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Major Goals: Transparent ceramics are of key interest for ballistic protection of armored tactical platforms in U.S. Army applications. MgAl2O4 spinel is among the materials of choice because of its high light transmittance, and chemical, mechanical, and thermal stabilities. The mechanical properties of polycrystalline spinel are highly dependent on its microstructure; and grain size refinement has been proven to enhance hardness to unprecedented levels. While we have recently demonstrated that grain sizes of 14 nm can lead to hardness above 27GPa (Vickers), these superstrong nanoceramics at ambient temperature show low fracture toughness, limiting their practical utility. Although progress has been made in enhancement of toughness with composites, for applications where transparency is required this has to be done without the inclusion of second phases (such as in dispersion strengthening that causes light scattering). This means that the properties need to be tailored by controlling atomistic mechanisms underlying the failure of the single phased material.
Mechanical behavior of nano-ceramics is strongly dependent on the grain boundary characters. However, the dearth of understanding of this relationship between the local characteristics of grain boundaries and the observed macro-properties hinders proper materials' design. In this project we propose a combination of novel synthesis and processing strategies to allow refined control of atomic structure and bonding at grain boundaries of single-phased nanostructured spinel and cubic zirconia. The goal of the strategies is twofold: (1) strengthen grain boundaries by using dopants prone to segregation. Very small amounts of rare-earth elements are expected to segregate to grain boundaries (due to elastic and electrostatic forces) and form more bonds between neighboring grains than the host ions (lowering the grain boundary energy). This segregation will also allow control of grain boundary energy distribution in the system that can be linked to improvement of fracture energy. (2) Create local polarizations of the grain boundaries to store high electric energy density, enough to influence crack growth. This approach is based on the fact that dielectric materials could potentially be polarized and their toughness increased proportionally to the applied field when this is parallel to the crack plane. Because grain boundaries are more likely to be polarized because of the higher mobility of cations at high temperatures, one can trap poled domains in nanocrystalline ceramics during processing, creating a new toughening mechanism.
The dual effort of targeting grain boundary energy and polarization will be achieved in two complementary tasks. Task 1: Nanoparticles of spinel and cubic zirconia will be synthesized using co-precipitation method. This process can lead to proper segregation of the dopant to the interfaces of the particles due to thermodynamic driving forces. The powders will be sintered to discs using a unique facility at UC Davis that enables grain sizes below 20 nm without residual porosities (that would affect mechanical properties). Samples will be studied in terms of mechanical properties: hardness and indentation toughness. Task 2: Nanoceramic samples will be subjected to high fields at high temperatures to allow grain boundary polarization. Fields up to 3kV/mm will be applied with electrodes not touching the sample. The mechanical behavior of these materials will be comparatively studied in

terms of hardness and flexural strength. The grain boundary energies before and after field application will be measured using microcalorimetric techniques and correlated with mechanical results. Microstructure will be studied with high resolution transmission electron microscopy (TEM). Grain boundary chemistry will be assessed by Electron Energy Loss Spectroscopy in Scanning TEM studies.

Accomplishments: Summary of accomplishments
[complete/detailed version can be found as an uploaded document]

The main goal of this STIR project was to develop fundamental understanding on the toughness of nanocrystalline ceramics, in particular spinel and zirconia, and explore new energy absorption mechanisms to promote enhanced performance. Two main mechanisms were proposed: (1) Grain boundary strengthening by grain boundary energy decrease; and (2) Polarization of grain boundaries by utilizing electric fields. Despite the short period of the project, we were able to stress the first mechanism and demonstrate its efficacy in increasing toughness of zirconia by about 20%. This opens a new research frontier that shall be explored in other oxides. Moreover, we could address the second mechanism, which should that although polarization can be induced by electric fields in the complex oxide $MgAl_2O_4$, the resulting effect on mechanical properties is too small. The results are consolidated in 1 submitted paper, and 4 other manuscripts in preparation (one already at near-submission stage). Note that in the context of the very short time available to accomplish this project (9 months), we consider this a great achievement. The papers will be submitted, but the limited funds to continue the project are certainly delaying the outcome reporting.

Papers submitted or in preparation:
(a) Title: Energetic design of grain boundary networks for toughening of nanocrystalline oxides, submitted.
Abstract: Improving the mechanical performance of nanocrystalline functional oxides can have major implications for stability and resilience of battery cathodes, development of reliable nuclear oxide fuels, strong and durable catalytic supports. By combining Monte Carlo simulations, experimental thermodynamics, and in-situ transmission electron microscopy, we demonstrate a novel toughening mechanism based on interplay between the thermo-chemistry of the grain boundaries and crack propagation. By using zirconia as a model material, lanthanum segregation to the grain boundaries was used to increase the strength of individual boundaries and simultaneously promote a smoother energy landscape in which cracks experience multiple deflections through the grain boundary network, ultimately improving fracture toughness.

(b) Title: Room temperature grain rotation in nanocrystalline ceramics, in preparation.
Abstract: The mechanical behavior of ceramics is generally dictated by its intrinsic higher interatomic cohesion due to ionic/covalent bonding character2. This feature not only increases the energy barrier for deformation, but also imposes additional restrictions for dislocation glide such as preservation of charge neutrality or ion coordinations3. As a result, plasticity in ceramic materials so far has been only been achieved at elevated temperatures, where the higher atomic mobility can accommodate deformation by dislocation motion and grain sliding. Here we demonstrate grain rotation occurring at room temperature in ZrO_2 bulk ceramics when the grains have diameters below ~27nm and samples are absolutely pore-free. The absence of pinning pores facilitates grain boundary dislocation-mediated grain rotation, which becomes the main mechanism of load accommodation as grain sizes are further reduced. This mechanistic observation fundamentally explains the nature of the inverse Hall-Petch relation (i.e. reduction of strength/hardness with decreasing grain size) in ceramics, while building a framework to explore the limits of ceramic (quasi) plasticity.

(c) Title: Electric field effect on grain growth of nanocrystalline $MgAl_2O_4$, in preparation.
(d) Title: Enhanced Grain Boundary Conductivity in La doped YSZ nanoceramics, in preparation.
(e) Title: Improved toughness in sodium doped $MgAl_2O_4$ nanoceramics, in preparation.

Training Opportunities: This projected partially supported a graduate student, Arseniy Bokov and Dereck Muche, towards their Ph.D. programs.

Results Dissemination: Given the short length of the project, only one paper has been submitted for publication for dissemination of the results. The PI will give an Invited Talk at TMS2018 about the results accomplished within this grant.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Ricardo H. R. Castro
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Arseniy Bokov
Person Months Worked: 9.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Dereck Muche
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

STIR: Grain boundary polarization to increase toughness of nanocrystalline transparent spinel

Award No: W911NF-17-1-0026

PI: Ricardo H.R. Castro
Department of Materials Science & Engineering
University of California, Davis

Period of funding: 01/01/2017 - 09/30/17

Final Report

1. Summary

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Petch relation (i.e. reduction of strength/hardness with decreasing grain size) in ceramics, while building a framework to explore the limits of ceramic (quasi) plasticity.

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2. Sintering Developments – High Pressure SPS

One of the major challenges in studying nanocrystalline materials is the expected high reactivity of the powders' surfaces. In metals, this leads to the formation of undesirable oxides, whist in ceramics, water and other gasses can be absorbed and dramatically affect thermodynamics and kinetics of processing. This last has been demonstrated to be a major problem in obtaining reliable nanocrystalline ceramics for a systematic mechanical study that can lead to a true and unquestionable theoretical framework. To overcome this challenge, within this project we have developed a technique in which the nanopowders are synthesized by using co-precipitation with target grain sizes <5nm, and further degassed under high vacuum to eliminate impurities. The powder is then maintained in inert atmosphere (dry and CO_2 free) before sintering. Since conventional sintering is known to provide significant concurrent grain growth, we developed a modification of the Spark Plasma Sintering by modifying dies to allow high pressure and high heating rates. As shown in Figure 1, the die is constitute of a Diamond/SiC punch, named Versimax©, and can withstand pressures up to 2GPa at temperatures as high as 1000°C. Although this temperature may not sound high in terms of densification mechanisms, note that driving force for sintering increases with pressure, and 2GPa can allow massive densification even at such low (or even lower) temperatures. The advantage of course is the limited grain growth that is barely activated at such low thermal conditions.

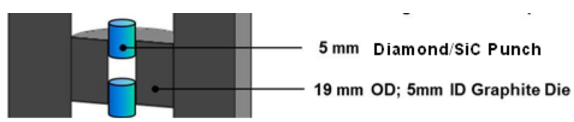

Figure 1. Die section used in HPSPS densification. Powder is added in between the SiC/Diamond punches.

Figure 2 shows a densification profile applied in the densification of 10mol% Yttria-Stabilized Cubic Zirconia (YSZ) powders for reference. Note that the whole densification process takes about 15min. In this case, the temperatures were limited to 800°C and the pressure up to 1.4GPa. This protocol resulted in fully dense, transparent, cubic zirconia, with grain sizes of 16nm.

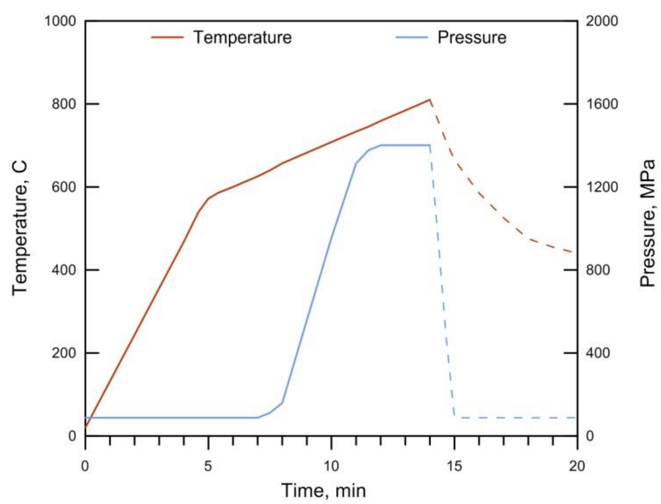

Figure 2. Sintering profile of HPSPS for Yttria-doped Cubic Zirconia. Starting powders were 5nm in grain size and final dense pellets were 16nm, demonstrating very limited coarsening during densification.

Although this (transparent YSZ with nanograined sizes) represents by itself a great achievement with no parallel in the literature, our group is interest in understanding the mechanical properties of the obtained samples. Therefore, we made efforts to tune the processing conditions to achieve fully dense samples with different grain sizes. Table 1 shows the parameters utilized to obtain the densification of YSZ with controlled grain sizes. Densities are not shown as they all are above 99.99% density as measured by Archimedes method.

Table 1. Sintering conditions, grain size, hardness and toughness of nanocrystalline YSZ samples.

Sintering profile	*comment*	*Grain size, nm*	*d-1/2, micron-1/2*	*Hardness, GPa*	*Std dev*	*Kic, Mpa m1/2*	*Std dev*
1140C, 0.8 GPa	no hold, ramp sintering	47.7	4.58	17.15	0.30	2.29	0.17
1090C, 1.0 GPa	no hold, ramp sintering	36.3	5.25	18.10	0.39	2.32	0.20
1040C, 1.2 GPa	no hold, ramp sintering	27.3	6.05	18.48	0.56	2.04	0.19
970C, 1.7 GPa	no hold, ramp sintering	21.5	6.82	17.97	1.12	1.79	0.26
955C, 1.8 GPa	no hold, ramp sintering	19.1	7.24	16.95	0.98	1.77	0.14
925C, 2.1 GPa	no hold, ramp sintering	16.8	7.72	16.36	0.99	1.58	0.19

High pressure SPS was also utilized to manufacture La doped YSZ. To this end, La was added in the salt form in the precursor of the coprecipitation method to achieve 0.5 to 1.5mol% La in YSZ. The sintering conditions were similar to those presented for YSZ, with equally high densities and small grain sizes. These samples were of particular interest to demonstrate the effect of dopant in reducing the grain boundary energy, as noted in a following session, to test the hypothesis regarding the increase in toughness.

Nanocrystalline $MgAl_2O_4$ was also manufactured utilizing HPSPS by utilizing coprecipitated powders. The sintering conditions are listed in Table 2. La^{3+} was tested as a dopant in the context of the improvement of toughness along with Na^+. As noted in the table, Na^+ allowed lower sintering conditions with reduced grain size. We attribute this effect to the increase in grain boundary shearing, which also results in an increased toughness as discussed later on this document, but more studies are required.

Table 2. Sintering conditions, grain size, and composition of nanocrystalline $MgAl_2O_4$ produced by HPSPS.

Grain Size, nm	Sintering Conditions	Composition	
19.50	**920C, 1.2 GPa** (no hold, ramp sintering)	MgAl2O4	
11.50	**830C, 1.8 GPa** (no hold, ramp sintering)	MgAl2O4	
14.50	**1080C, 1.1 GPa** (no hold, ramp sintering)	1 mol% La	
7.50	**810C, 1.4 GPa** (no hold, ramp sintering)	4 at.% of Mg substituted by Na	
8.90	**750C, 1.8 GPa** (no hold, ramp sintering)	4 at.% of Mg substituted by Na	
5.70	**810C, 1.4 GPa** (no hold, ramp sintering)	8 at.% of Mg substituted by Na	

3. Toughening Mechanisms

The nanocrystalline samples produced in this project allowed a systematic evaluation of toughening and also hardness of the materials as a function of grain size for the given compositions. Below we present the results for the specific materials that were studied.

3.1. Nanocrystalline Zirconia

The relative macroscopic fracture toughness was measured from the hardness impressions left by a Vickers indenter (Mitutoyo HM-220A) as the average between three equations: Lankford [1], Laugier [2], and Shetty-Wright-Mincer-Clauer [3]. These equations were proven to provide the smallest deviation from fracture toughness obtained by other techniques. Rather than relying on optical images, the obtained hardness impressions were imaged on Scanning Electron Microscope (SEM) FEI Nova NanoSEM430 using backscattered electrons, 5 kV accelerating voltage and 6.5 mm working distance. About 130 impressions were used for toughness calculations: roughly 32-33 for each composition including 11-12 for each indentation load (30 gf, 40 gf, 50 gf).

Toughness of nanocrystalline YSZ showed no improvement as compared to the microcrystalline samples, leveling at 1.74 MPa.m$^{1/2}$, demonstrating that nanosized grains alone do not contribute to toughening. This contrasts the literature on the topic, but the rational here is that clean grain boundaries do not allow grain boundary sliding for load accommodation, not enabling a toughening mechanism at the nanoscale, at least for YSZ.

3.2. La doped nanocrystalline YSZ

In order to create a mechanism of toughening in YSZ, we doped YSZ with La. The goal was to decrease the grain boundary energy, thus increasing bonding strength at the boundaries that would result in increased resistance to intergranular fracture. Figure 3 shows that indeed a correlation between fracture toughness and grain boundary energy exists. La content varied from 0.5mol% to 1.5mol% showed a systematic decrease in grain boundary energy, and an increase in toughness. However, from a crack energy perspective, the total energy decrease is likely not enough to stop crack movement, suggesting another mechanism operating, as will be discussed below.

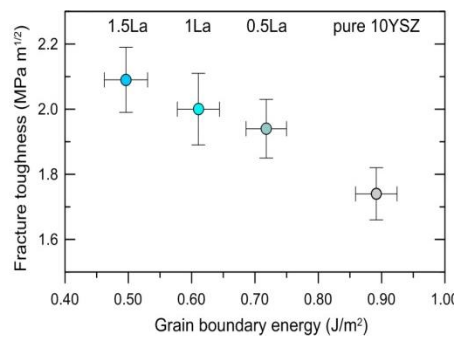

Figure 3. Fracture toughness as a function of grain boundary energy for La doped YSZ nanoceramics.

If the energy reduction helps but cannot stop by itself the crack propagation, there must exist another mechanism responsible for the improved properties. We looked than into the overall effect of the dopant on the population of grain boundaries by utilizing Molecular Dynamics simulations, instead of at the average, and learned that La lowers the overall energy but, more importantly, it decreases the energy difference in between grain boundaries in the system. That is, grain boundaries in the doped sample have more similar energies. This induces branching of the crack, which in turn increases toughness. Figure 4 shows the highlighted intergranular cracking and the cracks from indentation showing evidence of branching when doped with La. More details about this part of the work, which resulted in a submitted publication, can be found in the manuscript itself in ARO website list of publications from the project.

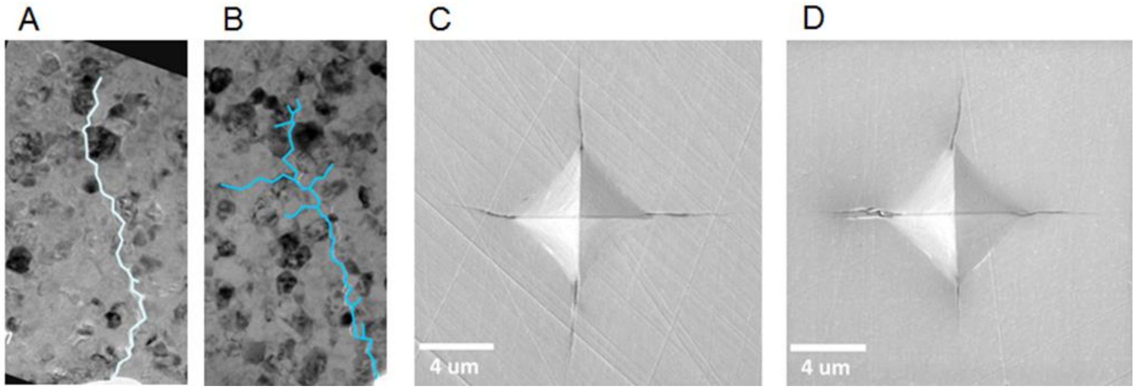

Figure 4. Selected images of tracered cracks observed after in-situ TEM fracture tests in 10YSZ (A) and La-doped YSZ (B). Selected SEM images for the impressions on 10YSZ (C) and 1.5La8.5YSZ (D) samples left by 50gf diamond pyramid.

3.3. Nanocrystalline doped and undoped $MgAl_2O_4$

Toughness in nanocrystalline $MgAl_2O_4$ ceramics was studied using same protocols as for YSZ and contrasted with the literature. Note that the literature does not have data with grain sizes even close the ones we reported here. Figure 4 shows the curve of fracture toughness as a function of log of the grain size for the studied compositions. Noteworthy, the $MgAl_2O_4$ data lies on the extrapolation of the results found in the literature. This suggests that size itself, in $MgAl_2O_4$ can be responsible for a slight increase in toughness. We noticed that La doping did not significantly increased toughness as demonstrated for YSZ. This is likely so because the grain boundary energies of $MgAl_2O_4$ are already generally smaller than from YSZ itself, and hence a dopant cannot significantly affect the distribution of energies and the toughness increase follows the grain sizes, rather than the composition.

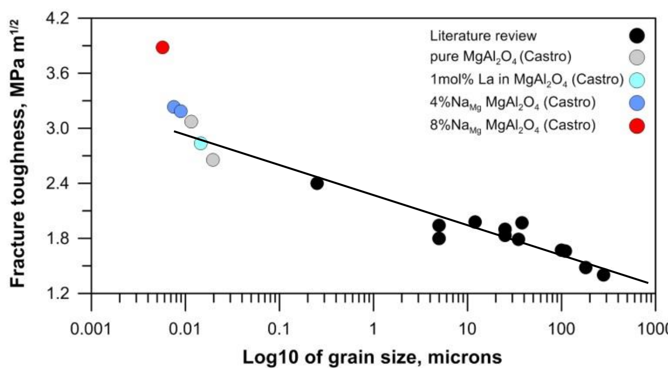

Figure 5. Toughness of spinel with different compositions as a function of grain size (log). Literature data marked in black circles for comparison and straight line predicts tendency.

Na^+, on the other hand, when in 8mol% caused a significant increase in toughness. The data for 4mol% already indicated an increase, but 8mol% is certainly outside any standard deviation. We are currently trying to explain why there is such pronounced increase in toughness, but we hypothesize it has to do with a change in the charge distribution at the grain boundaries that allow load accommodation. Further systematic studies are under way.

3.4. Field effects on toughness of $MgAl_2O_4$

One of the objectives of the proposal was to evaluate if grain boundaries can be polarized and store enough energy on them to allow crack arrest in a similar way as the well-known transformation toughening mechanism for partially stabilized zirconia. Preliminary calculations suggested that a high field of 2.4kV could trap energy consistent with the crack propagation energy. To evaluate this, we have prepared an extensive amount of samples of fully dense nanocrystalline $MgAl_2O_4$ with 25nm in grain size. The samples were than subjected to polarization at 800°C utilizing the setup shown in Figure 6 to apply 1.5kV. Control samples were produced under the same setup but without the field. This would assure the thermal inertia of the system is the same and allow true comparison.

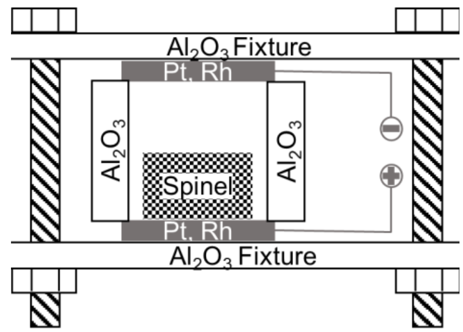

Figure 6. Apparatus used to polarize nano spinel pellets. Note the electrodes do not touch the samples to avoid electric current.

Table 3 shows the results of the grain sizes as a function of time of polarization. The first noticeable observation is the increase in grain growth observed for the samples prepared under the electric field (see Figure 7). The results suggest a change in either the mobility of the grain boundary or the grain boundary energy. We took this data as great encouragement for tests on mechanical behavior and thus performed hardness and toughness measurements to evaluate if the resulting polarization can also reflect on crack propagation and indentation at room temperature.

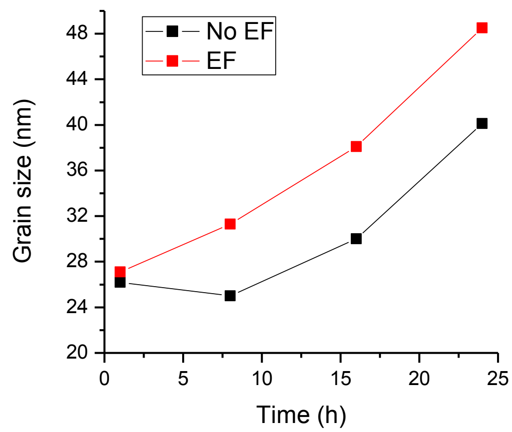

Figure 7. Grain size as a function of annealing time at 800°C with and without electric field (EF).

Table 4 shows a compilation of hardness and toughness data. A small decrease in hardness can be observed when comparing the samples with EF and without. Although this may sound intriguing, note that the hardness scales mostly with the different grain sizes observed in the samples, which follows a Hall-Petch relation in the context that larger grains would be less hard.

In order to evaluate toughness, we have observed the crack length in two directions: perpendicular the EF and in parallel to it. The logic was to look for a specific effect of a directionality of the field in arresting cracks. Table 4 confirms that samples with and without the field show statistically the same crack length regardless of the direction – suggesting same toughness. One could argue for a small decrease in the crack length along the EF for the polarized samples, but this is not statistically defendable. It is possible that more intense fields are

Table 3. Grain sizes (GS) as a function of time

Sample	GS (nm) **No EF**	GS (nm) **With EF**
MAS 1h	26.2±2.1	27.1 ±2.7
MAS 8h	25.0±1.9	31.3 ± 2.5
MAS 16h	27.0±2.7	38.1 ±3.5
MAS 24h	40.12±9.59	48.46 ±13.33

Table 4. Mechanical properties of $MgAl_2O_4$ pellets treated under EF. Indentations were taken along or perpendicular EF.

Sample	Hard (GPa) **No EF**	Hard. (GPa) **EF**	Crack Length (µm) **No EF**		Crack Length (µm) **EF**	
			Across EF	**Along EF**	**Across EF**	**Along EF**
MAS 1h (load 120g)	19.32±0.52	17.45±1.34	31.42±2.56	31.42±3.08	37.32±5.95	33.10±3.11
MAS 8h (load 80g	20.01±1.63	18.33±1.25	15.80±1.22	15.98±0.70	17.08±1.81	16.90±1.10
MAS 16h (load 80g)	18.66±1.09	17.83±1.02	17.42±1.89	16.47±1.69	17.62±1.64	16.44±1.45
MAS 24h (load 80g)	17.61±1.14	16.60±1.45	17.50±1.96	16.64±1.23	16.14±1.90	15.43±1.43

required to observe an effect that is visible, but it is equally possible the polarization energy is not high enough to disturb crack propagation. However, we believe that further studies are required since the growth behavior is indeed statistically significantly different, and thus suggest a change in grain boundary character. A manuscript is in preparation with this data (and more not shown for brevity).

4. Hardness

The existence or not of a breakdown in the Hall-Petch relationship has intrigued the community for many decades. Given the good quality samples we have prepared here, part of this project was dedicated to address this question. This part of the project was focused on YSZ ceramics.

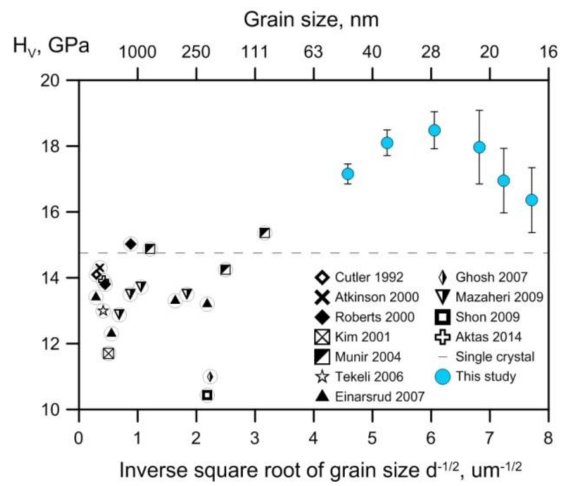

Figure 8. Hardness as a function of grain size for YSZ, including our data and from the literature.

Figure 8 shows a graph of hardness as a function of grain size in a typical HP plot for YSZ ceramics data from this project along with the literature data. Noteworthy, there is a clear inverse-relation for grain sizes below 27nm and raised the questions why this is observed for YSZ and not for $MgAl_2O_4$, which has been produced by our group and did not show a breakdown for grain sizes below 10nm. The answer was found in a mechanism of grain rotation occurring at room temperature. In collaboration with Dr. Dillon from Illinois, we observed grains rotating during in-situ loading of a nanocrystalline sample. The rotation was way more pronounced for samples with 17nm as compared to 48nm. Note these sizes are on opposite sides of the maximum curve shown in Figure 8. Figure 9 shows the results of in-situ electron diffraction showing grain rotation.

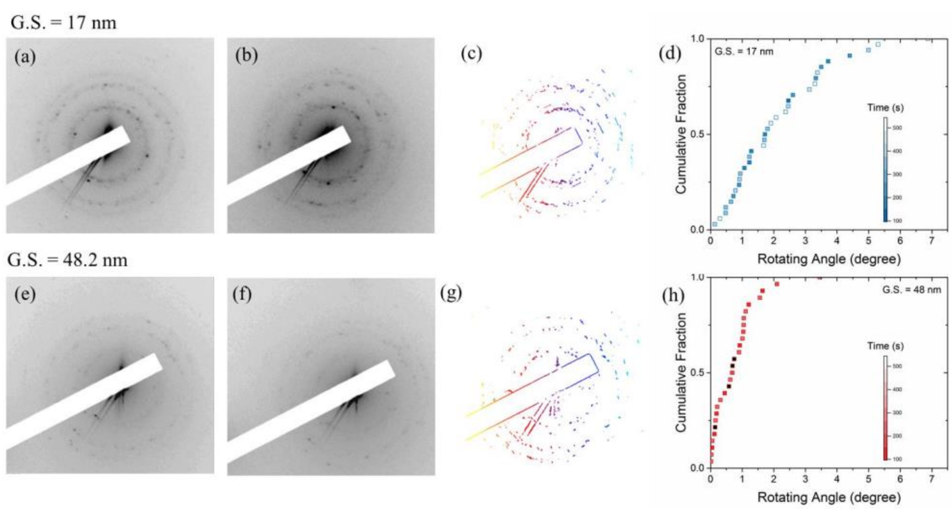

Figure 9. Evolution of electron diffraction patters under applied stress. Diffraction patterns obtained during in situ TEM indentation of 17nm (a-b) and 48nm (e-f) 10YSZ samples. Tracking trajectories shown in (c) and (g) represent the corresponding crystallographic rotation. Rotation angles of diffractions spots present in the initial state and the experimental time over which they are observable (d) and (h).

In principle, there seems to exist a competition between the traditional HP relation and room temperature grain rotation. As grains get smaller, the number of dislocations is reduced, and thus materials get harder within the classical grain boundary strengthening theory. However, for very small grains, depending on the disclination strength, rotation of grains by dislocation climbing at the grain boundaries could result in deformation of the part by accommodation of grains – macroscopically observed as reduced hardness. This model is under development and will be reported as a potential explanation for this behavior.

More studies are however needed to understand what is defining the disclination strength of the material. In principle, contaminated grain boundaries and high grain boundary energies (such as for YSZ) are both related to a relatively facile grain boundary rotation, while materials with low energy clean boundaries, will have this effect only observed at very small grain sizes (i.e. <10nm).

5. Conclusions and Future Perspectives

This STIR project opened a great deal of possibilities to be explored in terms of the mechanics of nanocrystalline ceramics. We have not only demonstrated the capability of manufacturing fully dense ceramics with grain sizes in the 10-20nm range, but we have developed unprecedented concepts to improve toughness of transparent ceramics without composites in which transparency (single phase) is always maintained. We need to better rationalize the toughening design by further systematic experiments. What are the best dopants and why? Moreover, we showed that electric fields can induce growth in nanocrystalline ceramics, but the results regarding toughness increase were inconclusive likely because the increment is very limited. The STIR project also generated data to clarify at certain level the conflicting data on hardness dependence on grain size, and started development of a model that attributes inverse HP to the initiation of grain rotation by dislocation climbing at grain boundaries.

The STIR opened new perspectives to be addressed in a subsequent project driven by the following questions:

1- How to select a dopant that optimally improves toughness of nanoceramics?
2- Is the grain boundary energy the most important parameter defining toughness in single phased nanocrystalline materials or is there any other aspect, such as dislocation climbing?
3- Is the inverse-HP relation found for hardness of YSZ an universal phenomenon even in good-quality samples?
4- Do the indentation measurements utilized in this STIR proposal are consistent with bending tests?
5- Can the electric field be ruled out as a toughening mechanism even when dopants are utilized – which could potentially increase toughness?

These and other underlying questions shall guide this exciting research area that will forge the foundations for new technologies for the Army.