial energies and the enthalpy of bulk amorphization.
- Crystalline materials with low interface energy and high amorphization energy show better performance at the nanoscale as compared to coarsened materials.

[1] Dey, S., et al., Radiation Tolerance of Nanocrystalline Ceramics: Insights from Yttria Stabilized Zirconia. Scientific Reports, 2015. 5; Dey, S., et al., Irradiation-induced grain growth and defect evolution in nanocrystalline zirconia with doped grain boundaries. Physical Chemistry Chemical Physics, 2016. 18(25): p. 16921-16929.

- However, while lowering this energy by using dopants prone to segregation to the interface regions can increase the stability of nanomaterials against production of defects, the allocation of dopants also alters the availability of interfaces as sinks for defects during irradiation cascade events.
- Moreover, nanomaterials will have always a tendency to irradiation induced grain growth. We prove this is not thermally activated grain growth but is rather a result of the mechanism of defect accommodation, which basically simulates positioning atoms at the interfaces. This mimics a crystal growth process at the interface that leads to microscopic grain growth.
- Since irradiation induced grain growth is not alike thermally activated grain growth, typical methods to avoid thermal growth, such as pinning agents and lowering grain boundary energies are ineffective.
- However, results indicate that if the grain boundary energy is lowered enough, the system can be posed in a situation where creating new grain boundaries can be more energetically favorable than eliminating it by grain growth. This can increase the life time of nanomaterials under irradiation for engineering applications.

The conclusions about the radiation effects of nanomaterials are of high impact and consequences to the nuclear community. However, to obtain that level of understanding, highly controlled nanomaterials needed to be manufactured. Therefore, to a great extension, this project sponsored development of techniques that enable the manufacturing of such unprecedented samples. From nanoparticles of oxides with sizes below 5nm to nanograined samples with grain sizes below 15 nm, the technique advancements opened perspectives for many others to test hypothesis of nano-effects on truly clean and nanocrystalline materials. Major scientific achievements related to this:

- Controlled process for the synthesis of oxides with particle sizes below 5nm, to allow manufacturing of dense samples with grains below 20nm, was developed based on coprecipitation. The method can be applied to a number of oxides.
- A densification die-set was designed and built to be working on Spark Plasma Sintering, to allow densification with minimal grain growth. This achievement created the possibility of studying nanograined samples of zirconia and ceria for this project not as thin films as typically reported in the literature, but as bulk pellets representing the real material property and without substrate influences.

In addition to manufacturing development, this project also developed new techniques to measure interfacial energies using calorimetry and theoretical backgrounds that allowed the control of interfacial energies, both surfaces and grain boundaries, by the usage of dopants. This served as a bridge of collaboration with the Los Alamos National Lab, Dr. Blas Uberuaga, that could atomistic simulate the role of dopants on interfacial energies for a direct comparison with experimental results provided by this project. Note that the fundaments here were key to develop the findings described above on the role of interfacial energies on the control of radiation tolerance of nanomaterials. Without these developments, the conclusions on that matter would've been incomplete and lacking proof. Some of the major scientific findings from this project on calorimetry and interface energy control:

- A novel method to measure the surface energy of oxide nanoparticles was developed. This is non-destructive and utilizes water as a molecule-probe and is based on the developed theoretical concept that the heat of adsorption of water on the surface of a particle can be directly linked to the surface energy if the right calorimetric experiment is performed. This allowed rapid characterization of surface energies for any given composition.
- The surface energy measurements allowed the building up of phase diagram for oxide in the nanoscale. That is, nanoparticles have a great fraction of surfaces that affect the total energy of the system significantly. In systems with two or more polymorphs, the stability of the

phase is determined by both surface energy bulk enthalpies. In this project we built phase diagrams for zirconia based systems. The predictive diagrams are considered the greatest advance in phase diagram science in decades and were developed within this project sponsorship.

- We demonstrated for the first time that a dopant, such as La or Mn, can lower surface and grain boundary energy of zirconia, ceria and other oxides. This was directly demonstrated by measuring surface and grain boundary energies using calorimetric techniques. The result enabled purpose lowering on interfacial energies to examine the role of interfacial energies on the radiation tolerance of nanomaterials. The concept of segregation of dopants to lower interfacial energies is now well consolidated and has several implications to nanostability and even mechanical properties, as reported in papers from the group within this project.
- As a different approach to manipulation of grain boundaries, we have demonstrated that high electric fields can modify the equilibrium position of atoms located at interfaces, changing the distribution of the space charge layers and affecting phenomena such as grain growth. Now that we have demonstrated this effect, future work lies on determining the effects of such novel grain boundary chemistry on the radiation tolerance of nanomaterials.

The interlinked successes described above are all reported in specific publications. Since some of them have been reported in previous reports, in this report we will focus on the papers published in this period (9 in total), with an extra session for data that is still not published, but should be submitted shortly to high impact journals.

1.1. Irradiation-induced grain growth and defect evolution in nanocrystalline zirconia with doped grain boundaries.
Published in Physical Chemistry Chemical Physics, 18, 16921(2016).

Abstract: Grain boundaries are effective sinks for radiation-induced defects, ultimately impacting the radiation tolerance of nanocrystalline materials (dense materials with nanosized grains) against net defect accumulation. However, irradiation-induced grain growth leads to grain boundary area decrease, shortening potential benefits of nanostructures. A possible approach to mitigate this is the introduction of dopants to target a decrease in grain boundary mobility or a reduction in grain boundary energy to eliminate driving forces for grain growth (using similar strategies as to control thermal growth). Here we tested this concept in nanocrystalline zirconia doped with lanthanum. Although the dopant is observed to segregate to the grain boundaries, causing grain boundary energy decrease and promoting dragging forces for thermally activated boundary movement, irradiation induced grain growth could not be avoided under heavy ion irradiation, suggesting a different growth mechanism as compared to thermal growth. Furthermore, it is apparent that reducing the grain boundary energy reduced the effectiveness of the grain boundary as sinks, and the number of defects in the doped material is higher than in undoped (La-free) YSZ.

1.2. Improving the Thermodynamic Stability of Aluminate Spinel Nanoparticles with Rare Earths
Published in Chemistry of Materials, 28, 5163 (2016).

Abstract: Surface energy is a key parameter to understand and predict the stability of catalysts. In this work, the surface energy of $MgAl_2O_4$, an important base material for catalyst support, was reduced by using dopants prone to form surface excess (surface segregation): Y^{3+}, Gd^{3+}, and La^{3+}. The energy reduction was predicted by atomistic simulations of spinel surfaces and experimentally demonstrated by using microcalorimetry. The surface energy of undoped MgAl2O4 was directly measured as 1.65 ± 0.04 J/m^2 and was reduced by adding 2 mol % of the dopants to 1.55 ± 0.04 J/m^2 for Y-doping, 1.45 ± 0.05 J/m^2 for Gd-doping, and 1.26 ± 0.06 J/m^2 for La-doping. Atomistic simulations are qualitatively consistent with the experiments, reinforcing the link between the role of dopants in stabilizing the surface and the energy of segregation. Surface segregation was experimentally assessed using electron energy loss spectroscopy mapping in a scanning transmission electron microscopy image. The reduced energy resulted in coarsening inhibition for the doped samples and, hence, systematically smaller particle sizes (larger surface areas), meaning increased stability for catalytic applications. Moreover, both experiment and modeling reveal preferential dopant segregation to specific surfaces, which leads to the preponderance of {111} surface planes and suggests a strategy to enhance the area of desired surfaces in nanoparticles for better catalyst support activity.

1.3. Stabilization of $MgAl_2O_4$ spinel surfaces via doping
Published in Surface Science 649, 138 (2016)

Abstract: Surface structure of complex oxides plays a vital role in processes such as sintering, thin film growth, and catalysis, as well as being a critical factor determining the stability of nanoparticles. Here, we report atomistic calculations of the low-index stoichiometric magnesium aluminate spinel ($MgAl_2O_4$) surfaces, each with two different chemical terminations. High temperature annealing was used to explore the potential energy landscape and provide more stable surface structures. We find that the lowest energy surface is {100} while the highest energy surface is {111}. The surfaces were subsequently doped with three trivalent dopants (Y^{3+}, Gd^{3+}, La^{3+}) and one tetravalent dopant (Zr^{4+}) and both the surface segregation energies of the dopants and surface energies of the doped surface were determined. All of the dopants reduce the surface energy of spinel, though this reduction in energy depends on both the size and valence of the dopant. Dopants with larger ionic radius tend to segregate to the surface more strongly and reduce the surface energy to a greater extent. Furthermore, the ionic valence of the dopants seems to have a stronger influence on the segregation than does ionic size. For both undoped and doped spinel, the predicted crystal shape is dominated by {100} surfaces, but the relative fraction of the various surfaces changes with doping due to the unequal changes in energy, which has implications on equilibrium nanoparticle shapes and therefore on applications sensitive to surface properties.

1.4. Synthesis of Ca-doped spinel by Ultrasonic Spray Pyrolysis
Published in Materials Letters 171, 232 (2016)

Abstract: $MgAl_2O_4$ is a stable catalyst support with potential for replacing gamma-alumina in several applications. However, synthesis of magnesium spinel requires elevated temperatures to avoid phase separation (in MgO and Al_2O_3) at low temperatures, leading to coarsening and reduction of active surface area. In this work, nano CaO-doped and undoped magnesium aluminate were successfully prepared by Ultrasonic Spray Pyrolysis (USP), using a simple adapted experimental set-up operating at 1100°C. During the process, the particles stay at high temperatures for a short period of time, allowing phase stability and limited coarsening. The influence of calcium oxide on the particles morphology and structure was investigated via X-ray diffraction, N_2 adsorption, X-ray fluorescence, scanning electron microscopy and transmission electron microscopy. The spinel nanopowders were obtained as spherical porous agglomerates of ~1µm. The resulting powder showed low crystallite sizes in the 5–10nm range and high specific surface area from 110.0 to $76.6 m^2 g^{-1}$.

1.5. Thermodynamic Strengthening of Heterointerfaces in Nanoceramics
Published in Chemistry of Materials 28, 2897 (2016)

Abstract: The properties of nanocomposites and layered materials with two or more crystalline phases are strongly dependent on their interfacial features. In terms of mechanical strength, this means a strong dependence on interfacial local bonding and coordination characters. From a thermodynamic perspective, these terms directly related to interfacial energy and thus reveal a significant link between the interface thermodynamics and the mechanical behavior - a connection not well explored in the design of nanocomposites with multiple crystalline phases. Here we demonstrate for the first time that a targeted reduction in the interfacial energy of a magnesium aluminate-zirconium oxide bi-phase nanocomposite can be used to remarkably increase the flexural strength of the ceramic nanocomposite. Interface energy reduction was achieved by introducing a dopant prone to segregation using Gibbs adsorption concepts. The remarkable energy decrease, from 1.09 J/m^2 to 0.38 J/m^2, was directly measured by using microcalorimetry and caused a two-fold increase in flexural strength of the nanocomposite.

1.6. Photocatalytic Nb_2O_5-doped TiO_2 nanoparticles for glazed ceramic tiles
Published in Ceramics International 42, 5113 (2016)

Abstract: TiO_2 nanoparticles are currently used as coating for self-cleaning building products. In order to achieve high self-cleaning efficiency for outdoor applications, it is important that titania is present as anatase phase. Moreover, it is desirable that the particle sizes are in nano-range, so that a large enough surface area is available for enhanced catalytic performance. In this work, TiO_2 nanoparticles doped with 0–5mol% Nb_2O_5 were synthesized by co-precipitation. Nb_2O_5 postponed the anatase to rutile transformation of TiO_2 by about 200°C, such that after calcination at 700°C, no rutile was detected for 5mol% Nb_2O_5-doped TiO_2, while undoped TiO_2 presented 90wt% of the rutile phase. A systematic decreasing on crystallite size and increasing on specific surface area of TiO_2 were observed with higher concentration of Nb_2O_5 dopant. Photocatalytic activity of anatase polymorph was measured by the decomposition rate of methylene blue under ultraviolet and daylight illumination and compared to commercial standard catalyst (P25). The results showed enhanced catalysis under UV and visible light for Nb_2O_5-doped TiO_2 as compared to pure TiO_2. In addition, 5mol% Nb_2O_5-doped TiO_2 presented higher photocatalytic activity than P25 under visible light. The enhanced performance was attributed to surface chemistry change associated with a slight shift in the band gap.

1.7. Grain growth resistant nanocrystalline zirconia by targeting zero grain boundary energies
Published in Journal of Materials Research 30, 2991(2015)

Abstract: Nanocrystalline ceramics offer interesting and useful physical properties attributed to their inherent large volume fraction of grain boundaries. At the same time, these materials are highly unstable, being subjected to severe coarsening when exposed at moderate to high temperatures, limiting operating temperatures and disabling processing conditions. In this work, we designed highly stable nanocrystalline yttria stabilized zirconia (YSZ) by targeting a decrease of average grain boundary (GB) energy, affecting both driving force for growth and mobility of the boundaries. The design was based on fundamental equations governing thermodynamics of nanocrystals, and enabled the selection of lanthanum as an effective dopant which segregates to grain boundaries and lowers the average energy of YSZ boundaries to half. While this would be already responsible for significant coarsening reduction, we further experimentally demonstrate that the GB energy decreases continuously during grain growth caused by the enrichment of boundaries with dopant, enhancing further the stability of the boundaries. The designed composition showed impressive resistance to grain growth at 1100 °C as compared to the undoped YSZ and opens the perspective for similar design in other ceramics.

1.8. Obtaining highly dense YSZ nanoceramics by pressureless, unassisted sintering
Published in International Materials Reviews 60, 353 (2015).

Abstract: For technological applications, zirconia is commonly blended with other oxides to stabilise the tetragonal and/or cubic phases at low temperature, being yttria the most frequently added dopant.

It is generally desirable to obtain highly dense ceramics while maintaining grain sizes in the nanoscale (< 100 nm). Small grains contribute to stabilise the tetragonal phase and to improve the toughness and flexural strength. Moreover, a higher ionic conductivity for cubic zirconia electrolytes is achieved with smaller grain size and lower thickness of the intergranular regions. The sintering onset temperatures required for nanometric particles are significantly reduced when compared to conventional micrometric powders. However, densification is generally accompanied by an undesirable grain coarsening. A Ramp and Hold Sintering (RHS) is the simplest densification schedule, consisting of heating up to the peak temperature followed by a holding time at that temperature. Another approach, called Two-Step Sintering (TSS) is based on the principle that the activation energy for grain growth is lower than the activation energy of densification. The key elements in this method are heating up to a high temperature to achieve a density >75% Theoretical Density (TD) to render the pores unstable, and then cooling down rapidly to a lower temperature to finish sintering and hinder grain growth. Alternatively, considerable efforts have been made in increasing the heating rate and/or reducing the hold time at the peak temperature during sintering cycles in processes that are generally referred to as ‘Fast Firing’ (FF) or ‘rapid sintering’. This review summarises the attempts in the literature for obtaining dense monolithic nanocrystalline Yttria-Stabilized Zirconia (YSZ) ceramics by pressureless sintering schedules carried out in conventional furnaces. RHS, FF and TSS schedules are reported only from YSZ as starting powders, i.e. without the aid of any additional dopant or grain growth inhibitor. For the sake of comparison, the discussion is focused mainly on YSZ nanoceramics with final densities >99% TD and average grain size < 100 nm. Powder and shaping effects on microstructure and properties of bulk nanoceramics are discussed. A comparison among sintering approaches is then made taking into account the microstructural development of the nanostructures and some key properties of the products.

1.9. DC Electric Field-Enhanced Grain-Boundary Mobility in Magnesium Aluminate During Annealing
Published in Journal of the American Ceramic Society, 99, 1951 (2016)

Abstract: Magnesium aluminate spinel was sintered and annealed at 1300°C under an applied 1000 V/cm DC electric field. The experiment was designed such that current could be removed as a variable and just the effect of a noncontact electric field was studied. Enhanced grain growth was observed for both samples that were sintered or annealed after densification in the presence of an electric field. Grain-boundary character distributions revealed that no microstructural changes were induced due to the field. However, the electric field was found to enhance the kinetic movement of cations within the lattice. Energy-loss spectroscopy experiments revealed cation segregation resulting in regions of Mg-rich and Al-rich layers adjacent the grain-boundary cores. The defects generated during segregation supported the generation of a space charge gradient radiating from the grain-boundary core out into the bulk, which was significantly affected by the applied field. The interaction between the field and space charges effectively reduced the activation energy for cation movement across boundaries thereby enhanced grain-boundary mobility and resultant grain growth.

1.10. Irradiation tolerance and grain growth resistance of Mn doped CeO_2
Manuscript in preparation

A literature survey and results from project suggested an uneasy hypothesis: From an energetic perspective, when a nanograined material is irradiated, its bulk energy is expected to increase as defects accumulate. At the same time, irradiation induced grain growth is trigged (regardless of the mechanism) and decreases the fraction of grain boundaries. However, at certain point, we may argue it is possible that the energy “cost” associated with the accumulation of defects in the bulk of the nanograin is higher than the energy decrease that grain growth brings to the system when irradiated induced grain growth is activated. This will create a specific grain size that should be resistant to irradiated induced grain growth. Because grain boundary energies are dependent on the crystalline planes meeting at the interface, this meta-equilibrium condition would be restrict to a few grains. However, one may also expect that, if the grain boundary energy of a system is generally very low, a relatively large grain may be prone to split into more grains during irradiation (forming new grain boundaries) because it is energetically more favorable than accumulating defects in the single large grain alone.

To test this hypothesis, we have studied the radiation damage on manganese doped CeO_2. Manganese has been observed by our group to segregate to the grain boundaries of CeO_2, significantly decreasing its average grain boundary energy. The grain boundary energy is lowered from 1.08 $J.m^{-2}$ for pure CeO_2 down to 0.3 $J.m^{-2}$. We have then produced nanocrystalline samples (pellets) using Spark Plasma Sintering (SPS) starting with nanoparticles prepared by co-precipitation [33] and irradiated using Kr^{++} ions at 400keV in collaboration with the Los Alamos National Laboratory (Dr. W. Wang). Figure 1 shows representative scanning electron transmission microscopy (STEM) images for the microstructures. Before irradiation, grains are pristine with an average grain size of 118 nm. After irradiation, small grains were formed at triple junctions, as indicated by the arrows in the figure. The average grain size then decreased to 78 nm, as a result of the presence of these small grains with less than 40 nm in the distribution. While this result is somehow surprising, it follows thermodynamics in the sense of decreasing the global energy of the system. It is also consistent with observations of the persistent small grains during irradiation of nanocrystalline gold mentioned above, in particular with respect to the proposed correlation to existence of low energy grain boundaries.

One could suggest a parallel between this phenomenon and grain refinement by plastic deformation, where alloys are plastically deformed to induce formation of dislocations which, when in high concentrations, align forming new grain boundaries. From a thermodynamic perspective, the dislocation alignment occurs to decrease the energy of the system, such that the total energy with nanocrystalline grains (new grain boundaries formed) would be smaller than larger grains with dislocations randomly distributed in the bulk. This image is comparable to our hypothesis, but of course ceramics cannot be deformed plastically enough to create such dislocation density, and the collision cascade events would be responsible for the defect generation and rearrangement. It is even plausible to consider that irradiation can eventually become a path to create nanostructures from large grained ceramics.

The data and hypothesis encourage research to obtain a more comprehensive understanding of the stability of nanograins upon irradiation. Evidences suggest it is feasible to tune the interface energies of a system such that all grains are made resistant to irradiation induced grain growth.

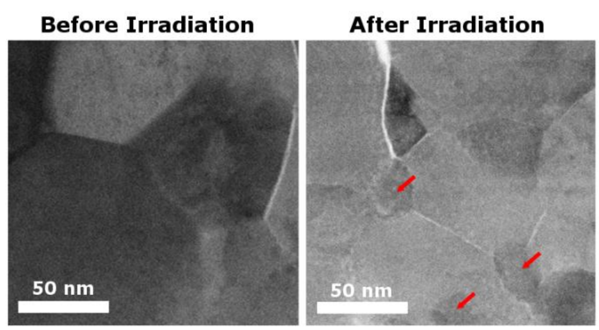

Figure 1. Manganese doped CeO_2 dense pellets before and after irradiation using heavy ions. Formation of new grains suggests a mechanism for lowering excess energy from defects in the crystal bulk.

1.11. Rare earth control of Grain Boundary Energies in Spinel Ceramics

Manuscript in preparation

Enhanced grain growth resistance in $MgAl_2O_4$ spinel nanostructure was achieved by grain boundary (GB) segregation of rare-earth trivalent dopants. The spinel was doped with 2 mol% of R_2O_3 (R = Y, Gd, and La) and dense nanostructures obtained using high temperature spark plasma sintering. GB energies of the undoped and doped samples were measured using microcalorimetry. The GB energy of the undoped spinel was 0.53±0.11 $J.m^{-2}$, which was reduced to 0.32±0.08 $J.m^{-2}$ for Gd-doped spinel, representing significant reduction in the driving force for grain growth. Segregation energies of the three dopants to the Σ3 (111) GB were calculated by atomistic simulation. The dopants with higher ionic radius tend to segregate more strongly to GBs. The GB energies were calculated from atomistic simulation and, consistent with experiments, a systematic reduction in GB energy with dopant ionic size was found. High temperature grain growth experiments were performed and revealed a significant reduction of grain growth in the doped nanostructures as compared to the undoped one, which was attributed to increased metastability or possibly also a GB dragging originated from the dopant segregation.

e. List of Papers

During this project, 20 papers have been published (9 since the last report), and manuscripts are in preparation:

List of Published or In Press since start of project (11) – ***2015-16 period marked with*** **(*)**

1. *Irradiation-induced grain growth and defect evolution in nanocrystalline zirconia with doped grain boundaries. *Physical Chemistry Chemical Physics*, 18, 16921(2016).
2. *Improving the Thermodynamic Stability of Aluminate Spinel Nanoparticles with Rare Earths *Chemistry of Materials*, 28, 5163 (2016).
3. *Stabilization of $MgAl_2O_4$ spinel surfaces via doping. *Surface Science* 649, 138 (2016)
4. *DC Electric Field-Enhanced Grain-Boundary Mobility in Magnesium Aluminate During Annealing. *Journal of the American Ceramic Society*, 99, 1951 (2016)
5. *Synthesis of Ca-doped spinel by Ultrasonic Spray Pyrolysis. *Materials Letters* 171, 232 (2016)
6. *Thermodynamic Strengthening of Heterointerfaces in Nanoceramics. *Chemistry of Materials* 28, 2897 (2016).
7. *Photocatalytic Nb_2O_5-doped TiO_2 nanoparticles for glazed ceramic tiles. Ceramics International 42, 5113 (2016).
8. *Grain growth resistant nanocrystalline zirconia by targeting zero grain boundary energies. *Journal of Materials Research* 30, 2991(2015).
9. *Obtaining highly dense YSZ nanoceramics by pressureless, unassisted sintering. International Materials Reviews 60, 353 (2015).
10. Radiation Tolerance of Nanocrystalline Ceramics: Insights from Yttria Stabilized Zirconia, *Scientific Reports*, 5, 7746 (2015).
11. Phase Stability in Nanocrystals: A Predictive Diagram for Yttria–Zirconia, *Journal of the American Ceramic Society*, 98, 1377 (2015)
12. Synthesis of stoichiometric nickel aluminate spinel nanoparticles, *American Mineralogist*, 100, 652 (2015).
13. Structure and Segregation of Dopant-defect Complexes at Grain Boundaries in Nanocrystalline Doped Ceria, *Physical Chemistry Chemical Physics*, 17, 15375 (2015).
14. Synthesis and Sintering Behavior of Ultrafine (<10 nm) Magnesium Aluminate Spinel Nanoparticles, Rufner, J., Anderson, D., van Benthem, K., Castro, R.H.R., *Journal of the American Ceramic Society*, 96, 2077-2085, 2014.
15. Mechanical properties of individual $MgAl_2O_4$ agglomerates and their effects on densification, Rufner, J. Castro, R.H.R, van Benthem, K., Holland, T., *Acta Materialia*, 69, 187-195, 2014.
16. Water adsorption and interface energetics of zinc aluminate spinel nanoparticles: Insights on humidity effects on nanopowder processing and catalysis, Quach, D., Bonifacio, A.R., Castro, R.H.R. *Journal of Materials Research*, 28, 2004-2011, 2013.
17. Water Adsorption Microcalorimetry Model: Deciphering Surface Energies and Water Chemical Potentials of Nanocrystalline Oxides, Drazin, J., Castro, R.H.R., *Journal of Physical Chemistry C*, DOI: 10.1021/jp5016356

18. On the thermodynamic stability of nanocrystalline ceramics, Castro, R.H.R., *Materials Letters*, 96, 45-56, 2013.
19. Analysis of Anhydrous and Hydrated Surface Energies of gamma-Al_2O_3 by Water Adsorption Microcalorimetry, Castro, R.H.R. and Quach, D., *Journal of Physical Chemistry C*, 116, 24726-24733, 2012.
20. Direct measurement of grain boundary enthalpy of cubic yttria-stabilized zirconia by differential scanning calorimetry, Quach, D. and Castro, R.H.R., *Journal of Applied Physics*, 112, 083527, 2012.

f. List of People Working on the Project

Castro, Ricardo – PI – one summer month
Dey, Sanchita – Postdoc – Partial support – 10 months
Bokov, Arseniy – Graduate Student, Partial Support – 9 months
Ferreira Muche, Dereck – Graduate Student, Partial support – 9 months
Li, Hui – Graduate Student, Partial Support – 6 months
Loyola, David – Undergraduate Student, Partial Support – 1 months

g. Cost status: (see table below)

Year 1 - 7/15/11 – 7/14/12 = $ 152,587
Year 2 - 7/15/12 – 7/14/13 = $ 152,587
Year 3 - 7/15/13 – 7/14/14 = $152,587
Year 4 - 7/15/14 – 7/14/15 = $152,587
Year 5 - 7/15/15 – 7/14/16 = $152,587

Total through 7/14/2016 = $762,935

All funds have been utilized in the project.

h. Future Perspectives

As described in previous sessions, this project has made impressive progress on the understanding of radiation tolerance of nanomaterials, establishing clear energetic boundaries to explain when nanomaterials are more stable under irradiation and when they are not. The future now reserves the refined control of the energetic parameters to allow improvement of radiation tolerance of nanomaterials to avoid the “unavoidable” irradiation induced grain growth. This can only be safely done by using direct measurements of interface energies, allowing tracking of the interfacial energies changes as a function of composition and processing (such as field induced modifications) and the corresponding damage profile during irradiation. Also, this proposal only used fixed dpa damage and room temperature irradiations. It remains necessary to explore the energetic hypothesis with regards to high temperature irradiation and varying doses of irradiation. Although this is relevant, other parallel processes, such as thermally activated grain growth, will overlap with the radiation damage and may confuse the picture of defect evolution. It may be useful to redesign utilizing collaborations with molecular dynamics to separate contributions.

i. Update list of other support (current and pending, federal and non-federal.)

Current
Source of the support: Department of Energy, NEUP
Title of the award: Thermally and Chemically Responsive Nanoporous Materials for Efficient Capture of Fission Product Gases, DE-NE0000704
Award period: 09/01/13 – 08/31/17
Total award amount for the entire award period (including indirect costs): $749,959
Number of person-months per year: 0
Description: This proposal focuses on the development of porous materials to enable capturing of fission products in fuel to avoid strain damage. There is no concept of interfaces being systematically addressed. Background learned from this project will be key to develop this current new proposal.

Current
Source of the support: UC Davis, FAPESP
Title of the award: Interfaces in Ceramic Processing
Award period: 7/1/16-6/30/18
Total award amount for the entire award period (including indirect costs): $20,000
Number of person-months per year: 0
Description: This project deals with the role of interfacial energies on processing of microstructure controlled ceramic oxides. This is a travel/exchanging grant with partners in Brazil (FAPESP)

Current
Source of the support: National Science Foundation
Title of the award: Thermochemistry of Nanoceramics: Understanding and Controlling Densification and Grain Growth
Award period: 7/1/16-6/30/19
Total award amount for the entire award period (including indirect costs): $375,000
Number of person-months per year: 1 (summer)
Description: This project deals with the role of interfacial energies on processing of microstructure controlled ceramic oxides using unprecedented calorimetric techniques.

Current
Source of the support: U.S. Army Research Office - STIR
Title of the award: Grain Boundary Polarization to Increase Toughness of Nanocrystalline Transparent Spinel
Award period: : 7/1/16-3/31/17
Total award amount for the entire award period (including indirect costs): $50,000
Number of person-months per year: 0.2 (summer)
Description: The project explores the role of grain boundary polarization using electric fields to create mechanisms for crack propagation tip arrest.

Pending
Source of the support: Advanced Materials and Devices, Inc. (AMAD)
Title of the award: Ultra-High Carbon Steel Bonded Tungsten Carbide Material for Armor Piercing Rounds
Award period: 7/1/16-4/30/17
Total award amount for the entire award period (including indirect costs): $50,000
Number of person-months per year: 0.2 (summer)
Description of how the funded/pending research differs from this application: This proposal focuses on the development of ultra-hard and heavy WC based projectiles.

Pending
Source of the support: National Science Foundation
Title of the award: Manufacturing of Fully Dense Ultrafine Nanocrystalline Oxides
Award period: 7/1/17 – 6/30/20
Total award amount for the entire award period (including indirect costs): $375,000
Number of person-months per year: 1 (summer)
Description: This project focuses on the development of a manufacturing technique for the production of fully dense nanocrystalline materials based on die design for spark plasma sintering.