

**Final Report**  
**STTR Phase I OPTION**  
**N04-T008**

**Nanograin Ceramic Optical Composite Window**

**Contract N00014-04-M0334**  
**March 31, 2005 – June 30, 2005**

**Final Report**

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## Report Documentation Page

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**Introduction and Executive Summary**

The principle objective of the Phase I STTR program was to demonstrate the feasibility of producing a dense, transparent nanocomposite material with final grain sizes less than 50 nm. The alumina/zirconia system was initially selected because it has been shown for larger scale systems that an immiscible phases are particularly effective in suppressing grain growth. The work was conducted by MetaMateria Partners (MMP) in collaboration with the Particulate Materials Center (PMC) at Penn State University. Key accomplishments done in Phase I were:

- Dense Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> composites with a microstructure under 50 nm were made on a repeatable basis by densifying Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanoparticulates with pressure-assisted sintering (sinter-forging). Primary starting particle size was 3-5 nm (surface area 200-500 m<sup>2</sup>/g).
- Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanoparticulate powders were prepared by two different methods: sonochemical processing at MMP and glycothermal processing at PMC. The sonochemical process gave finer particle sizes.
- Full densification was accomplished using sinter-forging followed by hot isostatic pressing (HIP) at 1250°C for 2 hours and 20,000 psi.
- Limited IR transmission measurements yielded in one sample ~ 50% transmission.

The Phase I STTR Option extended the work done during Phase I. The Option began in mid-April and focused on producing samples of the Al<sub>2</sub>O<sub>3</sub>:ZrO<sub>2</sub> nanocomposites using processes developed in Phase I, with a primary goal of increasing the IR transmission without an increase in grain size. Sinter-forging and post-HIP were used to achieve high density.

Phase I and the Option demonstrated an approach to making nanocomposite materials having a nanograin structure. At the beginning of the Option, it was believed that several factors could have contributed to blocking IR transmission in the nanocomposite materials. These factors were carbon impurities, pores, and larger grains. Oxygenation was also a factor but it appeared that soaking in oxygen at an elevated temperature was sufficient. The Option was directed to resolving these issues. Techniques were developed for reducing carbon and high density samples were produced using sinter-forging, followed by a post-HIP with minimal grain growth. However, these results did not lead to high IR transmission and in fact the IR transmission was generally low. The reasons for this are not understood but it is suspected that having multiple crystalline phases, impurities or defects related to oxygen concentration had a more significant effect than anticipated. The limited time available during the Option did not allow all of these factors to be investigated in detail.

During Phase I, it was thought that a probable contributor to lower transmission was residual carbon left in the sample that was not removed during presintering, sinter-forging and oxygenation. Generally after sinter-forging, the Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> samples had a deep gray to black

color. On oxygenation of lower density parts (~95 % of the theoretical density) these turned white. However, high density samples changed to a tan or brownish-white color and did not turn white. It was suspected that this coloration resulted from the presence of carbon that could not be completely removed during oxygenation. In the Option, carbon was measured in the as-produced and calcined powder and this did show that residual carbon existed in the starting materials. A fluidized bed was set up to allow oxygen gas to flow around the powder, which was calcined to completely remove carbon. This method did significantly reduce the carbon without affecting particle size.

While much was accomplished, the overall results obtained in the Option were disappointing and clearly a greater understanding of what affects IR transmission in these nanocomposites is needed, more than could be done during time available. While preparing materials with a nano microstructure is understood, more experimentation is needed (encompassing all the responsible factors) in order to successfully develop these nanocomposites as IR transparent materials (transparency higher than 80 %).

As described, IR transmission remained low no matter the powder processing route used. Even though the Option has ended, some additional work is being continued by MMP/PMC to better understand why higher IR transmission was not achieved. These understandings will be communicated.

Also in Phase I, parts were prepared from calcined powders made from both processes (sonochemical and glycothermal) and pellets prepared for sinter-forging runs. These would contain a metastable  $\text{Al}_{0.48}\text{Zr}_{0.52}\text{O}_x$  phase. Different ratios of  $\text{Al}_2\text{O}_3$  to  $\text{ZrO}_2$  were prepared, as well as compositions that started with mixtures of independently synthesized  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  particulates. Specimens were sinter-forged and some were further densified using HIP. IR transmission was measured after oxygenation and polishing at the PMC, where samples were further characterized.

### **Program Activities**

The Phase I Option was organized into 6 Tasks, shown below. The results obtained during the Option are discussed for each Task. More detailed background and experimental data is presented in the Phase I Final Report and is only discussed as needed to explain the Option work.

#### **Task 1: Preparation of Carbon-Free Nano Particulates**

This task was to evaluate and remove any residual carbon from the nanoparticles that might affect IR transmission. In Phase I high density samples were prepared without treatment and after sinter forging and hot isostatic pressing these never turned white in color during oxygenation. Lower density samples did turn white in color after oxygenation.

#### **Task 2: Use of Chemically-Aided Milling for Preparation of De-Aggregated Powder**

This task was to further optimize the method for preparing parts for sintering using calcined powder that was then de-aggregated using chemically-aided milling. These gave the best results during Phase I.

#### **Task 3: Preparation of Preforms for Sinter-Forging**

Preforms were made by pressing dry powders, which were then sintered, typically to 1100°C to obtain sufficient strength needed during the application of pressure during sinter-forging.

#### **Task 4: Densification using Sinter-Forging**

Preforms were densified using sinter-forging at conditions developed during Phase I. Heating rates, hold times and cyclic pressure were controlled.

**Task 5: HIP**

This task involved further densification of sinter-forged samples using hot isostatic pressing.

**Task 6: Oxygenation**

This task involved conditions for oxygenation of the Sinter-Forged/HIP'ed samples.

**Task 7: Characterization**

Oxygenated samples were polished and IR transmission measured. These samples were then used for determination of crystallite sizes using XRD techniques.

**Task 1: Preparation of Carbon-Free Nano Powders**

Because of concern that some residual carbon affected IR transmission in the specimens made in the Phase I program, attention was given to processing conditions that could provide full removal of carbon from the starting nanoparticulates. During this option period additional batches of Alumina-Zirconia colloids and powders were made using both sonochemical and glycothermal processes. The first approach (sonochemical synthesis) was developed at MMP for nanoparticle synthesis. This process results in amorphous particles that crystallize during further heat treatment. Sonochemical synthesis was used to produce the metastable as well as phase-pure  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  nanoparticles with sizes below 10 nm. The second process was a glycothermal synthesis approach practiced at the PMC. This approach resulted in formation of  $\alpha\text{-Al}_2\text{O}_3$  (~30 nm) where Boehmite was used as seeds. On seeding with 8 nm size  $\text{ZrO}_2$  particles, the glycothermal synthesis technique also resulted in formation of the metastable phase. Hydrothermal synthesis was used to make  $\text{ZrO}_2$  nanoparticle seeds (~8 nm)

The nanoparticulates were collected, dried and calcined using the fluidized bed method shown schematically below.

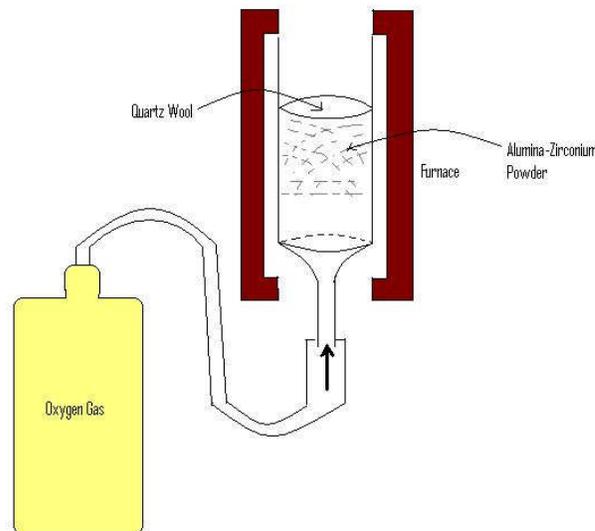


Figure 1: Schematic diagram of Fluidized bed oxygenation of  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  powder

Oxygen gas flow was used to remove carbon. Experiments were also conducted by simply calcining the powder in air as well as in a fluidized bed. Figure 1 shows a schematic of the fluidized bed setup used for removal of carbon. Oxygen was passed through a porous membrane distributor plate and flow rate was controlled such that the powder fluidized in the reactor. These carbon removal experiments were done at two different temperatures 500°C and 600°C. The heat treatment also resulted in crystallization of the powder.

Carbon content was measured by LECO Corporation on two of the powders which were calcined at 400°C and 500°C with just air and powders calcined by using fluidized bed method with oxygen gas flow at 500°C and 600°C and the results are shown in Table 1. As-prepared samples have shown carbon content above 1%, which has been significantly reduced after calcination. Additional carbon removal can be expected when the pressed parts are sintered in air at 1100°C.

**Table 1: Carbon content of the calcined Alumina-Zirconia powders analyzed by LECO**

Calcination Temperature	Carbon content (%)
400°C in Air	0.41
500°C in Air	0.15
500°C- Fluidized Bed Method with O <sub>2</sub> Gas	0.09
600°C- Fluidized Bed Method with O <sub>2</sub> Gas	0.09

As shown in the table, a lower carbon content was observed for powders heat treated by using fluidized bed. The result may be indicative of higher interaction of the powder with the O<sub>2</sub> in the fluidized bed than standard calcination. Using a fluidized bed generally exposed more particle surfaces to the gas than during the conventional calcination. Lower carbon content might also result from the use of the fluidized bed, as compared to the conventional calcination technique.

As mentioned previously, phase-pure Zirconia and Alumina powders were also prepared individually using sonochemical synthesis and calcined at 500°C. The surface area of the powders after heat treatment at 500°C were measured and shown in the Table 2.

**Table 2: Surface area and estimated particle size of the Alumina and Zirconia powders**

Material name	Surface area (m <sup>2</sup> /g)	Estimated particle size (nm)
Alumina	315.7	4.7
Zirconia	48.7	22

The phase purity was confirmed by XRD analysis. The XRD patterns of Alumina and Zirconia are shown in the Figure 2 and Figure 3 respectively. As shown in Figure 2,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> formed by calcining the sonochemically synthesized Al<sub>2</sub>O<sub>3</sub> at 500°C. However, both tetragonal and the monoclinic phase was observed for the ZrO<sub>2</sub> powder.

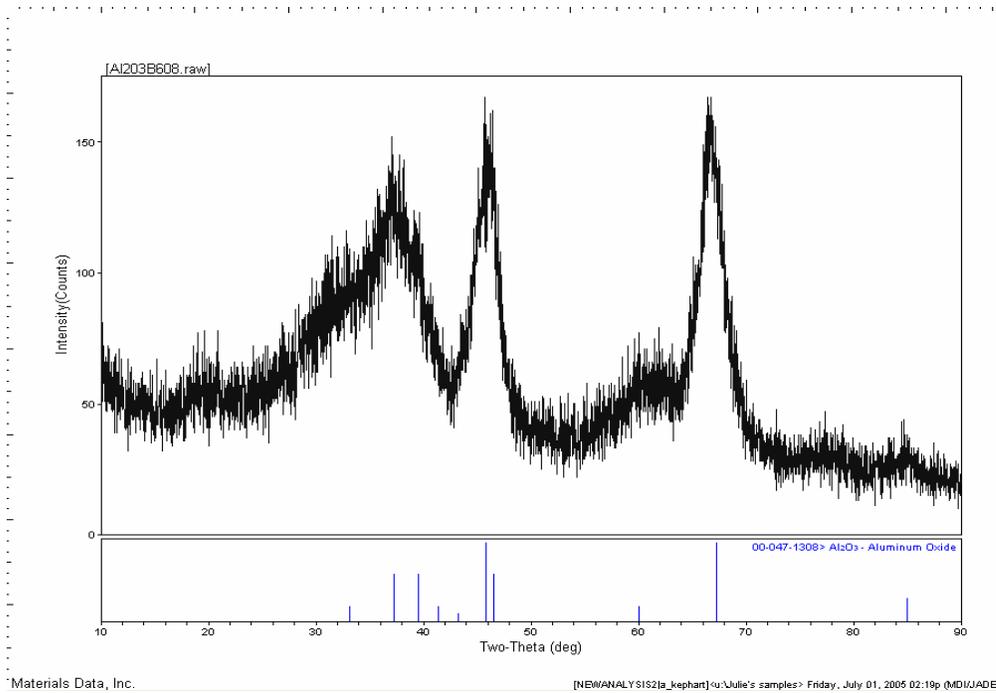


Figure 2: XRD patterns of alumina powder prepared by sonochemical method

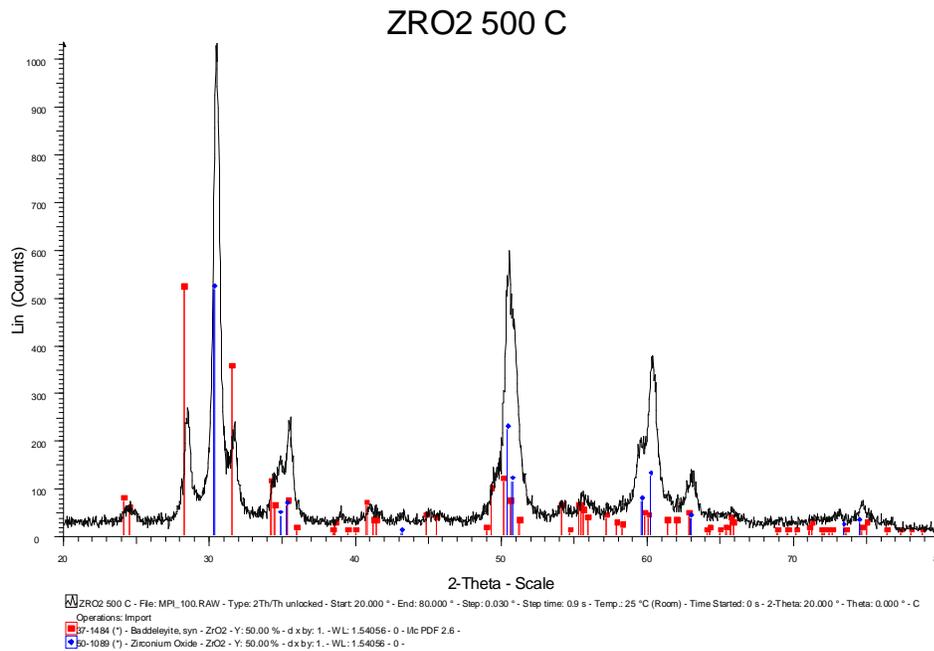


Figure 3: XRD patterns of zirconia powder prepared by sonochemical method

**Task 2: Use of Chemically-Aided Milling for Preparation of De-Aggregated Powder**

The best results during Phase I were found using calcined powder that was then de-aggregated using chemically-aided milling. This approach was continued during the Option, with more characterization and adjustment of the processing conditions.

In the Phase I Option, all calcined powders were chemically-aided milled for deaggregation, whether they were simultaneous precipitated or simply mixed in the desired ratio from independently synthesized powders. After milling any large aggregates that were still present were separated by using a simple sedimentation approach. Calcination of powder leads to agglomeration of particles; however, the use of a chemically-aided milling technique, as described in earlier reports was used to deagglomerate these aggregates.

Powders produced by this method were also directly used to make parts for pressure-assisted sintering or sinter forging. In a typical chemical aided milling approach, a suspension of the agglomerated particles is broken down in an attrition mill in the presence of surface active chemicals. The pH of the suspension is controlled. Surface active solutes contribute to the mechanical breakdown of the particles by promoting internal wetting. The surface active solutes also contribute to the size reduction by lowering the strength of the solid, an effect reported by Reh binder and his colleagues. Originally, this effect was interpreted simply as a lowering of surface energy by adsorption and hence reduction of the work required to produce new interfaces; but it must also include the creeping of surface-active substances along grain boundaries or dislocations while the body is under stress. The various effects introduced by the presence of a surface-active solute in wet milling are: (a) stabilizing new interfaces by adsorption, (b) wetting of the constituent particles (primary or aggregate) of an aggregate with elimination of air, (c) reduction of viscosity by preventing flocculation, and (d) creeping of the surface active substances under stress (Reh binder effect). All these effects operate simultaneously and may be difficult to separate during practice.

**Task 3: Preparation of Preforms for Sinter-Forging**

The deaggregated powder produced using chemically aided milling was then dried and pressed into pellets or preforms. The preforms were sintered, typically to 1100°C, to obtain the required strength for sinter-forging. Work during Phase I showed that sintering to this temperature did not affect grain growth.

A number of solid preforms made from Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> colloids were fabricated for sintering studies using pressure casting techniques described in earlier reports.

**Task 4: Densification using Sinter-Forging**

In this task sinter-forging of preforms was done using conditions developed during Phase I. Again, a number of samples were prepared using sinter-forging, where a uniaxial compressive stress is applied to the sample during sintering in a cyclic manner [an oscillating load with oscillation of 10 % (of the constant load) superimposed on a constant load]. A temperature was selected where plastic deformation of the ceramic occurs. Typical temperatures used in this program were 1250 °C-1450 °C. Samples were allowed to deform and densify simultaneously. No constraining dies are used during sinter forging, compared to hot pressing, thereby allowing lateral movement of grains and minimizing contamination. Zirconia felt was used as a separator from the graphite ram. The load was always applied in a cyclic fashion. All sintering experiments were conducted in a vacuum.

Table 3 is a summary of processing parameters and the densities achieved for samples made with pressure-assisted sintering (Sinter forging).

**Table 3: Processing parameters of Alumina-zirconia pellets made by sinter forging**

<b>Sample Number</b>	<b>Composition (Mole%) ZrO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub></b>	<b>Sintering Temperature (°C)</b>	<b>Sintering Time (Hours)</b>	<b>Maximum Pressure (Lbs)</b>	<b>Archimedes Density (g/cc)</b>
SF-AlZr-092	50/50	1350	4	3000	NA
SF-AlZr-093	50/50	1350	5	3000	NA
SF-AlZr-095	50/50	1350	5	3500	5.13
SF-AlZr-096	50/50	1400	5	3500	5.14
SF-AlZr-124	30/70	1400	6	3500	3.96
SF-AlZr-126	30/70	1350	6	3500	3.42
SF-AlZr-127	28.5/71.5	1350	6	3500	3.22
SF-AlZr-128	28.5/71.5	1400	6	3500	NA
SF-AlZr-129	30/70	1250	6	2000	NA
SF-AlZr-130	5/95	1400	6	3500	3.76
SF-AlZr-131	5/95	1450	6	3500	NA
SF-AlZr-132	5/95	1400	6	4000	NA
SF-AlZr-133	5/95	1350	6	3500	NA
SF-AlZr-134	5/95	1400	6	2000	NA
SF-AlZr-135	5/95	1400	6	2000	NA
SF-AlZr-136	5/95	1400	6	3500	NA
SF-AlZr-137	5/95	1450	6	3500	3.39
SF-AlZr-138	5/95	1450	6	3500	4.18
SF-AlZr-139	5/95	1400	6	2000	4.24
SF-AlZr-140	5/95	1400	6	3500	4.26
SF-AlZr-141	52.7/47.3	1400	6	3500	4.18
SF-AlZr-142	52.7/47.3	1350	6	3500	4.21
SF-AlZr-143	52.7/47.3	1250	6	3500	3.94
SF-AlZr-144	52.7/47.3	1250	4	2000	NA
SF-AlZr-145	52.7/47.3	1450	6	3500	4.46
SF-AlZr-146	52.7/47.3	1450	6	4500	4.45
SF-AlZr-147	52.7/47.3	1400	6	4000	4.21
SF-AlZr-148	30/70	1400	6	4000	3.76

### **Task 5: Densification using Hot Isostatic Pressing (HIP)**

Following densification by sinter-forging, samples were subjected to hot isostatic pressing for elimination of residual porosity.

A few samples that measured near 100 % of the theoretical density (using Archimedes principle) were taken through a HIP cycle with temperature of 1375°C for 2 hours under 40,000 psi of maximum pressure. A 95 % dense sample that showed 50 % IR transmission was also HIP'ed.

### **Task 6: Oxygenation**

This task was to evaluate the time/temperature conditions needed for full oxygenation of the sinter-forged and HIP'ed samples.

As-prepared pressure assisted sintered samples (both sinter forged and hot pressed) were found to have a characteristic dark color that results from the reduction of  $ZrO_2$ . These samples needed to be re-oxygenated, which was done at 1200°C. A few samples were also oxygenated at 1300°C; however, these samples showed grain growth at the surfaces.

Samples that were densified using pressure assisted sintering (sinter forging and hot pressing) under vacuum tend to be reduced, resulting in a darkening (deep gray to black color) of the sample. This was believed to be primarily due to a loss of oxygen from zirconia ( $ZrO_2$  to  $ZrO_x$ ) or  $Al_2O_3$ . After oxygenation these samples turned from deep gray to white as shown in Figure 4 and Figure 5. However, some darker coloration was also observed in dense samples. Overall, the change to a white color after oxygenation indicates that the tan to brownish white color observed in Phase I most likely resulted from the presence of unremoved carbon. During the Option the carbon content was reduced and this resulted in white colored samples (with some darker areas) after oxygenation. Final carbon content in the samples after oxygenation were however, not determined.

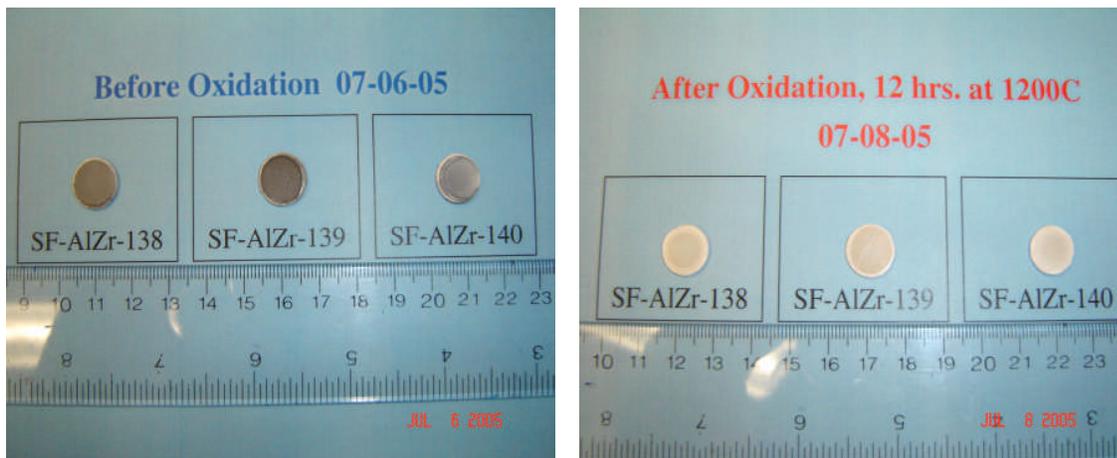


Figure 4: Digital pictures of sinter-forged Alumina-Zirconia pellets before and after oxygenation

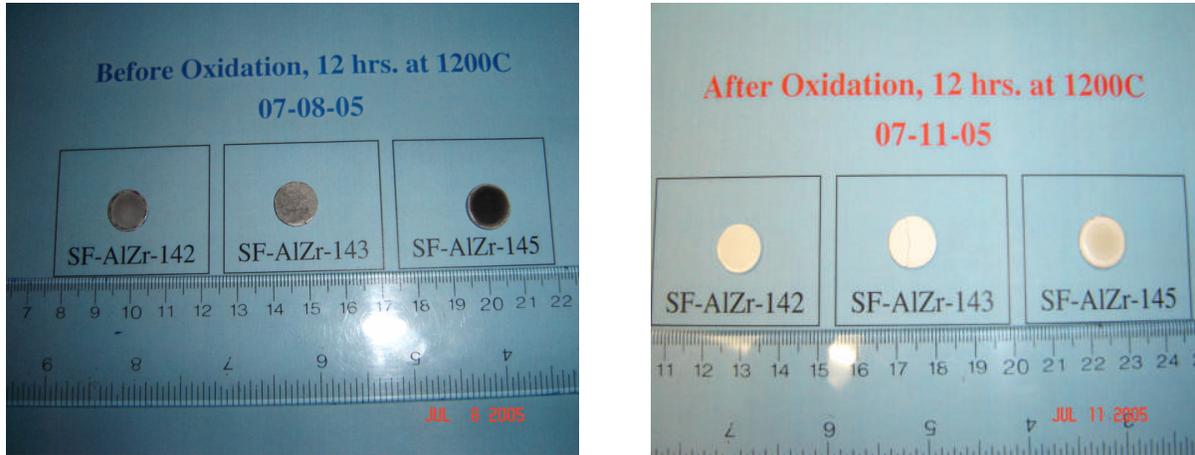


Figure 5: Digital pictures of sinter-forged alumina-zirconia pellets before and after oxygenation

**Task 7: Characterization**

As previously mentioned, more than two phases were found in most of samples, which is now believed to be at least part of the reason for lower IR transmission. Table 4 summarizes the starting powder characteristics and final crystalline phases for all of the samples. The phase assemblage was determined from the XRD patterns. The crystallite size was also determined from some of the XRD patterns.

**Table 4: Powder characteristics and the final phase assemblage for samples prepared during Phase I Option**

Sample Number	Composition (Mole%) ZrO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>	Method of preparation	Type of preparation	Phases from XRD
SF-AlZr-017	52.7/47.3	Glycothermal	Mixing of Individual materials	Corundum Al <sub>2</sub> O <sub>3</sub> , Baddeleyite ZrO <sub>2</sub> and meta stable phase of Aluminum-zirconium oxide
SF-AlZr-092	50/50	Sonochemical	Simultaneous	Corundum Al <sub>2</sub> O <sub>3</sub> , Baddeleyite ZrO <sub>2</sub>
SF-AlZr-093	50/50	Sonochemical	Simultaneous	Corundum Al <sub>2</sub> O <sub>3</sub> , Baddeleyite ZrO <sub>2</sub>
SF-AlZr-095	50/50	Sonochemical	Simultaneous	Corundum Al <sub>2</sub> O <sub>3</sub> , Baddeleyite ZrO <sub>2</sub> and meta stable phase of Aluminum-zirconium oxide
SF-AlZr-096	50/50	Sonochemical	Simultaneous	Corundum Al <sub>2</sub> O <sub>3</sub> , Baddeleyite ZrO <sub>2</sub> and

				meta stable phase of Aluminum-zirconium oxide
SF-AlZr-124	30/70	Glycothermal	precipitation with Zirconia seeds	Corundum Al <sub>2</sub> O <sub>3</sub> , Baddeleyite ZrO <sub>2</sub>
SF-AlZr-126	30/70	Glycothermal	precipitation with Zirconia seeds	Corundum Al <sub>2</sub> O <sub>3</sub> , Baddeleyite ZrO <sub>2</sub>
SF-AlZr-127	28.5/71.5	Glycothermal	precipitation with Zirconia seeds	Corundum Al <sub>2</sub> O <sub>3</sub> , Baddeleyite ZrO <sub>2</sub> and meta stable phase of Aluminum-zirconium oxide
SF-AlZr-128	28.5/71.5	Glycothermal	precipitation with Zirconia seeds	Corundum Al <sub>2</sub> O <sub>3</sub> , Baddeleyite ZrO <sub>2</sub> and meta stable phase of Aluminum-zirconium oxide
SF-AlZr-129	30/70	Glycothermal	precipitation with Zirconia seeds	XRD in progress
SF-AlZr-130	5/95	Sonochemical	Simultaneous	XRD in progress
SF-AlZr-131	5/95	Sonochemical	Simultaneous	XRD in progress
SF-AlZr-132	5/95	Sonochemical	Simultaneous	XRD in progress
SF-AlZr-133	5/95	Sonochemical	Simultaneous	XRD in progress
SF-AlZr-134	5/95	Sonochemical	Simultaneous	XRD in progress
SF-AlZr-135	5/95	Sonochemical	Mixing of Individual materials	XRD in progress
SF-AlZr-136	5/95	Sonochemical	Mixing of Individual materials	XRD in progress
SF-AlZr-137	5/95	Sonochemical	Mixing of Individual materials	XRD in progress
SF-AlZr-138	5/95	Sonochemical	Mixing of Individual materials	XRD in progress
SF-AlZr-139	5/95	Sonochemical	Mixing of Individual materials	XRD in progress
SF-AlZr-140	5/95	Sonochemical	Mixing of Individual materials	XRD in progress
SF-AlZr-141	52.7/47.3	Glycothermal	Mixing of	XRD in progress

SF-AlZr-142	52.7/47.3	Glycothermal	Individual materials Mixing of Individual materials	XRD in progress
SF-AlZr-143	52.7/47.3	Glycothermal	Individual materials Mixing of Individual materials	XRD in progress
SF-AlZr-144	52.7/47.3	Glycothermal	Individual materials Mixing of Individual materials	XRD in progress
SF-AlZr-145	52.7/47.3	Sonochemical	Individual materials Mixing of Individual materials	XRD in progress
SF-AlZr-146	52.7/47.3	Sonochemical	Individual materials Mixing of Individual materials	XRD in progress
SF-AlZr-147	52.7/47.3	Sonochemical	Individual materials precipitation	XRD in progress
SF-AlZr-148	30/70	Glycothermal	with Zirconia seeds	XRD in progress

**Crystallite Size:** Rietveld analysis was used to estimate the crystallite size (grain size) of the sample. It was originally conceived as a refinement method for crystal structures using neutron diffraction data. But today it is also used for X-ray diffraction. Briefly, the Rietveld method requires knowledge of the approximate crystal structure of all phases of interest. The input data required to calculate a synthetic pattern includes the space group symmetry, number of atoms, atomic positions, temperature factor, site occupancies, and lattice parameters. The refinement is conducted by minimizing the sum of the weighted, squared differences of this calculated pattern and the observed intensities every step in a digital powder pattern. In a typical refinement, individual scale factors (related to the weight percents of each phase) and profile, background, and lattice parameters are varied. In favorable cases the atomic positions and site occupancies can also be successfully varied. Since the method uses all lines, severely overlapping reflections are not a problem. The method can obtain the lattice parameters, accurate phase quantification, crystallite size and strain, site occupancies and atomic positions.

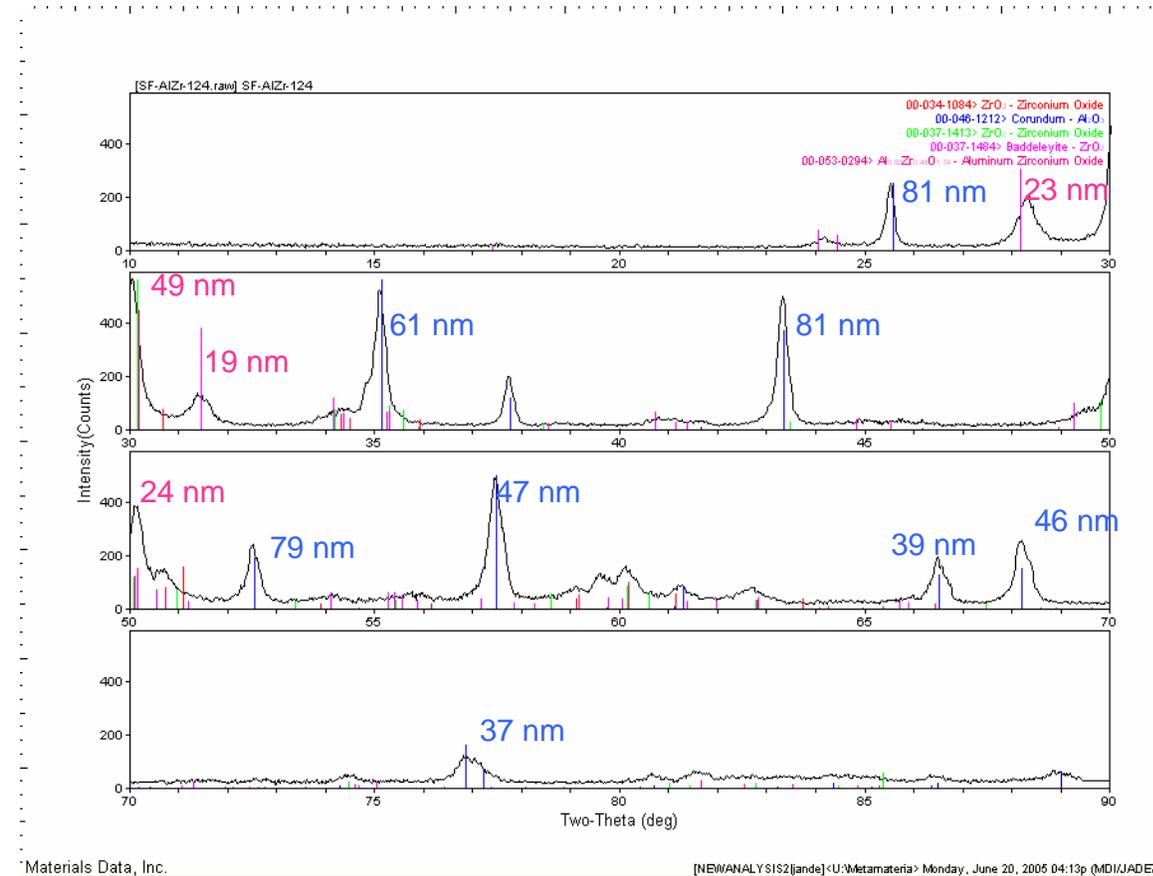


Figure 6: XRD pattern for the SF-AlZr-124 sample. The sample was sinter-forged at 1400°C for 6 hrs. The crystallite size is estimated using Rietveld analysis. The composition of the sample was 30/70 mol% Zirconia to Alumina. Crystallite sizes are given for each peak of Zirconia (pink) and Alumina (Blue).

Figure 6 shows the XRD pattern of the SF-AlZr-124 sample with the composition of 30/70 mol% of Zirconia to Alumina. The phases observed in this sample are Corundum  $\text{Al}_2\text{O}_3$ , Baddeleyite  $\text{ZrO}_2$  and another  $\text{ZrO}_2$  phase. The metastable phase was not observed. As shown in the figure, the crystallite sizes of zirconia are found to be below 50 nm even after sinter-forging at 1400°C for 6 h. The crystallite sizes of Alumina are below 81 nm.

Figure 7 shows the XRD pattern of SF-AlZr-127 sample with the composition of 28.5/71.5 mol% of Zirconia to Alumina. The phases observed in this sample are Corundum  $\text{Al}_2\text{O}_3$ , Baddeleyite  $\text{ZrO}_2$  and the metastable phase. As shown in the figure, the crystallite sizes of zirconia and alumina are found to be below 100 nm even after sinter-forging at 1350°C for 6 h.

SF-AlZr-128 sample also has the same composition with 28.5/71.5 mol% of Zirconia to Alumina and was sinter-forged at 1400 °C for 6 hrs. As shown in Figure 7, the metastable aluminum zirconium oxide phase is observed in this sample along with zirconia and alumina phases. All grain sizes are below 100 nm. Another sample (SF-AlZr-96) with a composition of 50/50 mol% of Zirconia to Alumina was sinter-forged at 1400°C for 6 hrs and also shows the metastable aluminum zirconium oxide phase. Crystallite sizes are shown in the Figure 8. The metastable aluminum zirconium oxide phase shows large grains, where as the zirconia and alumina phases shows grain sizes below 50 nm and 100 nm respectively.

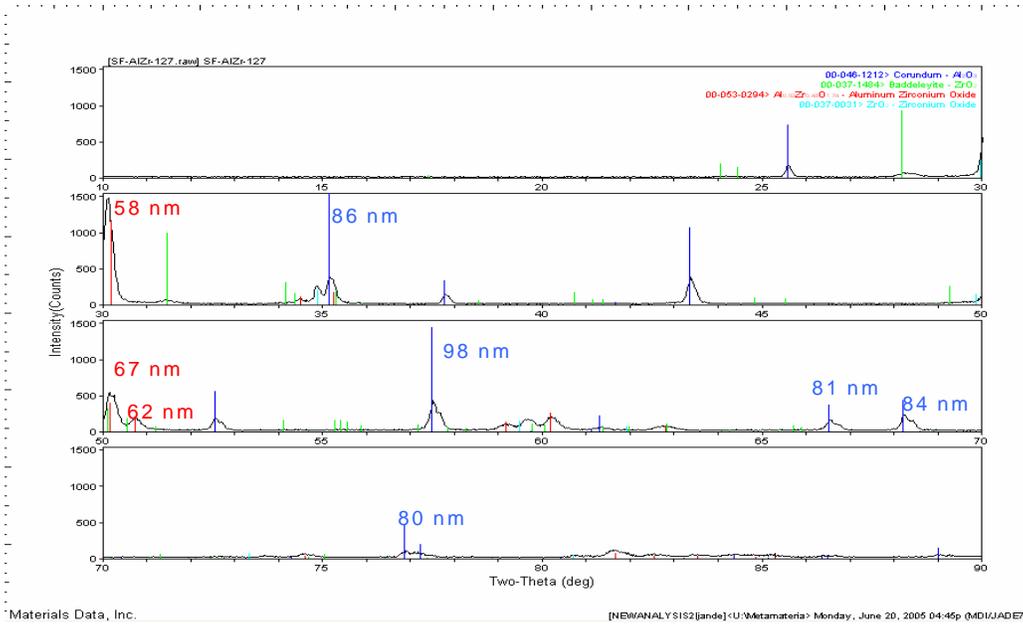


Figure 7: XRD pattern for the SF-AiZr-127 sample. The sample was sinter-forged at 1350°C for 6 hrs. The crystallite size is estimated using Rietveld analysis. The composition of the sample was 28.5/71.5 mol % Zirconia to Alumina. Crystallite sizes are given for each peak of metastable Aluminum Zirconium oxide phase (Red) and Alumina (Blue).

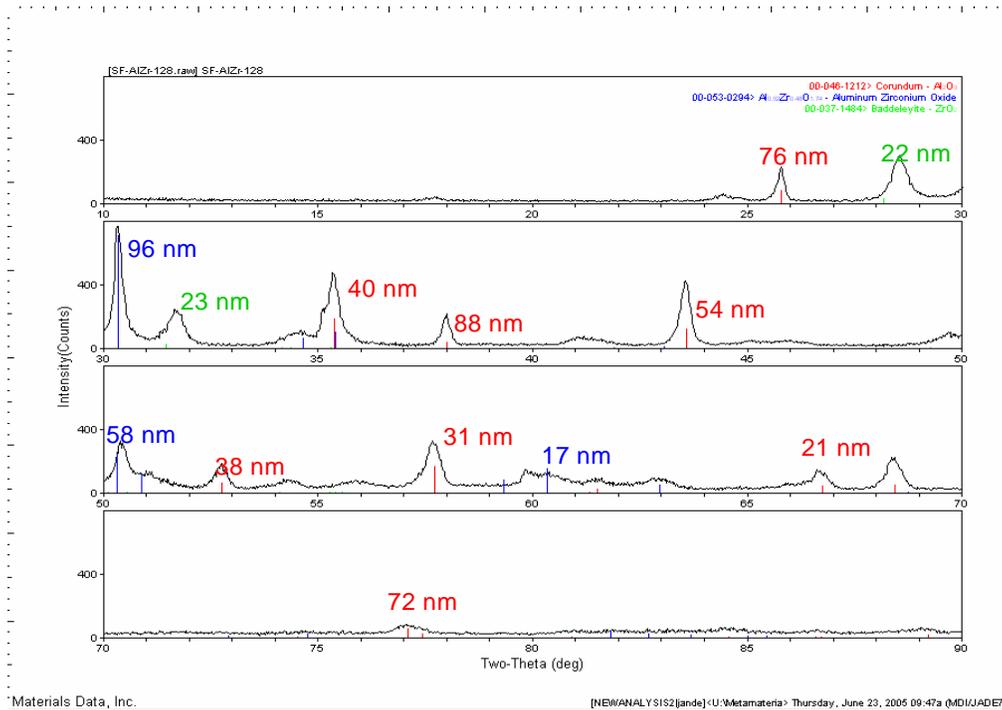


Figure 8: XRD pattern for the SF-AiZr-128 sample. The sample was sinter-forged at 1400°C for 6 hrs. The crystallite size is estimated using Rietveld analysis. The composition was 28.5/71.5 mol% Zirconia to Alumina. Crystallite sizes are given for each peak of Zirconia (Green), Alumina (Red) and metastable Aluminum Zirconium oxide phase (Blue).

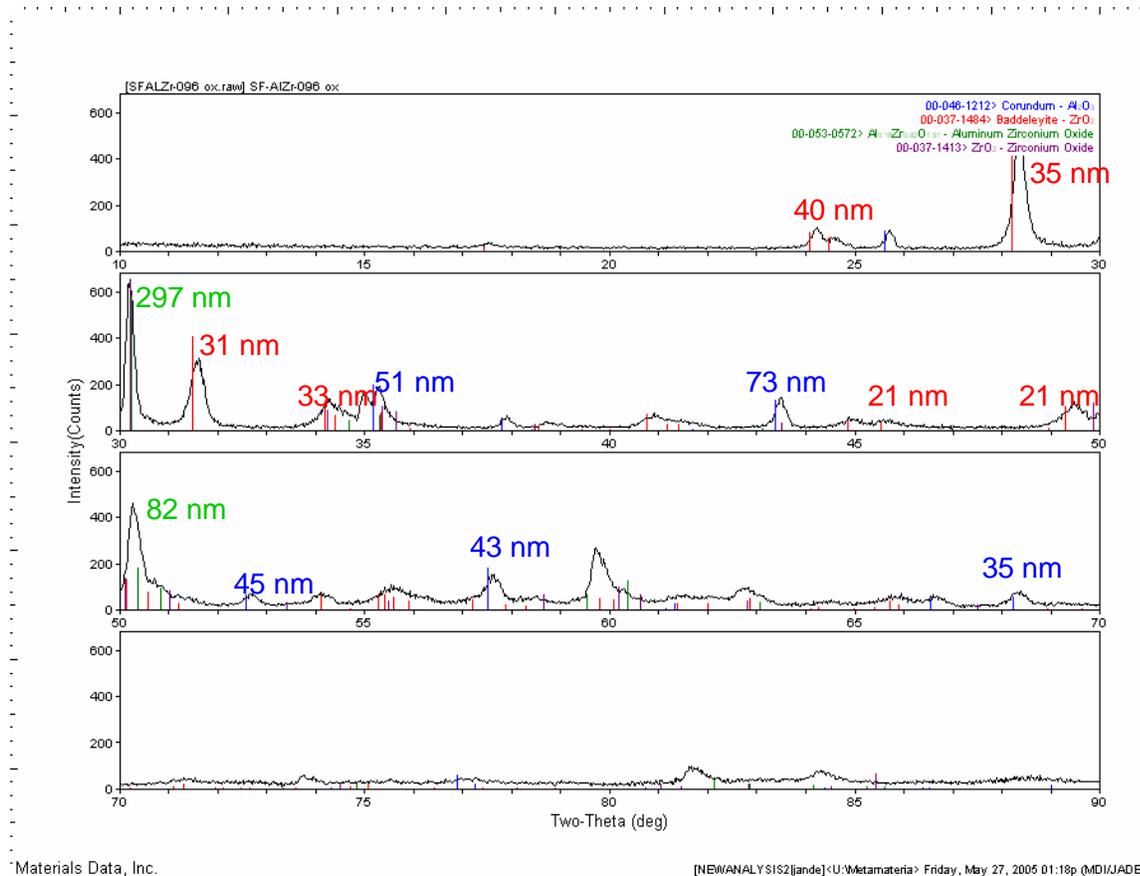


Figure 9: XRD pattern for the SF-AlZr-96 sample. The sample was sinter-forged at 1400°C for 6 hrs. The crystallite size is estimated using Rietveld analysis. The composition of the sample was 50/50 mol % Zirconia to Alumina. Crystallite sizes are given for each peak of Zirconia (Red), Alumina (Blue) and metastable Aluminum Zirconium oxide phase (Green).

**IR Measurements:** IR measurements were done at PMC on oxygenated samples that were polished. IR transmission was measured using a *Thermo Nicolet: Nexus 670 FT-IR*, for wavelengths between 2.5 $\mu\text{m}$  (4000 $\text{cm}^{-1}$ ) to 25 $\mu\text{m}$  (400 $\text{cm}^{-1}$ ). All IR data reported were corrected for background signal collected for the environment in the sample chamber. Background correction was verified before and after running the samples by collecting IR transmission spectra for empty cavity of the sample holder. An IR spectrum for a polished single crystal sapphire was used in each run as a standard.

Figure 10 shows IR transmission of Al-Zr-017 sinter-forged at 1250°C for 4 hrs and oxygenated at 1200°C for 12 hours. It can be seen that 45% transmission was observed after oxygenation and decreased to less than 20% after HIP'ing. IR transmission increased back to around 50% after oxygenation. The results suggests that no further densification resulted during HIP'ing

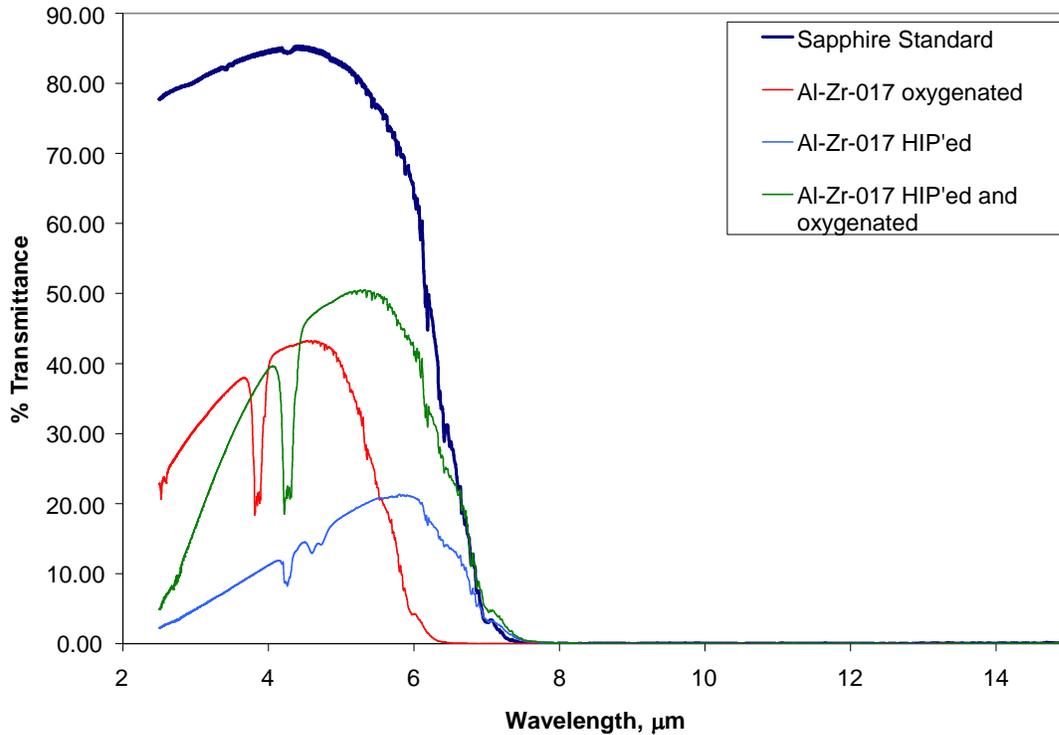


Figure 9: IR transmission of sinter forged Alumina-Zirconia sample before and after HIP'ing

IR transmission spectra were measured for many other samples and no significant IR transmission was found. Extended oxygenation did increase transmission slightly; however, nothing close to the 50% transmission showed in Figure 9. Typical examples are shown in Figures 11 and 12. Both of these samples (SF-AlZr-142 and SF-AlZr-145) only showed an IR transmission of 2% after oxygenation.

The IR transmission results obtained during the Option are both puzzling and disappointing. At the end of Phase I, it was believed that higher density would naturally lead to higher IR transmission. Not only was this not the case, it has not been possible to replicate the 50% transmission results obtain in the Al-Zr-017 sample, even though considerable effort was made trying to do this. In the Option, the effect of residual carbon has been minimized, if not eliminated. Porosity is low or non-existent. Grain size, while not as low as desired for alumina, still is on a par or lower than that found for the -017 sample.

Phase assemblage is now believed to possibly play an important role but its exact nature is not understood. What is of concern is that more than 2 phases are almost always present. The selection of zirconia as the phase to inhibit grain growth, while generally successful in this objective, may have indices of refraction different from alumina. The formation and subsequent breakdown of the aluminum zirconium oxide metastable phase may also be contributing to the drop in IR transmission.

In order to make a nanocomposite material, grain growth must be impeded, which generally requires an immiscible phase and lower processing temperatures. Pressure-assisted sintering of nanoparticulates certainly does provide an approach to making nanocomposites; however,

additional work is needed to understand the influence of the crystalline phases and to better optimize the nanocomposite grain structure.

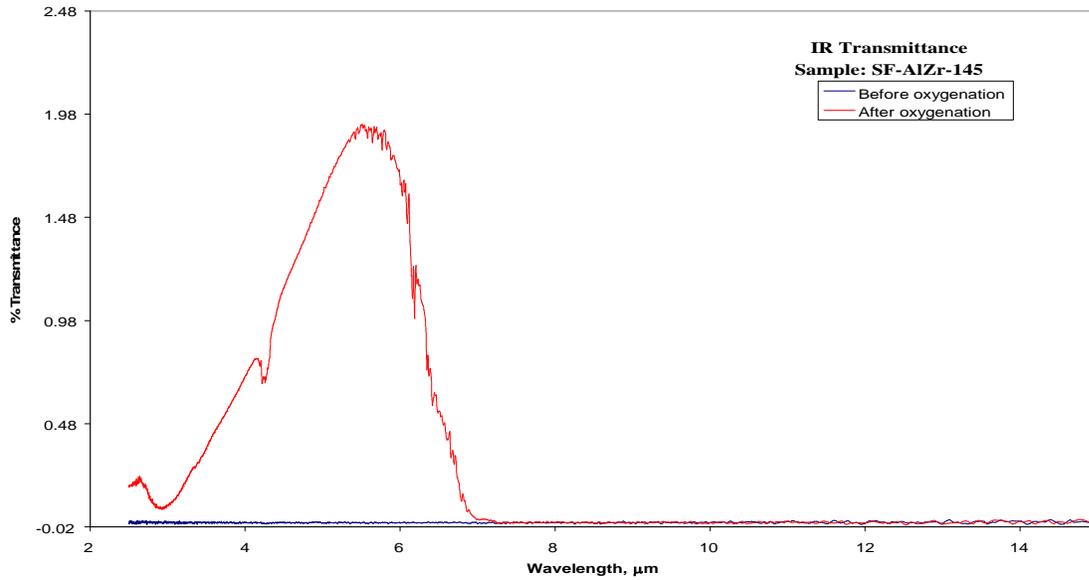


Figure 11: IR transmission of a sinter-forged specimen SF-AlZr-145 before and after oxygenation

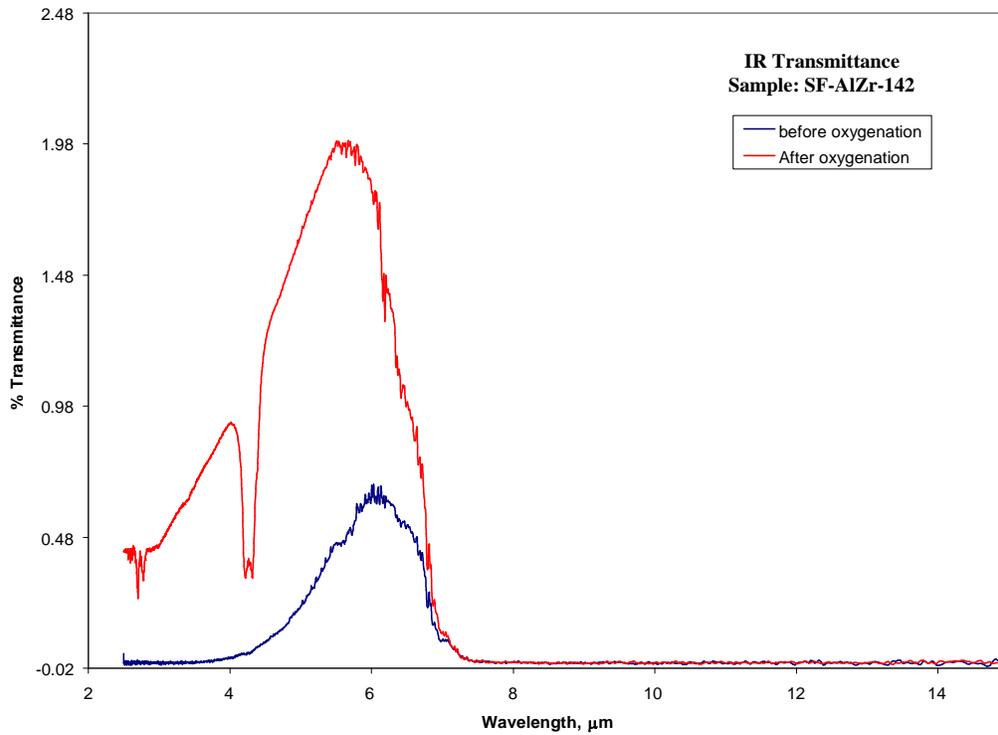


Figure 12: IR transmission of a sinter-forged specimen SF-AlZr-142 before and after oxygenation

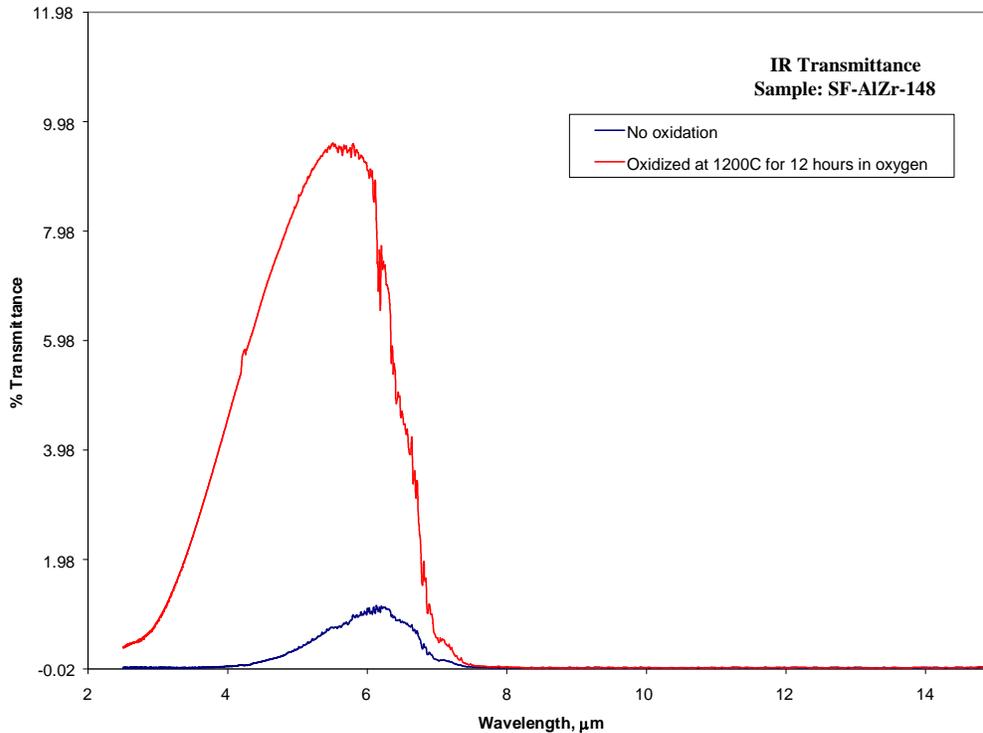


Figure 13: IR transmission of a sinter-forged specimen SF-AlZr-148 before and after oxygenation

The IR transmission results in the Al-Zr-O nanocomposite samples are not encouraging at this stage of the work. Causes for lower IR transmission includes

- inadequate oxygenation
- unfavorable phase assemblage
- inadequate pore removal
- grain growth of some phases not identified by XRD
- residual carbon content

Clearly, further work is necessary for developing a proper understanding of the impact of various factors, especially phase assemblage on the IR transmission in nanocomposite materials. This understanding would lay the foundation for the further process optimization in the development of an IR transparent nanocomposite material. While the Option has ended, some work is being continued to try to better understand the nature of what is occurring and additional results will be forwarded if IR transmission improves.

### **Conclusions/Recommendations**

In summary, during Phase I and the Option, a method was developed for preparing alumina and zirconia nanoparticles under 10 nm with a surface area of 200 to 400 m<sup>2</sup>/g and these could be used to form a dense nanocomposite. It was found that in addition to starting materials, a metastable alumina-zirconia phase could form during heat treatment. Colloids/dispersions were able to be prepared of the nanoparticulates produced using both sonochemical and glycothermal methods. A fluidized-bed technique was developed for reducing residual carbon in the powder. Chemical-aided milling was found particularly useful for de-aggregating and re-dispersing

calcined powders. Solid preforms were prepared using pressure casting techniques and also by dry pressing calcined powders. Drying of parts with nano-scale pores was difficult but procedures were developed that permitted successful drying of parts.

Pressureless sintering was not found useful for densification, although it was used to prepare samples for sinter-forging. Pressure-assisted sintering (sinter-forging) was able to consistently produce 100% dense parts (Archimedes density) with little grain growth at modest temperatures (above 1275°C) and while optimization is needed, this approach looks very promising. HIP (hot isostatic pressing) represents an alternative method for taking advantage of the plastic deformation properties developed during sinter-forging but insufficient time existed to explore this method. However, in an unrelated program described briefly below, HIP will be used to prepare dense samples of nanocomposites for armor testing and some additional evaluation will be done on alumina-zirconia by including some samples in these HIP cycles.

While high density was achieved, often with little grain growth, IR transmission was low and the reasons for this are not fully understood and additional work would be required to develop this understanding. A grain size of less than 50 nm was routinely obtained, although some growth in alumina grains always occurred. The presence of multiple phases was believed to be a deterrent to IR transmission, but this was not directly studied. It is believed that pressure-assisted sintering combined with a grain growth inhibitor does indeed offer the opportunity to prepare nanocomposite materials.

Zirconia may not have been the correct grain growth inhibitor and future work needs to examine other systems, such as a MgO-rich alumina spinel where two cubic phases can be formed: cubic MgO and cubic spinel. Metastable powders of the proper composition can be made using Bernie Kear's plasma process at Rutgers, which NanoDynamics/MetaMateria has recently licensed. Fully dense plasma processed powders of an alumina rich spinel have been used to make fully dense materials by HIP that have exceptional mechanical properties, exceeding those of alumina. HIP of these metastable powders is done below 1400°C to form a nanocomposite with grain sizes below 30nm.

The opportunity provided in this SBIR Phase I and Option to examine preparation of dense nanocomposite materials has provided substantial understandings of the requirements for making these materials. It has also indicated that much more work is needed to understand composition and processing conditions necessary for high IR transmission. Overall, while the principal objective of this SBIR has not yet been accomplished, considerable useful information was obtained that may enable future achievements.