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Fabrication of Phosphorescent Oxide Coatings Using the Aerosol Deposition Technique

Jacob Mahaffey, Shannon E. Murray, Caroline Winters, Elizabeth Jones, Amanda Jones, Wendy Flores-Brito, and Kathryn Hoffmeister

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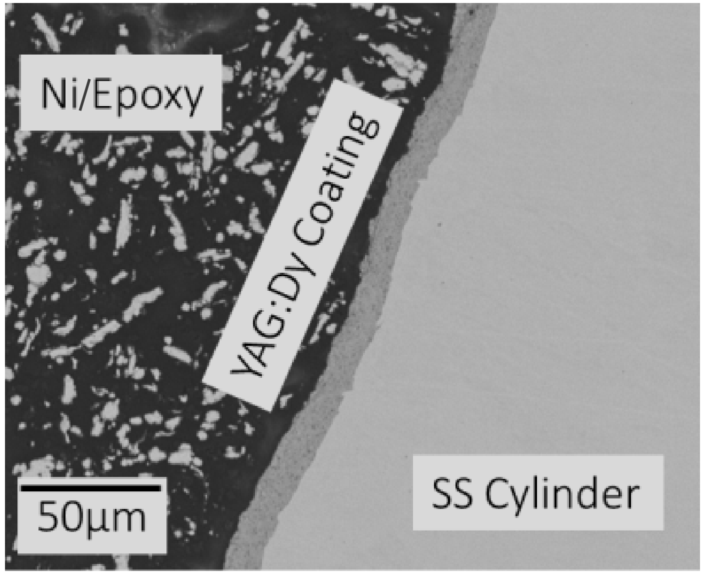
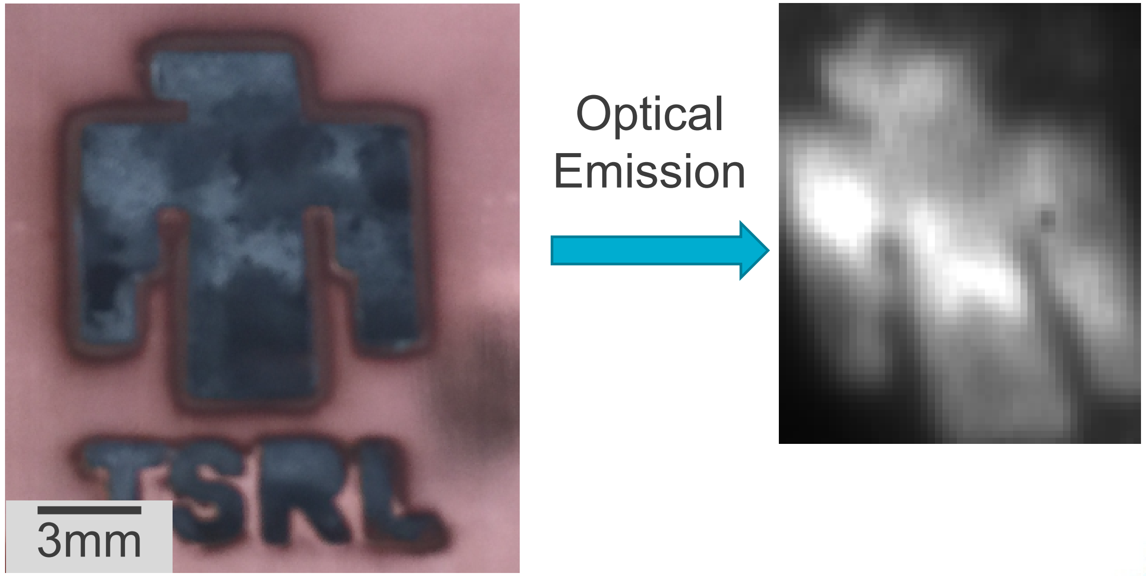
Outline of Talk

- Overview of Phosphorescent Materials
- Overview of Aerosol Deposition
- Material Characterization of Aerosol Deposited Phosphor Films
- Phosphor Film Optical Characterization
- Applications and On-going work

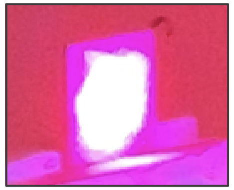




Phosphorescent Materials and Non-Contact Temperature Sensing

Phosphor Sample

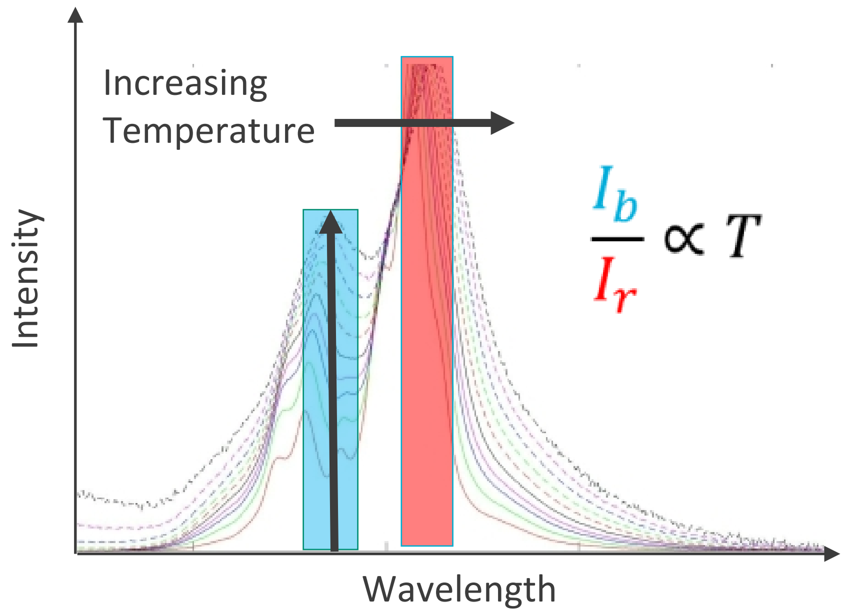
UV Excitation



Visible Emission

Activator atoms excited by UV light will be in an elevated electronic state for some period of time before relaxing to the ground state by emitting visible photons

Ratio Method



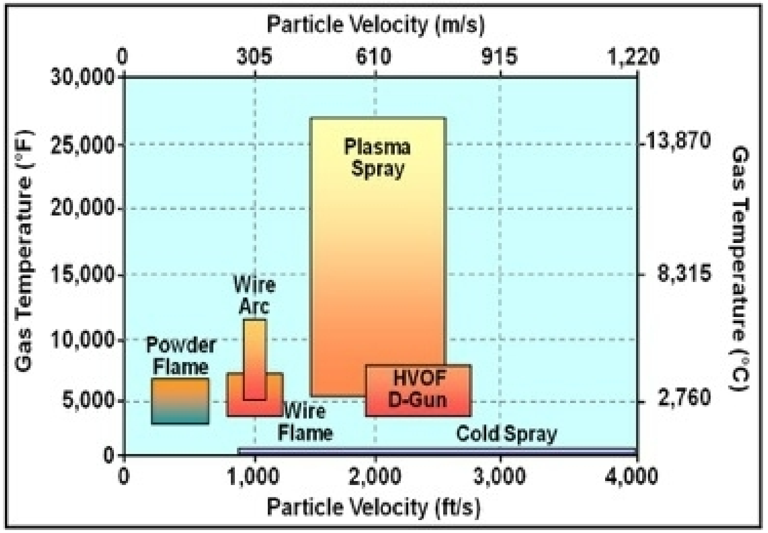
Use two cameras (each with a unique wavelength filter)
→ Infer the T of the area via pixel-to-pixel correlation

- Traditional IR measurements can become increasingly inaccurate in extreme environments as emissivity changes and background blackbody radiation increases
- Phosphors offer precise temperature, and emit light at shorter wavelengths to reduce background saturation
- Ratio method allows for the use of two filtered cameras to obtain 2-dimensional field of view
- This work explored the use of Yttrium Aluminum Garnet doped with 1-3% Dysprosium (YAG:Dy) and $Mg_4F_2GeO_4$:Mn (MFG)
- Conventional processing of these phosphor films done by ethanol drying and mixing in epoxy
  - Both methods have significant drawbacks for coating application

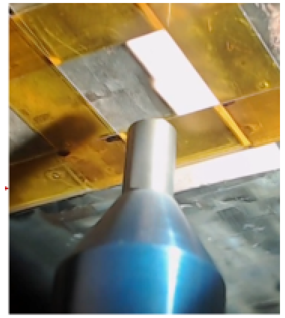
Overview of Aerosol Deposition

Thermal Spray Coating Techniques – Melt and Kinetic Deposition

- Thermal Spray encompasses many techniques used to produce coatings of Metals, Ceramics, and CerMets
- These technologies span a wide variety of particle states (temperature and velocity)
- Typically think of "thick films"

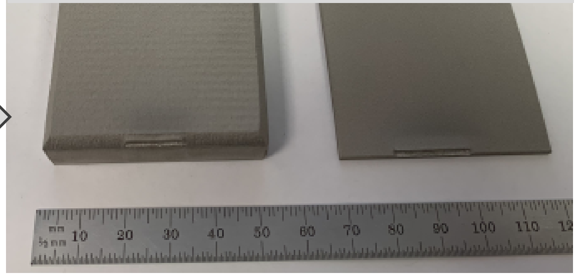


*Adapted from plots by R.C. McCune, Ford Motor Co. & A. Papyrin, Ktech Corp.



Aerosol Deposition

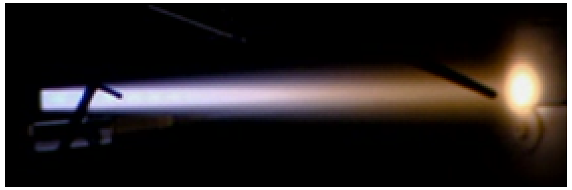
Cold Spray



Cold spray coating, ~3mm, .2mm thick

Air Plasma Spray

Twin Wire Arc Spray

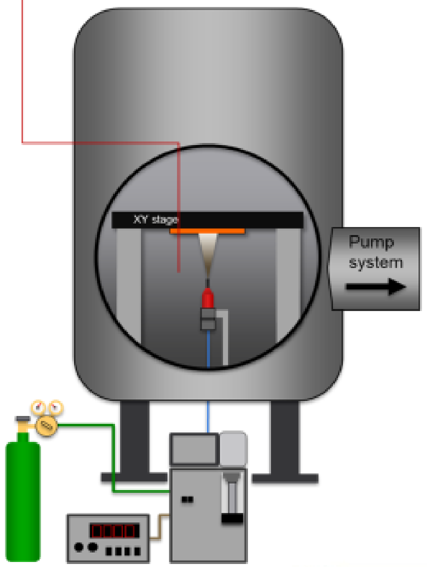


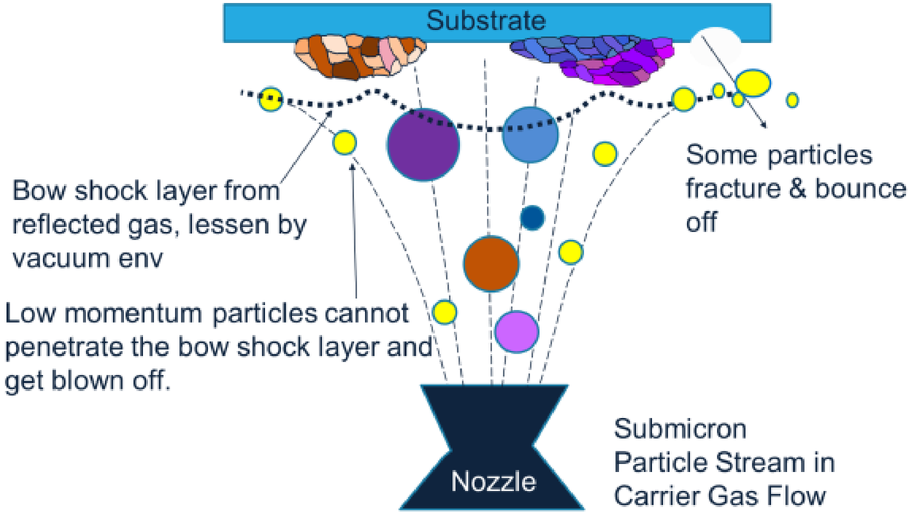
High Velocity Oxy-Fuel (HVOF)

Aerosol Deposition – A New "Thin" Film Thermal Spray Technique

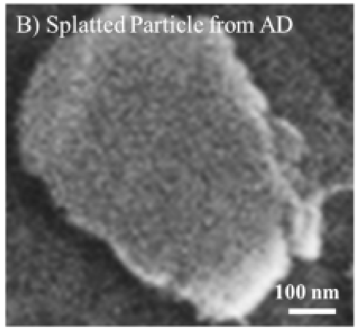
- Aerosol Deposition (AD) is a room temperature impact consolidation process that uses sub-micron dry powder to create dense coatings of ceramics, metallics, and other materials.
- Aerosols are formed by mixing sub-micron particles with Helium or Nitrogen carrier gases and accelerated through a de Laval nozzle into a vacuum (NO BINDERS).
- Resulting microstructures consist of crystallite sizes in the 10's of nanometers, and typically contain large residual compressive stresses.

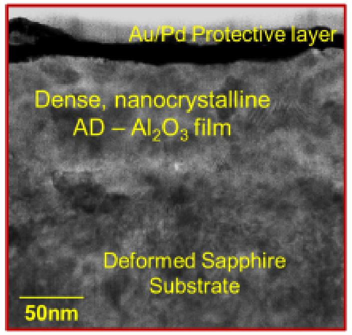
AD Cu on Al_2O_3 Substrate





Al_2O_3 Coating on Sapphire Substrate:

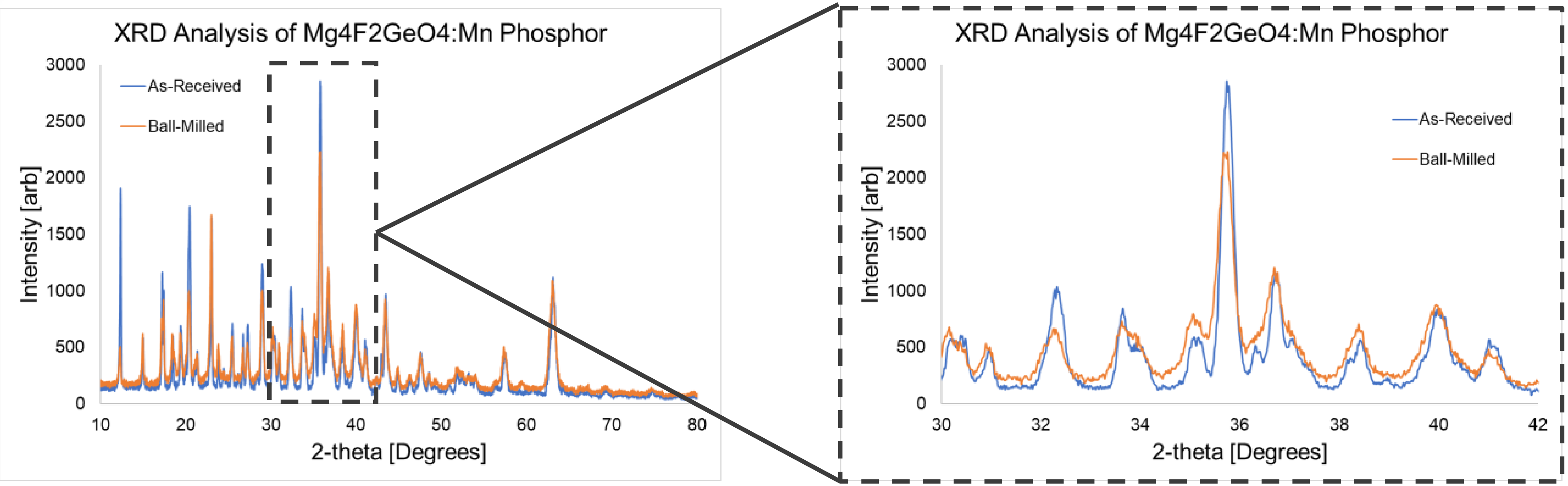




*Work on AD Al_2O_3 courtesy of Pylin Sarobol *Schematic of AD process courtesy of Jesse Adamczyk

Material Characterization of Aerosol Deposited Phosphor Films

XRD Analysis of AD $Mg_4F_2GeO_4$:Mn Powders: Pre-Processing



- As-received powder feedstock was verified using coulter size analyzer to ~1micron size
- Ball-milling is used to induce additional defects within the crystalline lattice to improve fracture mechanics during deposition
  - Powder milled in Pulverisette 7 high energy planetary mill in water
- Slight broadening in XRD spectral response (refinement needed to determine significance)
- Powder dried and sieved before spraying

Conventional Processing Technique vs Aerosol Deposition of Phosphors

Conventional Processing

Epoxy Doping (after 400C exposure)

Ethanol Drying

Aerosol Deposition

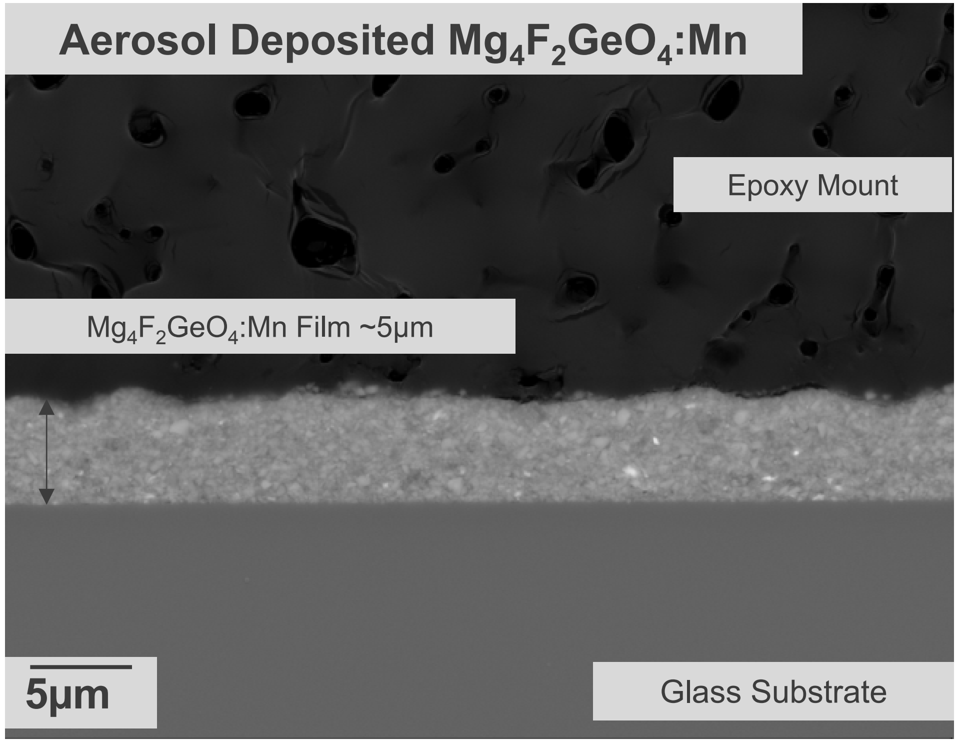
YAG:Dy Film

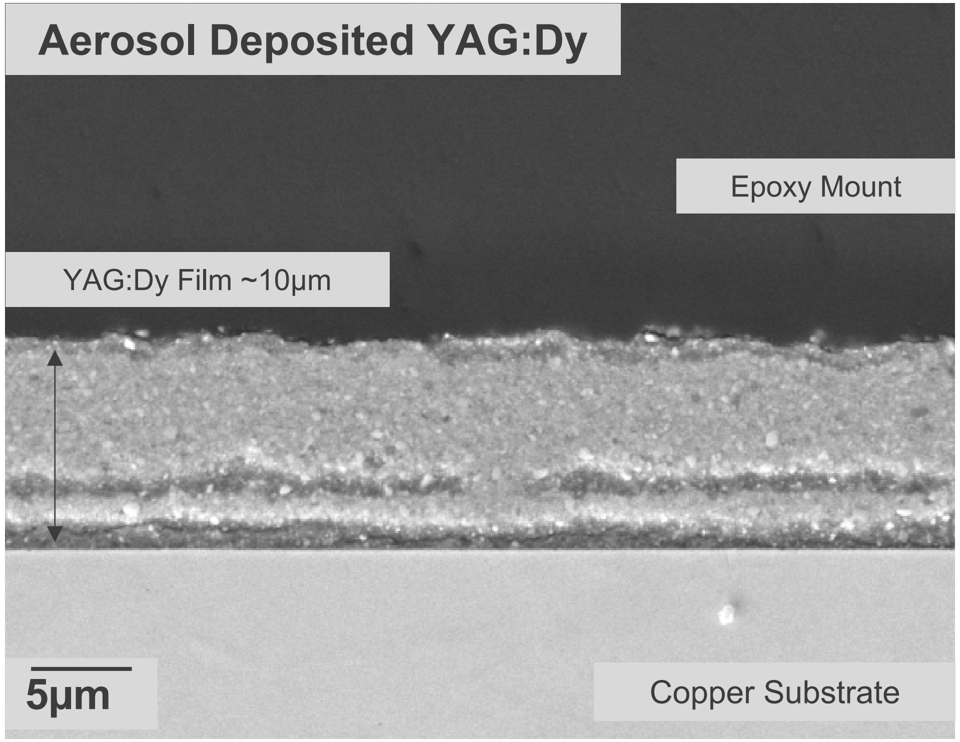
$Mg_4F_2GeO_4$:Mn Film

- Previous attempts at applying phosphor to surface utilized epoxy doping and ethanol drying
  - Produced poor bond, spallation, high porosity, low pyrolysis temperature, very thick films
- Aerosol Deposition was used to fabricate thin films of phosphor materials on the surface of ceramics (and metals)
  - Yttrium Aluminum Garnet doped with 1-3% Dysprosium (YAG:Dy) sprayed onto Al_2O_3 substrate
  - $Mg_4F_2GeO_4$:Mn sprayed onto borosilicate glass
- Coatings appeared uniform and were well adhered to the substrate
  - Tape-tests used to test coatings for adherence

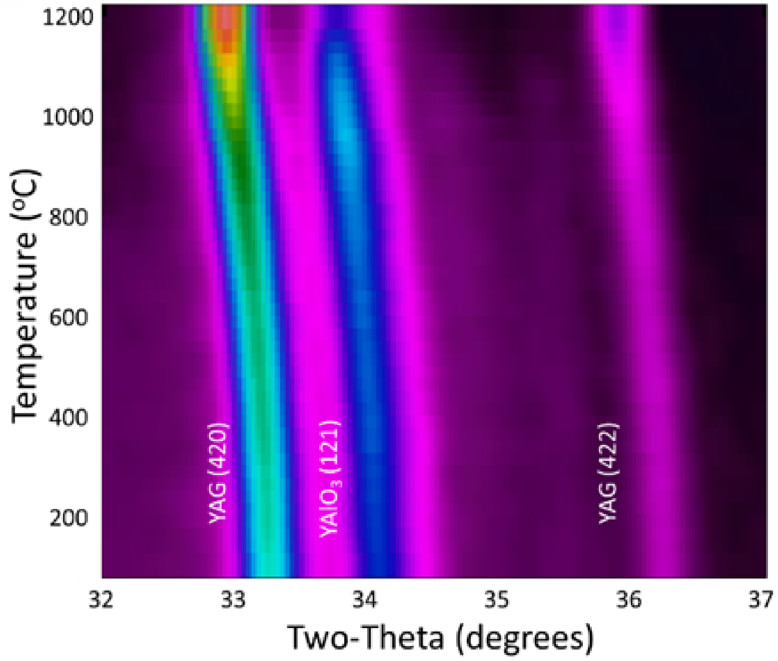
SEM Analysis of AD Phosphor Materials

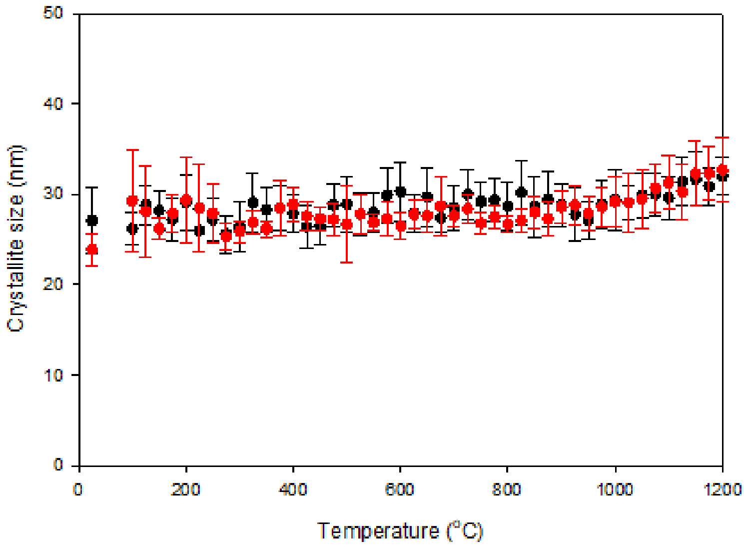
- SEM micrographs of both phosphors were obtained to determine microstructure
- Both coatings were comprised of smaller fractured particles which were conformal to the substrate surface
- Some cracking was observed in the YAG:Dy film
  - Could be caused by increase in residual stress from the 2x thickness of the coating (compared to the other phosphor)





XRD Analysis of AD YAG:Dy Coatings

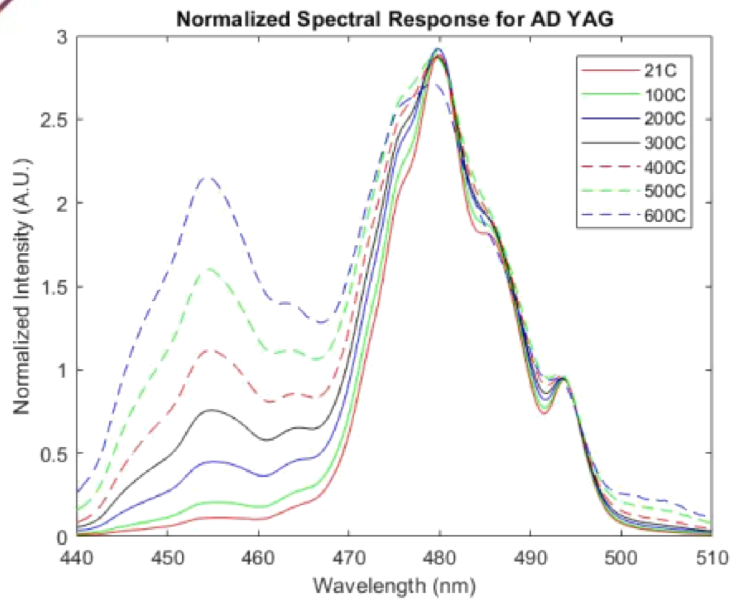




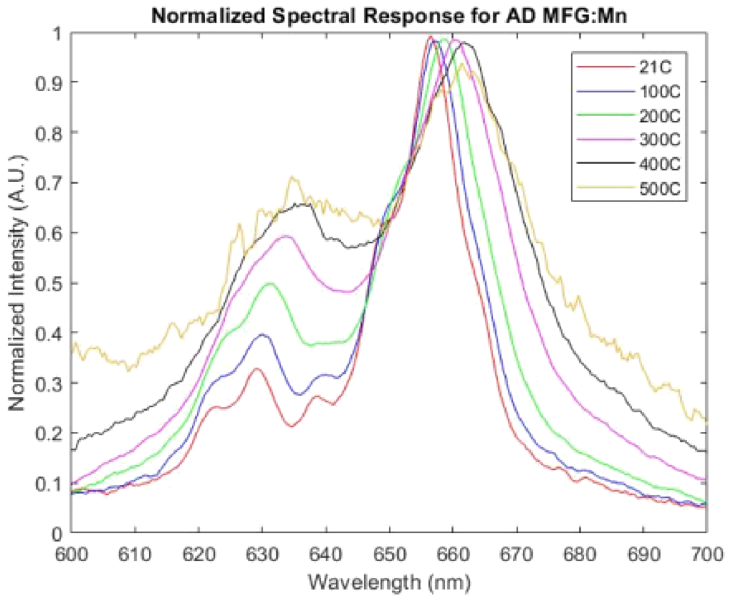
- X-Ray Diffraction measurements were taken while heating the YAG:Dy films to understand possible phase/microstructure changes
- Initial film contained Yttrium Aluminum Perovskite (YAP) impurity according to XRD
  - Likely due to starting powder purity
- Heating of the film above 1000°C resulted in a phase change from the YAP to YAG.
- Room temperature measurements showed that the as-sprayed film had a crystallite size of ~20-30nm
  - Consistent with literature measurements for AD ceramic films
- Slight peak narrowing occurs when heating above 1000°C which indicates grain coarsening
  - Error bars in crystallite size represent 3σ
- Slight peak shifting during heating likely represents strain relief
  - Common for AD films to have large compressive residual stress

Phosphor Film Optical Characterization

Spectral Response of AD Phosphor Films

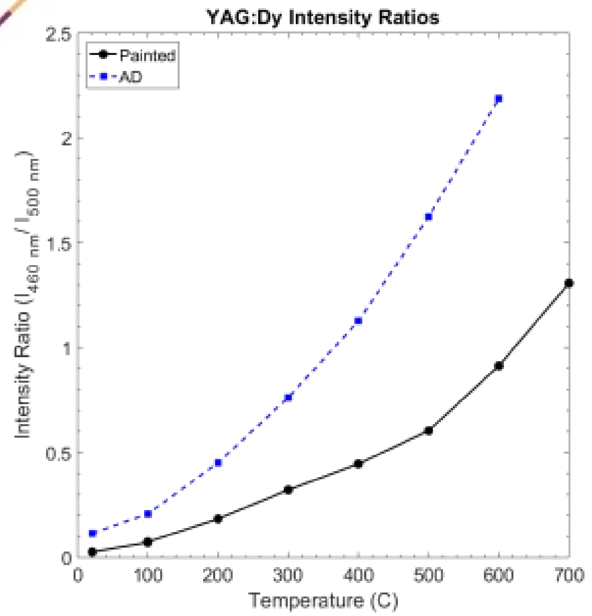


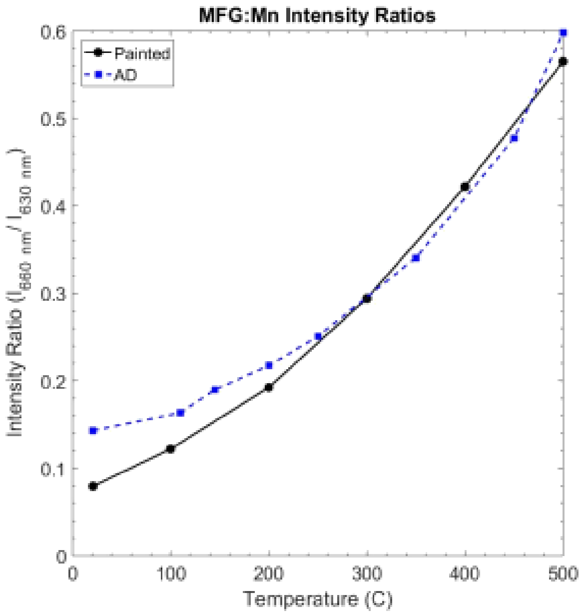
- Both AD films were excited with 355 nm UV light
- YAG:Dy (3%) phosphor (top figure) demonstrates similar behavior as non-processed YAG:Dy phosphor
  - The $^4I_{15/2} \rightarrow {}^6H_{15/2}$ transition band at 440 nm – 465 nm increases due to energy transfer processes between the populations of the $^4F_{9/2}$ and $^4I_{15/2}$ upper states
  - Overall signal decreases as temperature increases



- AD films of $Mg_4F_2O_4Ge:Mn$ phosphor, have similar spectral response to non-processed phosphor
  - The Stokes vibronic band (660 nm) peak shifts wavelength as temperature increases
    - This is a red-shift to longer wavelengths
  - The Stokes band also experiences thermal quenching
  - The anti-Stokes vibronic band (633 nm) increases with temperature due to population gain

Calibration Curves for AD Phosphor Films





- The intensity ratio versus temperature was computed by comparing the signal at two different transitions
- Two different processing strategies are presented
  - 1) Spectra with background subtraction
  - 2) Normalized spectra with background subtraction

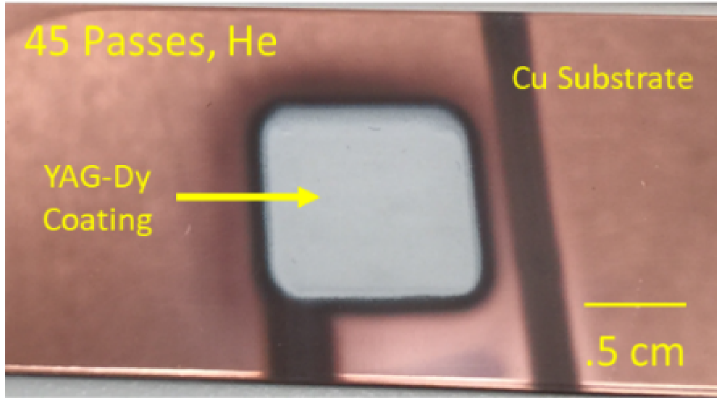
- Thermographic behavior of YAG:Dy is determined by the ratio between the $^4I_{15/2} \rightarrow {}^6H_{15/2}$ transition (460 nm) and the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition (500 nm)
  - Temperature sensitivity is limited by signal-to-noise of the AD film

- Thermographic behavior of $Mg_3F_2O_4Ge:Mn$ is determined by the ratio between the anti-Stokes (633 nm) and Stokes (660 nm) vibronic bands
- YAG:Dy is sensitive over a wider temperature range (25 – 600 C) than Mg3F2O4Ge:Mn (25 – 500 C)

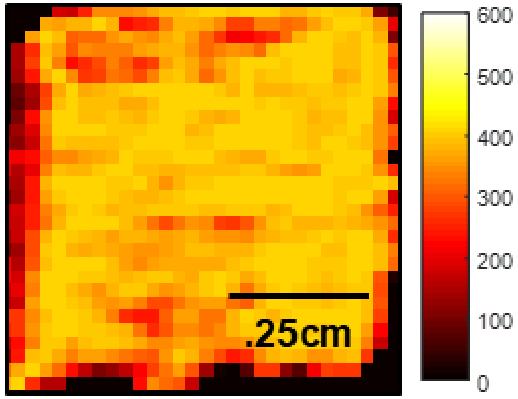
Applications and On-going work

2-Dimensional Temperature Profile of AD YAG:Dy Films

YAG:Dy Deposition on Copper Substrate

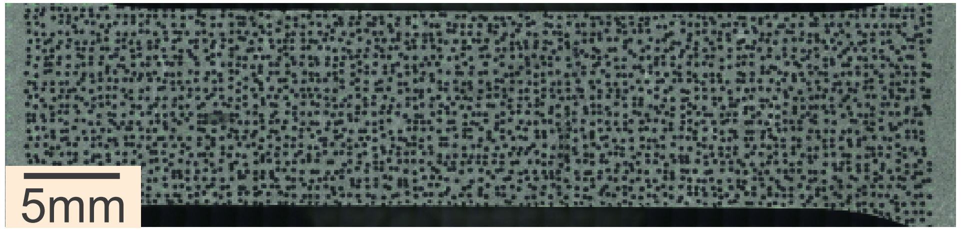


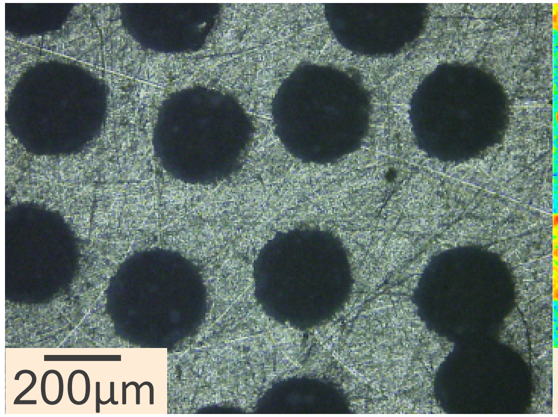
Extreme substrate oxidation at ~500C prevented higher temperature testing

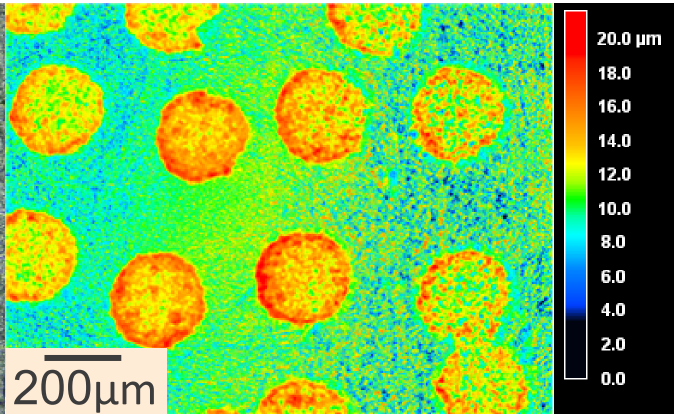


- 2-D Temperature profile obtained for AD YAG:Dy coatings using two color pyrometry
- Calibration curve determined previously used to correlate optical emission to temperature
- Measurement stopped at 500°C due to extreme oxidation of copper substrate
- Good resolution difficult for pure coatings due to ability to correlate between cameras
- Ceramic substrates and coatings have survived thermal cycling up to 1000°C (XRD samples)
- Conventional Epoxy mixed YAG:Dy coatings were shown to pyrolyze at 400°C

Temperature and Strain Measurements of Tensile Bars using $Mg_4F_2GeO_4$:Mn AD Patterns



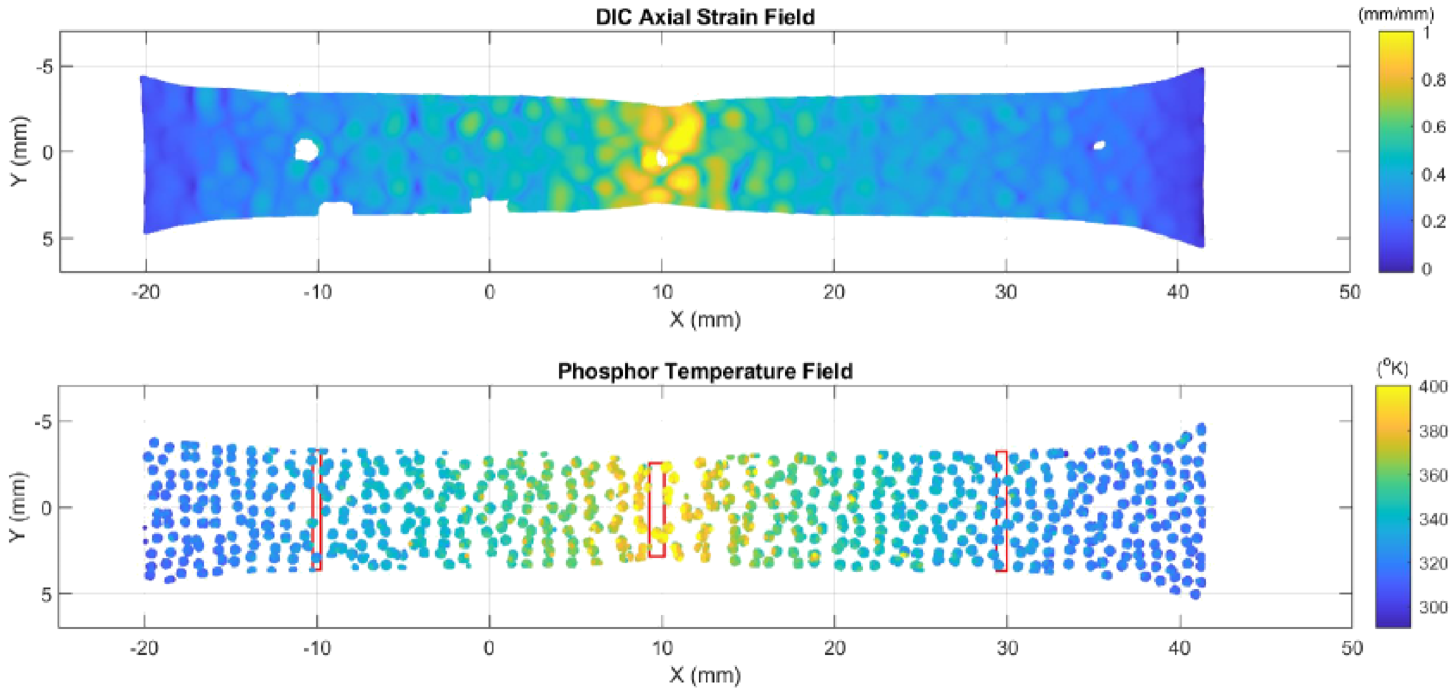




- Digital Image Correlation (DIC) patterns were produced on an area of ~47mm x 10mm on the surface of 304L stainless steel tensile bars
- Spots were produced at 0.010in (.25mm), 0.020in (.51mm), and 0.040in (1.2mm) diameter using laser cut Kapton masks
- A laser-based surface profilometer was used to observe the coating on the surface
- Less uniformity was observed for the spots than larger surface area films
  - Could be caused by gas turbulence from the small coating area compared to the thickness of the Kapton

Temperature and Strain Measurements of Tensile Bars using $Mg_4F_2GeO_4$:Mn AD Patterns

- Simultaneous temperature and strain data was successfully demonstrated using AD phosphor films
- DIC correlation process allows precise matching of a single point on the sample to sub-pixel (0.02 px) locations each of the cameras
  - Matching facilitates more precise intensity ratios and thus phosphor temperatures
- Emission intensity increases immediately with initial deformation during tensile testing
  - We believe this could be caused by strain relief mechanisms such as cracking



Thank You For Your Time