Optical and Mechanical Properties of Nano-Composite Optical Ceramics

*C. Scott Nordahl, Thomas Hartnett, Todd Gattuso, Richard Gentilman
Raytheon Integrated Defense Systems
c_scott_nordahl@raytheon.com

Submicron and Nanostructured Ceramics

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**Optical and Mechanical Properties of Nano-Composite Optical Ceramics**

See also ADM002307. ECI International Conference on Sub-Micron and Nanostructured Ceramics Held in Colorado Springs, Colorado on 7-12 June 2009, The original document contains color images.
Introduction

• Background
  – Current MWIR transparent materials
  – Nano-composite oxides
• Processing/Microstructures
• Optical Properties
• Mechanical Properties
• Summary
Acknowledgements

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Raytheon NCOC Project Team

- Raytheon IDS
- Scott Nordahl

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- Todd Stefanik

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Maximizing the Optical and Mechanical Performance

The goal is to achieve all of the following simultaneously:

**DARPA Goals:**
- High Strength - equivalent to Sapphire
- Scaleable Method - able to produce 3” domes
- MWIR Transparent - equivalent to Spinel

**Raytheon “Stretch Goal”**
- MWIR Transparency - equivalent to Yttria

To achieve these goals:
- No pore phase (large $\Delta n \sim 0.8$ = scatter)
- Minimize grain size / grain growth (G.S. $< \lambda/20$ for transparency)
- Uniform 2-phase microstructure (small $\Delta n < 0.2$)
- Avoid MWIR absorptions due to Si-O and Al-O bonds
Project Approaches

Raytheon Group
Densify nano-powders to make domes

Rutgers / UC-Davis Group
Plasma sprayed powders
Spark plasma sintering

UConn Group
Direct plasma deposition of dome shapes

• Material test and characterization
• Optical material modeling
Background

Sapphire (single crystal Al₂O₃) is the current MWIR dome material of choice.

- High strength
- Excellent erosion durability (rain/sand)
- High thermal shock resistance
- Low optical scatter
- Intrinsic birefringence
- Lacks full 3-5µm transparency (absorption at 5µm)
- Significant MWIR emission at elevated/operating temperatures
- High temperature mechanical properties degradation
- High cost due to single crystal growth and optical finishing
Objective:
Make much stronger dome materials and retain full MWIR transmittance

<table>
<thead>
<tr>
<th>Optical Properties</th>
<th>Mechanical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapphire</td>
<td><img src="image" alt="image" /></td>
</tr>
<tr>
<td>Spinel</td>
<td><img src="image" alt="image" /></td>
</tr>
<tr>
<td>ALON</td>
<td><img src="image" alt="image" /></td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td><img src="image" alt="image" /></td>
</tr>
<tr>
<td>MgO</td>
<td><img src="image" alt="image" /></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td><img src="image" alt="image" /></td>
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<tr>
<td>YAG</td>
<td><img src="image" alt="image" /></td>
</tr>
</tbody>
</table>

Oxide Nano-Composites

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Maximizing the Optical Performance

Problem: Most durable MWIR dome materials contain Al-O bonds. However, Al-O bonds absorb at $\lambda > 4$ microns.

Solution: Select nanocomposite systems without Al-O bonds ($Y_2O_3$, MgO, ZrO$_2$)
Nanocomposite Composition

Baseline Material System:
Yttria : Magnesia

Y₂O₃:MgO
20:80 Mol% → Y₂O₃:MgO
50:50 Vol%

Liquid
H·Y₂O₃ ss
H·Y₂O₃ ss + Liq.
C·H
C·Y₂O₃ ss + Liq.
C·Y₂O₃ ss
MgO ss + Liq.
MgO ss

1 µm

XRD

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Nanocomposite Optical Ceramics: A new class of MWIR dome materials

Approach: Reduce grain size of transparent polycrystalline ceramics to increase strength: Hall Petch relation: \( \sigma \propto (g.s.)^{-1/2} \)

Problem: Processing conditions (high T & P) required to densify to optical clarity promote grain growth

Solution: Use significant volume fractions of two or more mutually insoluble transparent ceramics (e.g. MgO + Y_2O_3)

Problem: Refractive index differences between phases cause scattering by the grains

Solution: Reducing the grain size to < \( \lambda/20 \) eliminates scatter and transparency is restored: 4\( \mu m/20 = 200 \) nanometers!
Nanopowder Production via Liquid Flame Spray Pyrolysis

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Process Overview

Powder Process

- Starting powders produced by Flame Spray Pyrolysis
- Densified by Sinter + HIP
- Slip Casting – alternate forming method
- SPS densification – smaller grain size
Nanocomposite Microstructure

Backscattered electron images. 50:50 Vol% Yttria:Magnesia

Uniform microstructure with ~150nm grain size.
Optical Properties

MgO:Y$_2$O$_3$ Nanocomposites

In the visible band

In the MWIR band
Fracture strength improved with optimized powders and processing.

New material systems and/or more energetic processing needed for 1200 MPa!
## Material Property Goals

### Material Property Metrics for 3-5 micron Nano-Composite Optical Ceramics

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Units</th>
<th>Phase I Metrics</th>
<th>Achieved</th>
<th>Phase II Metrics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Coefficient (ave, 3-5µm)</td>
<td>cm⁻¹</td>
<td>≤ 0.1</td>
<td>0.05</td>
<td>≤ 0.1</td>
</tr>
<tr>
<td>Optical Scatter (Fwd TIS @ 3.39µm)</td>
<td>%</td>
<td>≤ 2.0</td>
<td>0.6</td>
<td>≤ 0.5</td>
</tr>
<tr>
<td>Fracture Strength at 600°C (average of 10 biaxial disks)</td>
<td>MPa</td>
<td>≥ 600</td>
<td>650</td>
<td>≥ 1200</td>
</tr>
<tr>
<td>Hardness (µ-indent: 50g load)</td>
<td>kg/mm²</td>
<td>≥ 2200</td>
<td>2350</td>
<td>≥ 2200</td>
</tr>
<tr>
<td>Thermal Shock Resistance (requires thermal conductivity measurement)</td>
<td>calculated FoM: R’</td>
<td>- - -</td>
<td>1.3 X Sapphire</td>
<td>≥ 2X Sapphire</td>
</tr>
<tr>
<td>Sand Erosion Resistance (blowing sand – conditions TBD)</td>
<td>grams/std test</td>
<td>- - -</td>
<td></td>
<td>≥ 2X Sapphire</td>
</tr>
<tr>
<td>Water Drop Threshold Velocity (Marshall SFC – 3mm drop)</td>
<td>m/s</td>
<td>- - -</td>
<td></td>
<td>≥ 2X Sapphire</td>
</tr>
</tbody>
</table>
Spark Plasma Sintering

- Pressure
- Powder
- Graphite Die
- Vacuum Chamber
- Pyrometer
- DC Pulse Generator

Pulsing Electric Field → Joule Heating → Low T, Fast Sintering
Spark Plasma Sintering

Modeling die geometries to improve temperature uniformity in scaled-up process

YZ temp on x=0

max: 1.49
x: 1.45
w: 1.40
v: 1.35
u: 1.30
t: 1.25
s: 1.20
r: 1.15
q: 1.10
p: 1.05
o: 1.00
n: 0.95
m: 0.90
l: 0.85
k: 0.80
j: 0.75
i: 0.70
h: 0.65
g: 0.60
f: 0.55
e: 0.50
d: 0.45
c: 0.40
b: 0.35
a: 0.30
min: 0.30

Scale = E3

3” Diameter Disk

Uniform Microstructure
Direct Deposition

Precursor Droplet → Evaporation → Breakup and Precipitation → Pyrolysis → Sinter → Melt → Splat Deposit
Direct Deposition

50:50 MgO:Y$_2$O$_3$

Microstructure

Polished Cross-section

3.3mm thick

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Summary

• MgO:Y₂O₃ based nanocomposite ceramics have been developed using traditional ceramic processing routes and demonstrated:
  – Sapphire equivalent mechanical durability
  – Yttria equivalent MWIR optical transparency

• New nanocomposite material systems show potential for greater mechanical durability with inherently more durable crystallographic phases.

• More energetic fabrication techniques are showing promise for refined microstructures and improved mechanical properties.