Nuclear Science and Security Consortium
Virtual Scholar Showcase 2020

Synthesis of Li-containing Garnet Ceramics for Dual-mode Detection

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NSSC
NUCLEAR SCIENCE and SECURITY CONSORTIUM

Introduction

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SCINTILLATION MATERIALS RESEARCH CENTER

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NSSC Focus Area: Nuclear Instrumentation

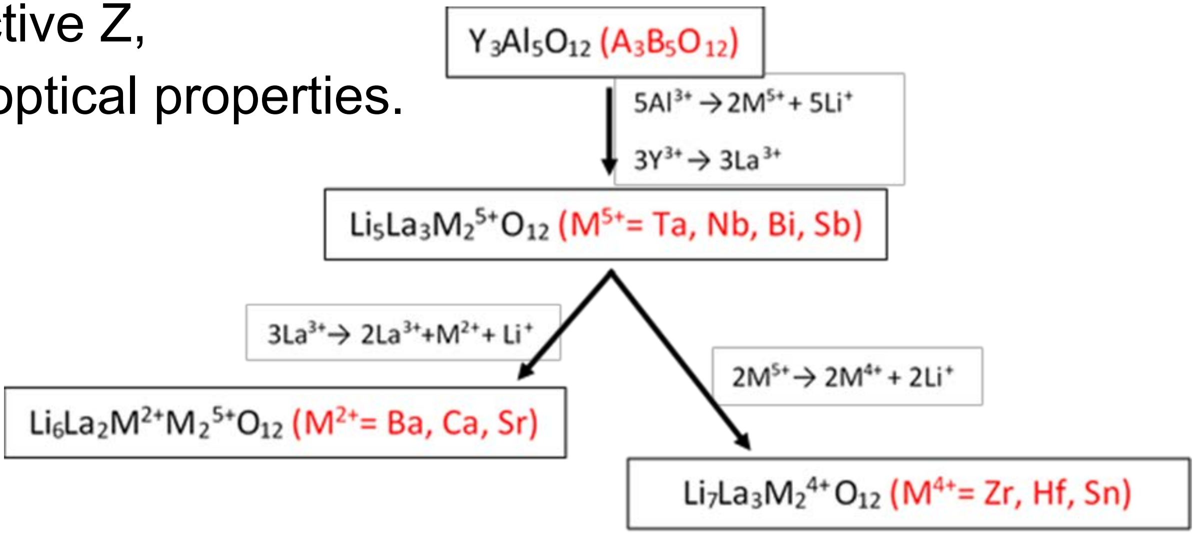
Radiation Detection and Instrumentation

Motivation

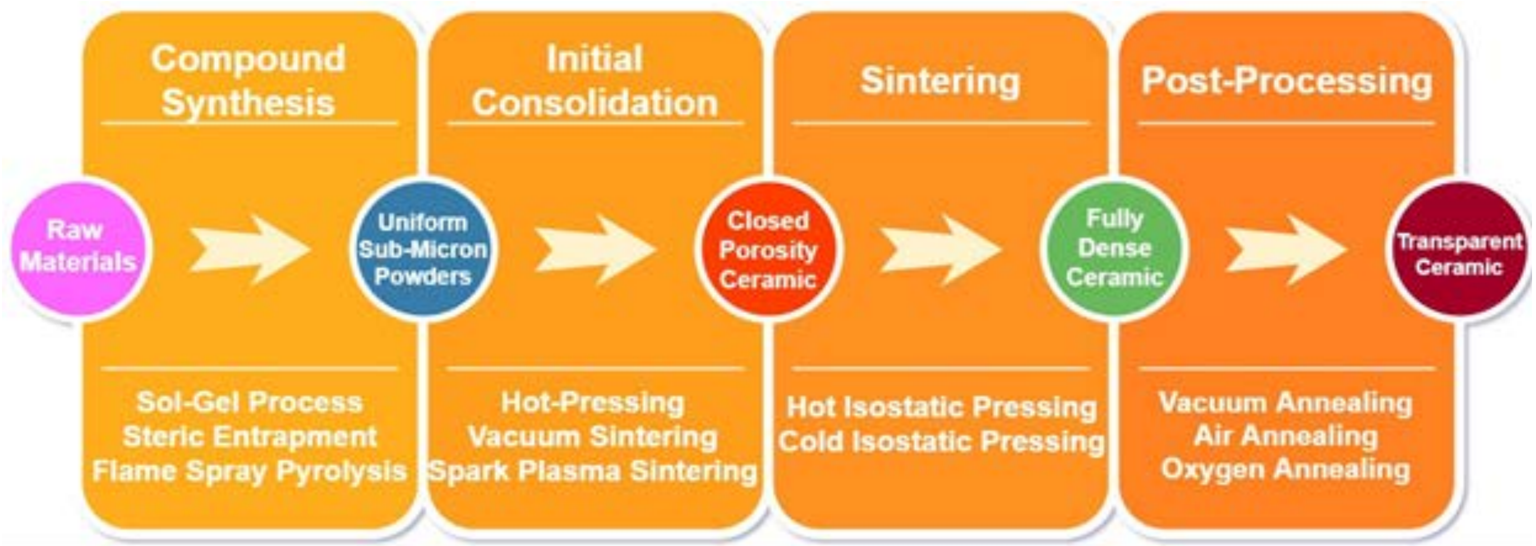
- One of the goals of the NNSA is to **“develop technologies to detect nuclear and radiological proliferation worldwide”.**
- Wide spread use of novel dual-mode inorganic scintillators such as LiI:Eu and Cs_2LiYCl_6:Ce (CLYC) has been prevented by their high cost and low yields from current single crystal growth methods
- Transparent ceramic scintillators could provide a quicker and cheaper method of producing high performance scintillators in near net shapes

Family of Li-containing Garnets

- **Initially researched for solid state electrolytes for Li-ion batteries due to high Li-content and garnet structure**
- **Among these, $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (LLTZx) garnets are promising for efficient dual mode ceramic detectors due to their:**
  - high Li content,
  - high density,
  - high effective Z,
  - isotropic optical properties.



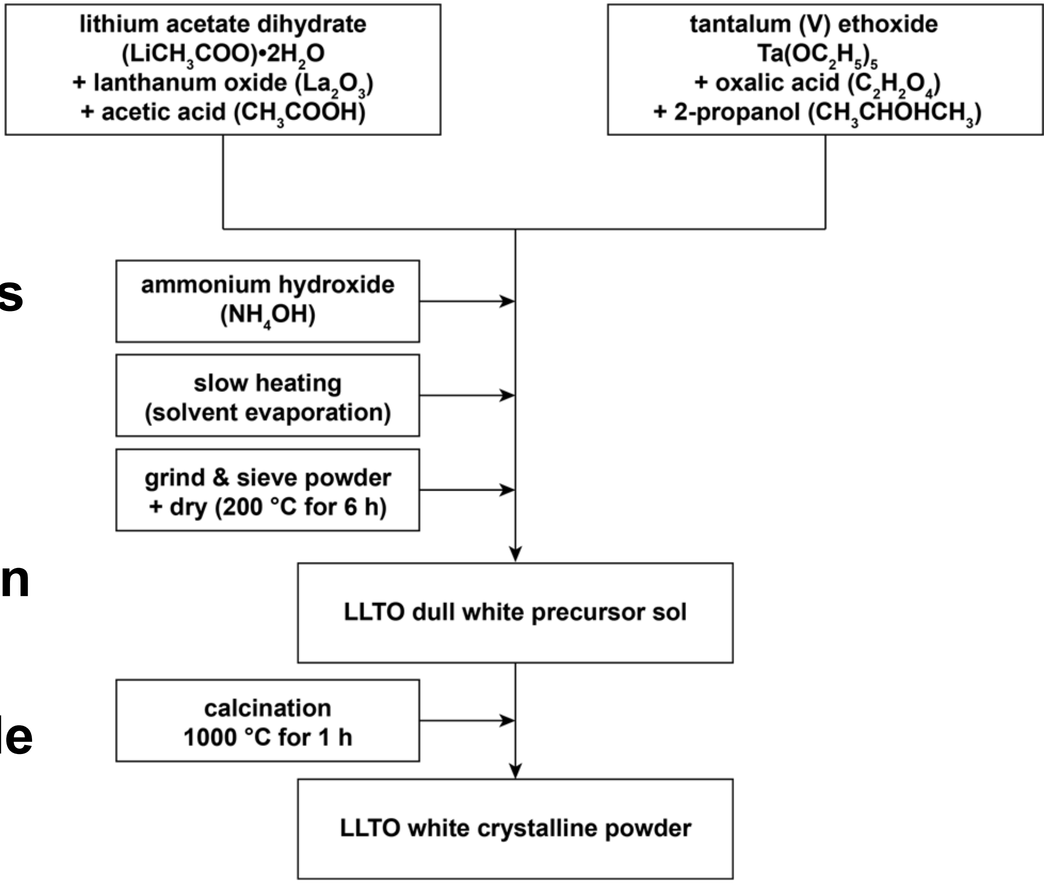
A Process for the Synthesis of Transparent Ceramics



- **A general process for synthesizing transparent ceramics**
- **Several challenges include:**
  - Secondary phases from volatilization of Li during high temperature stages
  - Intragranular pores from imbalance of grain growth and pore removal

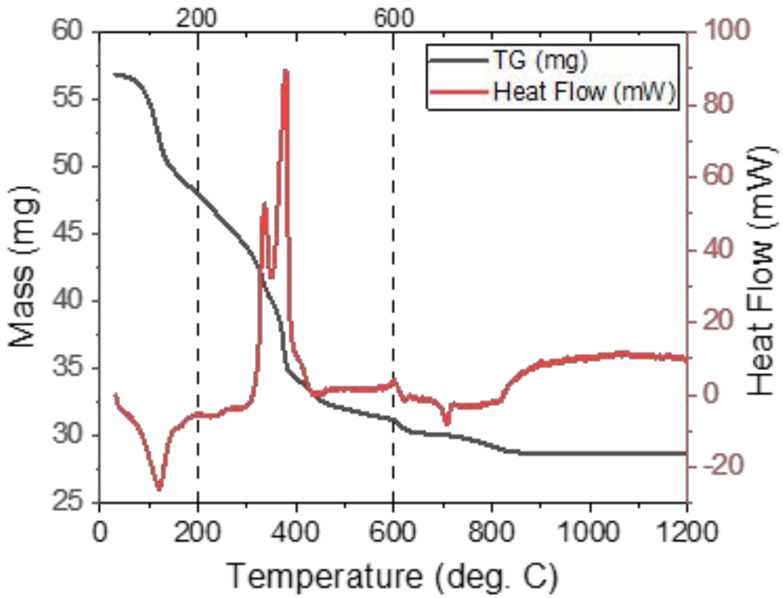
Compound Synthesis via Sol-gel Process

- A flexible alkoxide sol-gel process developed with LANL for the synthesis of $Li_5La_3Ta_2O_{12}$ (LLT)
- Solubility of Li-intermediates necessitates solvent evaporation
- Li-volatility at high temperatures requires compensation by inclusion of excess Li-acetate
- Substitution of Ta-ethoxide for Zr-isopropoxide for LLTZx



Establishing Boundary Conditions for Thermal Processing

Simultaneous DSC/TGA of dried sol-gel cake to better understand transformation to crystallized oxide

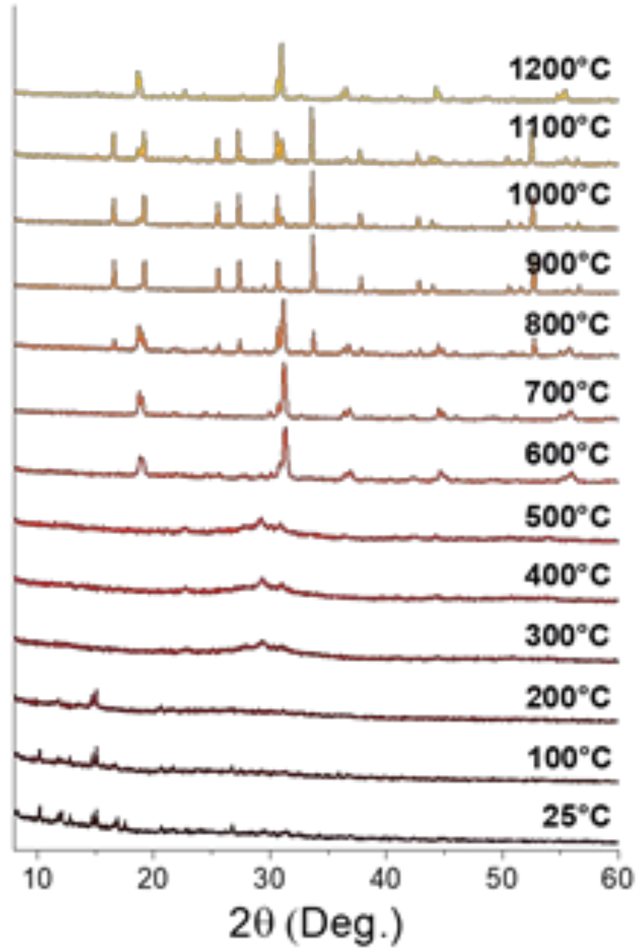


- **20°C- 200°C**
  - Removal of residual water and volatile organics
- **200°C- 600°C**
  - Decomposition of oxalates and acetates to carbonates/oxycarbonates
- **600°C and up**
  - Decomposition of carbonates/oxycarbonates, crystallization and glass transition related to reconfiguration

Establishing Boundary Conditions for Thermal Processing (Continued)

Equilibrium High Temperature X-Ray Diffraction of dried sol-gel cake

- **20°C- 200°C**
  - Low angle peaks likely from residual organics
- **200°C- 600°C**
  - Low intensity peaks around 30° are likely from carbonates/oxycarbonates
- **600°C and up**
  - $LiLa_2TaO_6$ phase first appears, then transitions into $Li_5La_3Ta_2O_{12}$ which then begins to break down from Li-volatilization



Study of Li-volatility During Initial Consolidation

Li-volatility during crystallizing and initial consolidation necessitates excess Li to compensate

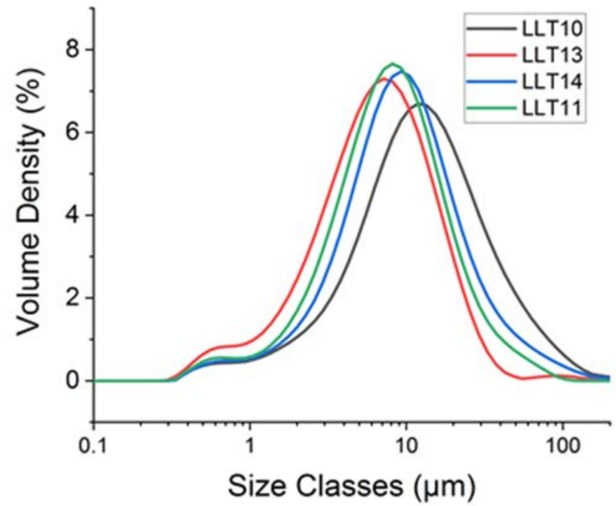
- **3 batches of powder were made with varying amounts of excess Li following the same sol-gel procedure**
- **1 batch was made with excess La**

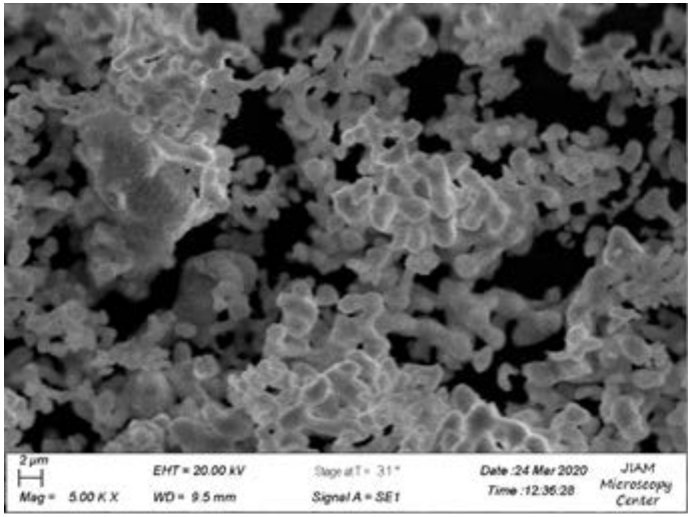
Sample	Wt% Excess Li	Excess La
LLT10	10	No
LLT13	12.5	No
LLT14	12.5	1 Wt%
LLT11	15	No

Particle Size Distribution and Powder Morphology

Particle size distribution was analyzed for each batch of powder using Dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM)

- **Uniform size distribution of each of the powder batches with similar mean size**
- **Observation using SEM shows sintering of particles during crystallization resulting in larger agglomerates.**





Initial Consolidation by Uni-axial Hot Pressing

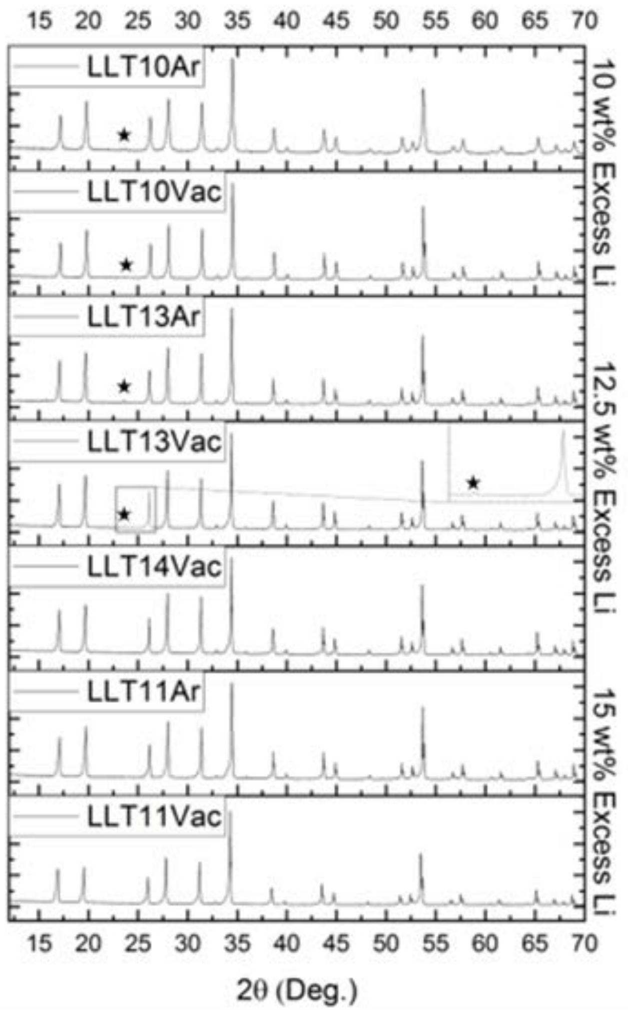
- ~4.5 g green bodies at 182 MPa in a 12 mm diameter stainless steel die
- Green bodies are then loaded into a 12 mm diameter grafoil-lined graphite die and hot pressed at 1200 °C and 80 MPa for 1 hr under vacuum or flowing Ar.

Sample	Wt% Excess Li	Excess La	Hot Pressing Atmosphere	Density [g/cm^3]	Secondary Phases
LLT10Ar	10	No	Ar	6.17 (97.5% TD)	$LiTaO_3$, $Li_7La_3Ta_2O_{13}$
LLT10Vac	10	No	Vacuum	6.18 (97.6% TD)	$LiTaO_3$, $Li_7La_3Ta_2O_{13}$
LLT13Ar	12.5	No	Ar	6.28 (99.2% TD)	$LiTaO_3$, $Li_7La_3Ta_2O_{13}$
LLT13Vac	12.5	No	Vacuum	6.32 (99.8% TD)	$LiTaO_3$, $Li_7La_3Ta_2O_{13}$
LLT14Vac	12.5	1 Wt%	Vacuum	6.15 (97.2% TD)	$Li_7La_3Ta_2O_{13}$
LLT11Ar	15	No	Ar	6.12 (96.7% TD)	$Li_7La_3Ta_2O_{13}$
LLT11Vac	15	No	Vacuum	6.20 (97.9% TD)	$Li_7La_3Ta_2O_{13}$

Secondary Phase Formation and the Effect of Excess Li

X-Ray Diffraction of hot pressed samples show near single phase ceramics.

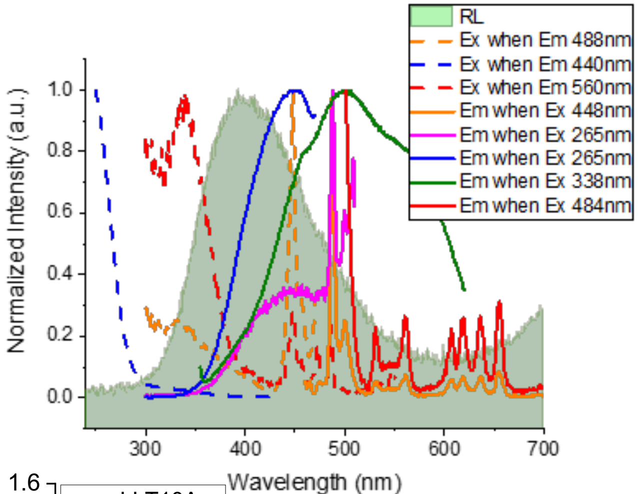
- **Low intensity peak at ~23° from $LiTaO_3$ secondary phase**
- **Garnet peaks show low angle asymmetry from formation of Li-stuffed $Li_7La_3Ta_2O_{13}$ garnet phase**
- **Rietveld refinements using GSAS II resulted in poor fits from asymmetry of garnet peaks**

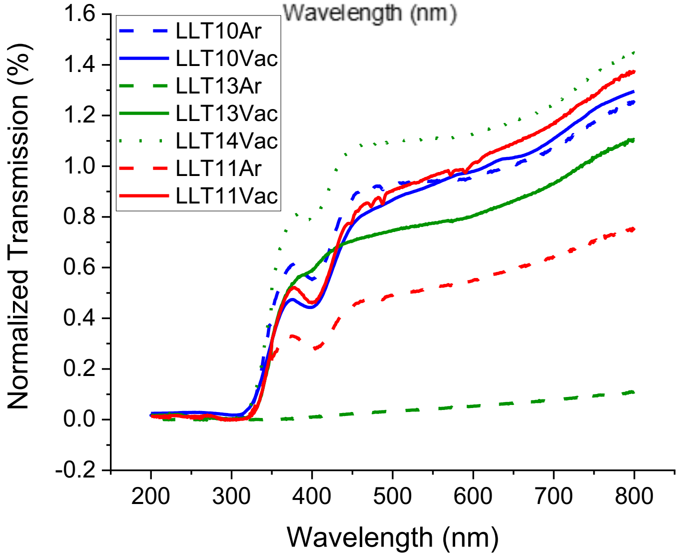


Complex Emission Profile of Hot Pressed LLT ceramics

Broad X-Ray excited radioluminescence and photoluminescence emission from self-trapped exciton tantalate intrinsic emission

- **Multiple line emissions above 480 nm likely from a 4f-4f transition in some rare-earth impurity.**
- **In-line transmission spectra show a degree of transparency in the area of emission**



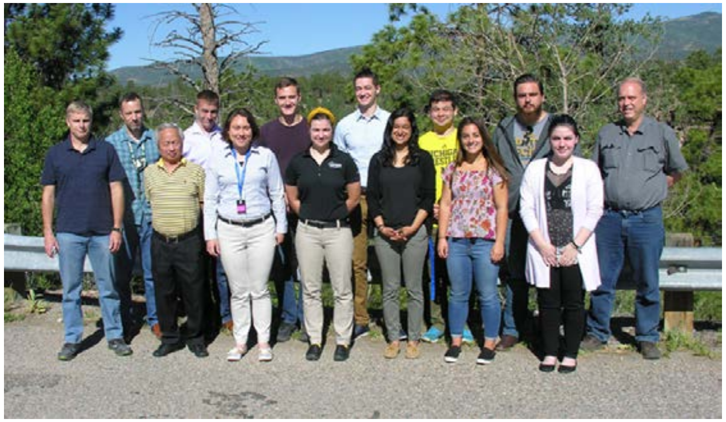


Future Plans

- **Hot isostatic pressing of consolidated ceramics**
- **Expand sol-gel process to include Zr**
- **Investigate activation by Ce^{3+} and Pr^{3+} using the sol-gel process**
- **Investigate pulse shape and pulse height discrimination techniques for neutron-gamma discrimination**

NSSC Experience

- **LANL School of Nukes 2018**
  - Non-destructive assay short course
- **NSSC-LANL Keepin Non-proliferation Summer Program 2018**
  - Resulted in a continued collaboration on the synthesis of nano-powders and transparent ceramics with Dr. Chen (LANL)
- **GW Bootcamp on Nuclear Security Policy 2019**
  - An in-depth introduction to Nuclear Security policy and job opportunities
- **Several Conferences and Presentation Opportunities**



Acknowledgements

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