

CFP 06 ID: (TA-01-SL01):

Fabrication of Large-Volume, Low-Cost Ceramic Lanthanum Halide Scintillators for γ -Ray Spectroscopy

Pin Yang*, Timothy J. Boyle, Nelson S. Bell,
Mark A. Rodriguez, Margaret R. Sanchez,
Leigh Anna M. Ottley, and Richard P. Grant

Sandia National Laboratories

June 27, 2007
(Quarterly Review – DHS Headquarters)

Outline

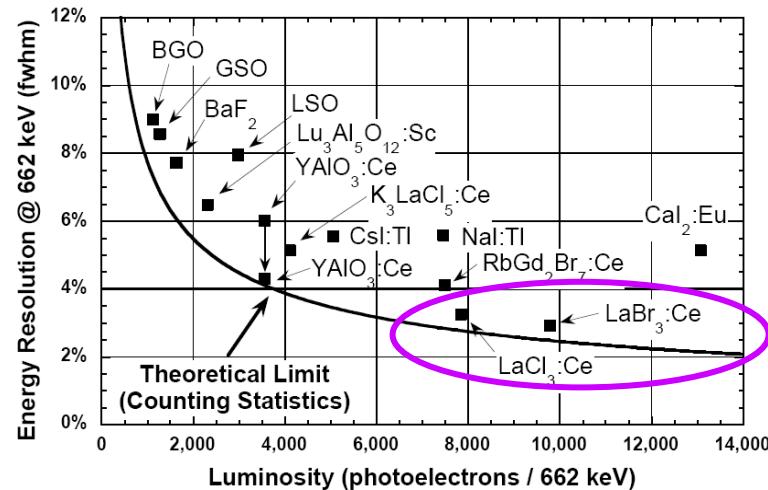
- **Conceptual Overview**
- **Project Objectives**
- **Phase II Task Review/Remaining Issues from Phase I**
- **Development Approach**
- **Progress Summary and Key Issues**
- **Future Work and Contingent Plan**
- **Cumulative Funding Profile and Project Status**



Fabricating Low-Cost & Rugged Lanthanum Halide Ceramic Scintillators

Conceptual Overview

- **Opportunity: Lanthanum halide scintillators show superior performance for γ -ray detection over most materials**
 - Higher light output per detected gamma (γ)
 - Better energy resolution for spectroscopy
 - More proportional output.
- **Problem: Lanthanum halide crystals are fragile and expensive**
 - Large single crystals are mechanically fragile and temperature sensitive
 - Expensive to grow crystals due low yield.
- **Approach: Make crystallographically aligned (or “textured”) lanthanum halide ceramics to**
 - Reduce light scattering
 - Enhance mechanical performance
 - Increase production yield and reduce cost.
- **Expected Results: The resultant lanthanum halide material will be**
 - Superior scintillator for γ -ray detection
 - Mechanically rugged
 - 10 times less expensive to produce in large sizes than single-crystal growth processes.



Fabrication High-Performance, Low-Cost Ceramic Scintillators

Project Objectives

- Project goal:

- Develop a ***low-cost ceramic manufacturing*** process to produce ***rugged large size, optical quality*** lanthanum halide scintillator materials for γ -ray detection.

Spectral Energy Resolution Target	Light Yield Target	Cost Target*
< 3% at 622 keV	~ 63,000 photons/MeV	➤ 10 \times cost reduction

*(Raw powder: \$1.00/gram; Single crystal: \$30.00/gram)

- Phase II Tasks:

- Task 1: Material and process development

To address several remaining issues from previous phase so robust processes for powder synthesis, seed particle fabrication and densification of textured ceramic can be established.

- Task 2: Investigation of composition-microstructure-property relationship

To provide an integrated solution from powder synthesis to final scintillation performance evaluation.



$\text{La}_{0.9}\text{Ce}_{0.1}\text{Br}_3$ powder luminescing under black light



Task 1: Material and Process Development

Phase II Task Review

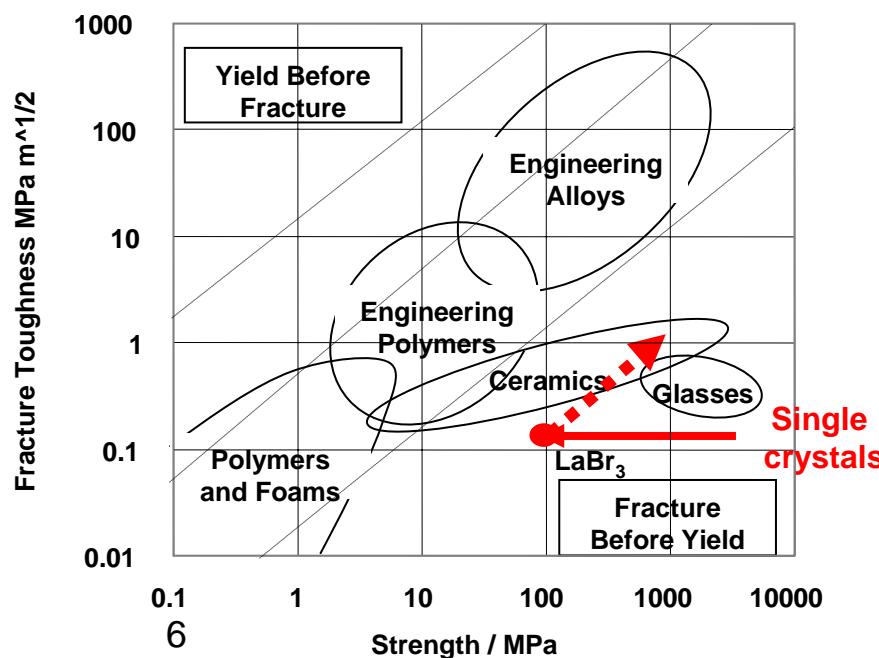
- **(1.1) Chemical synthesis of ultrafine, high purity lanthanum halide powders**
 - Large scale batch processing development
 - Size/Morphology control
 - Elimination of water.
- **(1.2) Seed crystal preparation**
 - Pursue different solvent systems or precursor generation method
 - Understand solvent incorporation and removal process
 - Morphology control.
- **(1.3) Densification of textured ceramics**
 - Characterization of ceramic/seed crystal interface
 - Optimization of solid state conversion and densification processes
 - Development of highly textured, optical quality ceramics
 - Fabrication of large size ceramic scintillator for property evaluation.



Task 2: Investigation of Composition-Microstructure-Property Relationship

Phase II Task Review

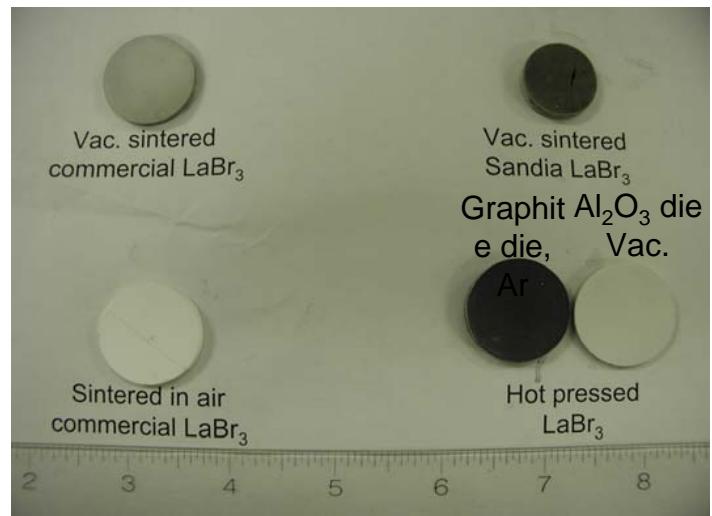
- Optimize the dopant level for maximum luminosity.
 - Establish LaBr_3 - CeBr_3 phase diagram
 - Characterization scintillation properties
- Evaluate the effect of microstructure on mechanical and optical properties of textured ceramics.
 - Grain size
 - Degree of texture
 - Light scattering



Key Remaining Issues from Phase I

- Task 1: LaBr_3 powder synthesis (new CeBr_3 synthesis)

- Identify origin and remove of “gray” color of densified pellets.
 - Develop large scale batch processing



- Task 2: Seed particle preparation

- Optimize seed crystal morphology
 - Optimize thermal stabilization procedure for seeds
 - Characterization of seed particles

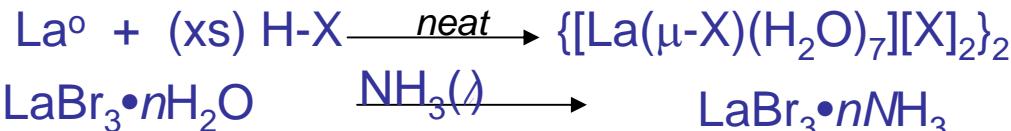
- Task 3: Densification of textured ceramics

Fabricating Low-Cost & Rugged Lanthanum Halide Ceramic Scintillators

Development Approach – Task 1

- **Synthesis Ultrafine, High Purity Lanthanum Halides (Timothy J. Boyle)**

- Direct acidification
- Solvent exchange

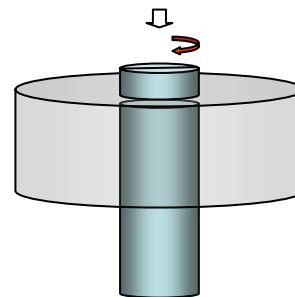


- **High Aspect Ratio Seed Crystal Preparation (Nelson S. Bell)**

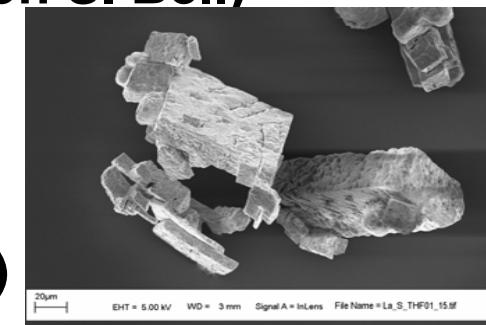
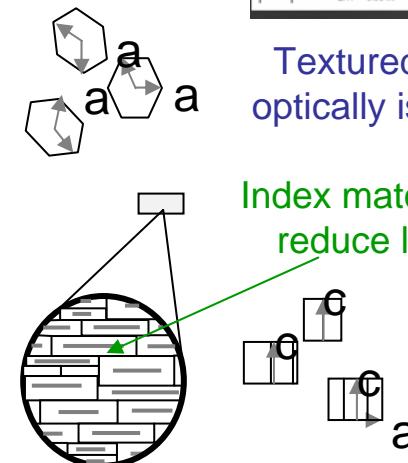
- Hot solution recrystallization
- Seeding during dehydration
- Vapor phase synthesis

- **Developing a highly Textured Ceramics (Pin Yang)**

- Rotation shear forming
- Solid-state conversion



After high temperature densification



Textured ceramics are optically isotropic along c axis

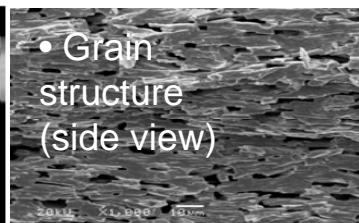
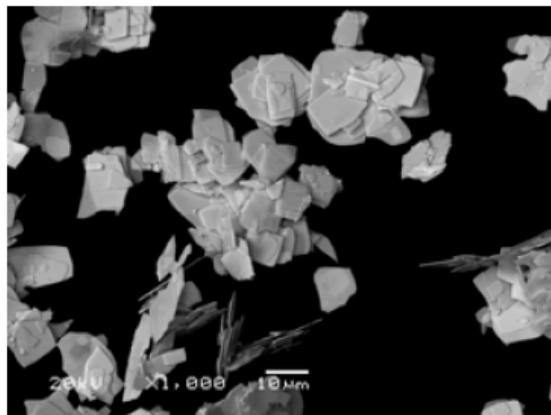
Index matching interface – reduce light scattering



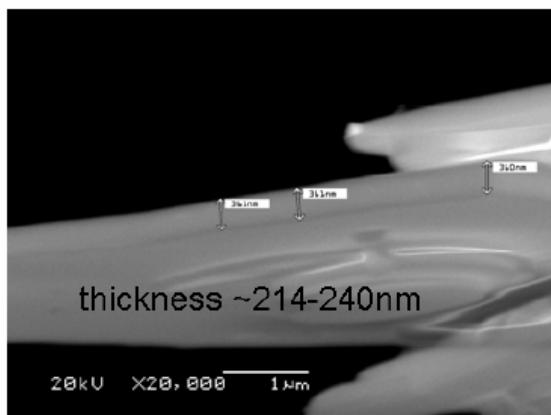
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Creating an Optical Isotropic Axis from Birefringent Materials to Enhance Optical Properties

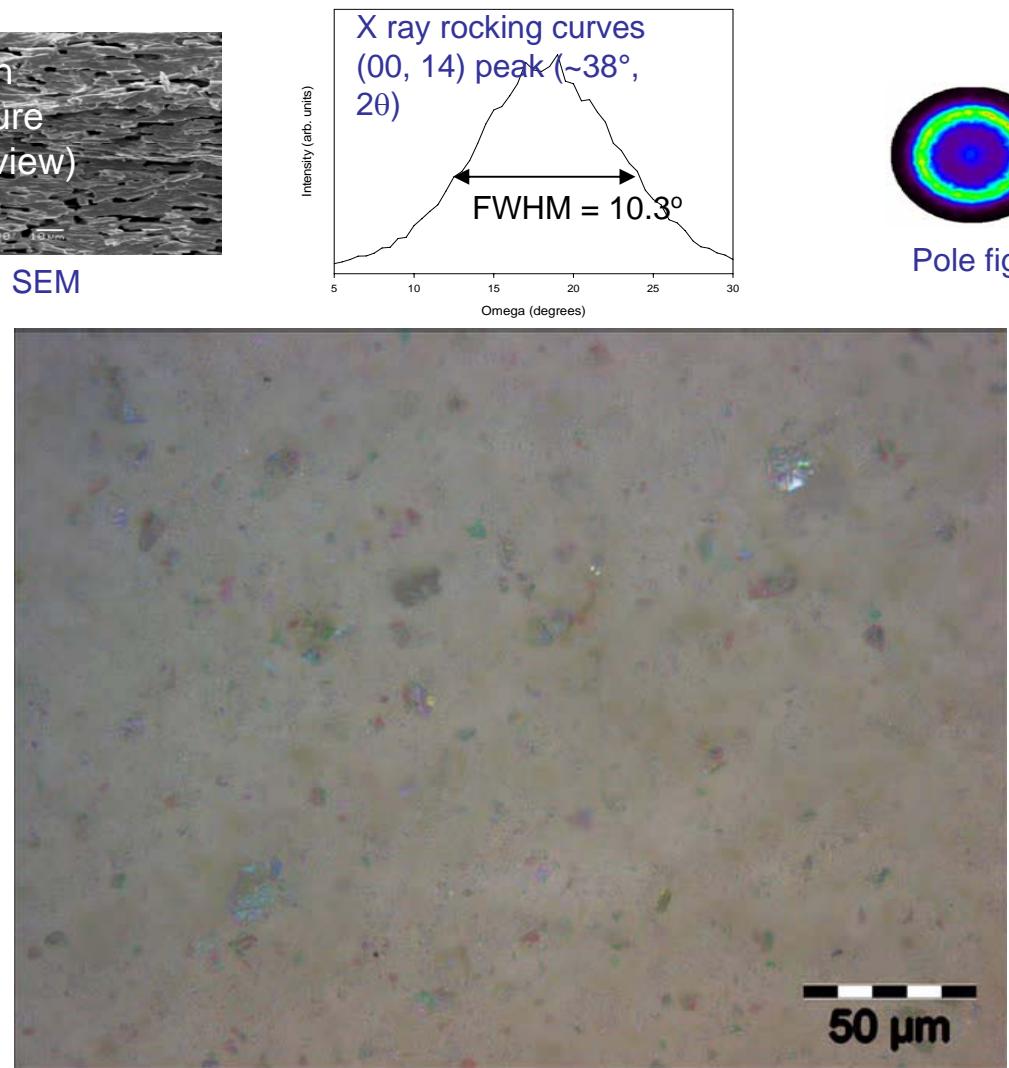
(Through a highly textured ceramic)



SEM



Seed particles of $\text{Bi}_4\text{Ti}_3\text{O}_{13}$ synthesized using a molten salt synthesis.



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Progress Summary and Key Issues

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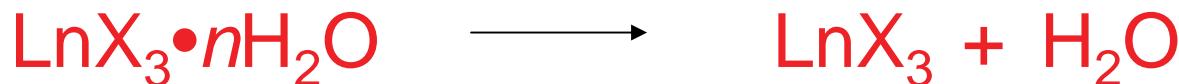
- (1) Powder synthesis – Tim J. Boyle
- (2) Seed particle preparation – Nelson S. Bell
- (3) Developing a highly textured ceramic – Pin Yang

Recap (Powder Synthesis) : Simple, clean, synthesis of LnX_3 Materials Has Been Realized.

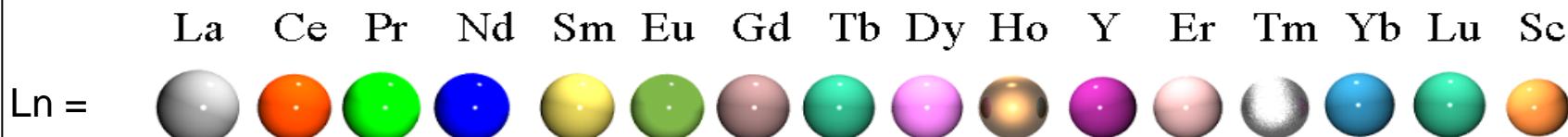
- Developed a simple route that is amenable to the synthesis of all $\text{LnX}_3 \bullet n \text{H}_2\text{O}$ materials on a large scale, reproducibly.



- Dehydration of the aqueous solvate was determined by TGA/DTA to be at 180 °C under argon atmosphere to form phase pure LaX_3 as determined by BeD-XRD.

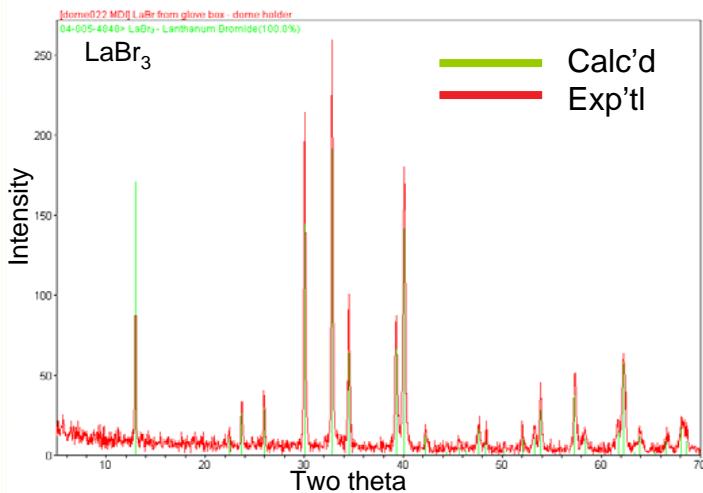


$\text{X} = \text{Cl, Br, I}$



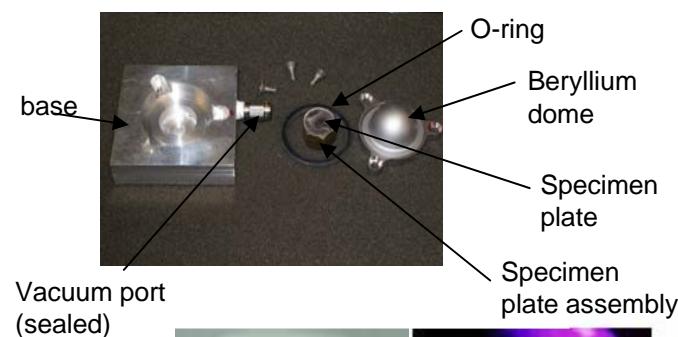
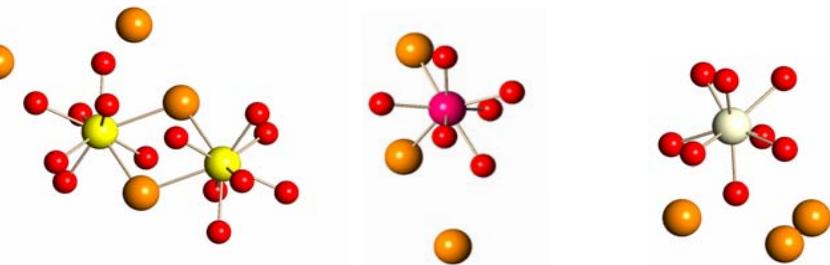
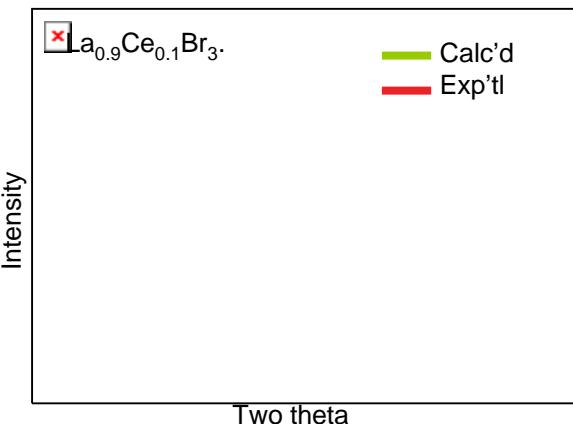
Recap: All $\text{LnX}_3 \bullet n\text{H}_2\text{O}$ and LnX_3 compounds have been fully characterized.

- Three general structure types observed across the $\text{LnBr}_3 \bullet n\text{H}_2\text{O}$ series:



- Phase pure LaBr₃ formed upon drying as identified by BeD-XRD.

- Due to their structural similarities, CeBr₃ was easily doped into LaBr₃ forming a solid-solution of La_{0.9}Ce_{0.1}Br₃.



- Exposure to black light.



TASK 1.1: Source of 'black' thought to be due to residual organic led to syntheses in new lab.

- The synthesis process was successfully transferred to the new chemistry laboratory

A large batch of CeBr_e (> 80 grams) powder was produced.



- All previous results *successfully reproduced* by a novice chemistry technician on large scale.

- Processing of 'new' LaBr_3 still yielded 'black' materials.



Conclusion

Reaction is transferable and reproducible but source of black still an issue!

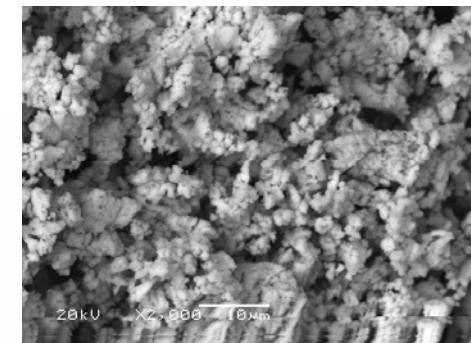
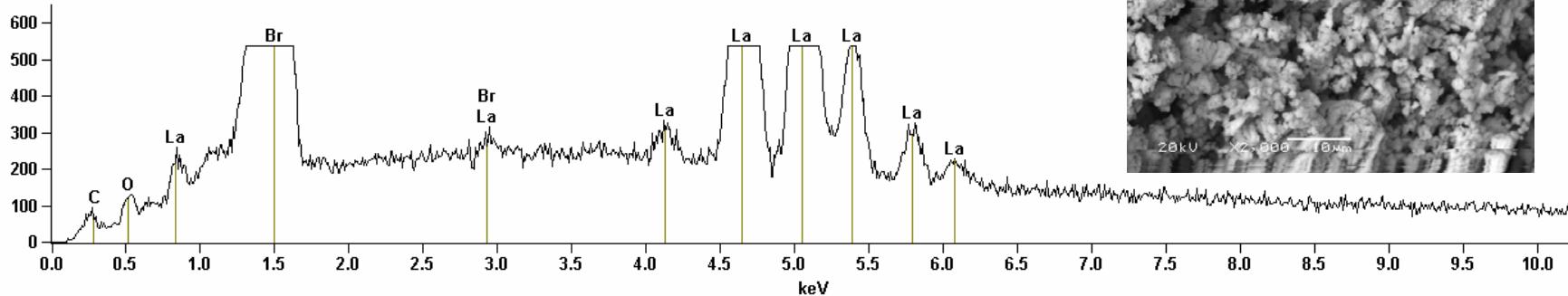


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Task 1.1 Carbon and Oxygen were detected in powder and hot pressed pellets.

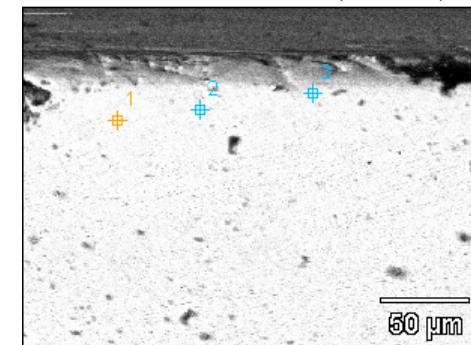
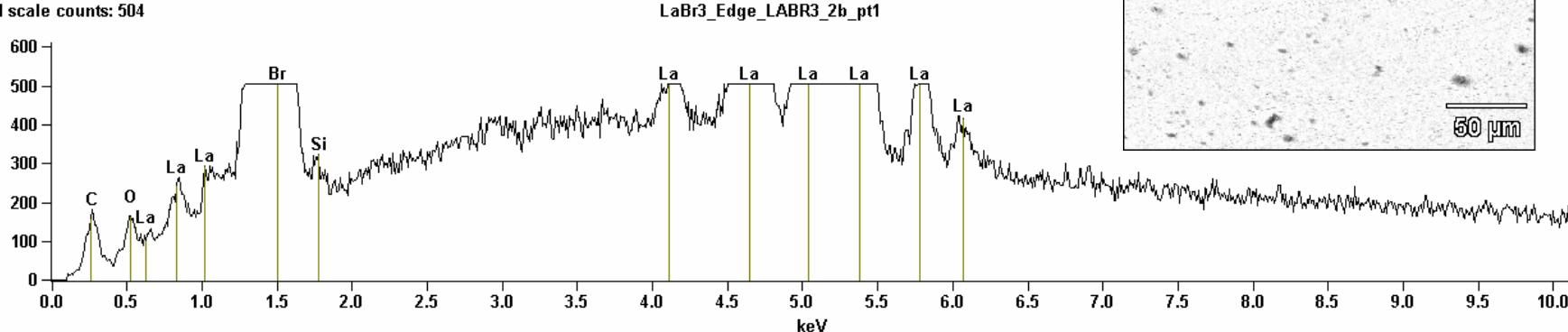
(A) LaBr₃ powder after dehydration

Full scale counts: 536



(B) Hot pressed LaBr₃ pellets

Full scale counts: 504



TASK 1.1: Source of 'Black' proven NOT to be from Residual Organic Solvents.

- No **Organic** solvents used in box but 'black' occurred again.
- NMR data reveals no presence of **'trace organics'** in HX materials.

1H NMR Spectrum of HBr
(TJB)

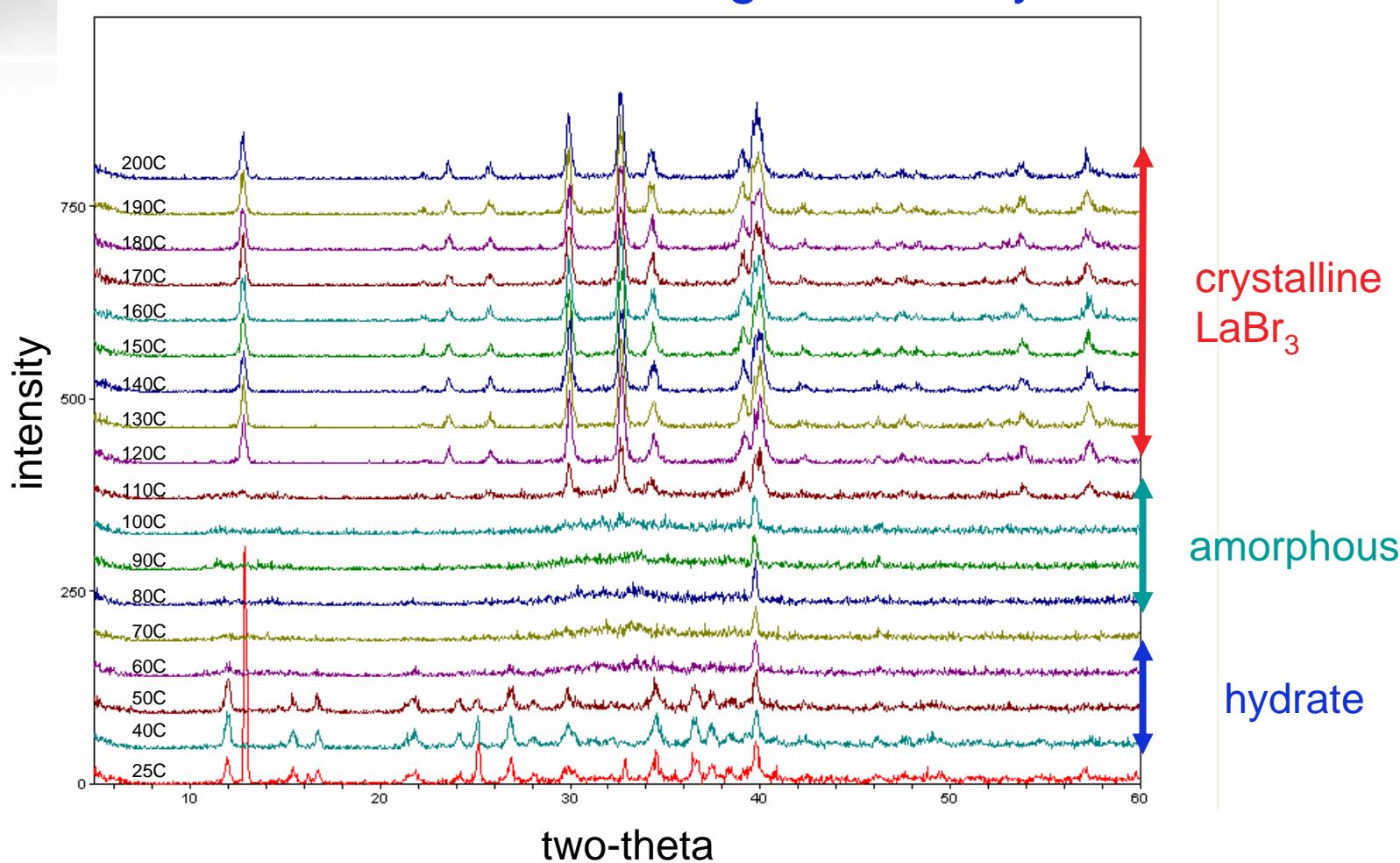
Conclusion

Solvent contamination is not the source of the 'black'!

Task 1.1 Potential sources for darkening (“Black”)

- Non stoichiometry
 - Loss of Br during the drying process
- Vacancies formation – color centers
- Thermally reduced LnX_3
 - Formation of black LaBr_2 or La_2Br_5 phases
 LaBr_3 can be reduced to LaBr_2 (black hexagonal platelets of graphite-like appearance; hexagonal, $\text{P}6_3/\text{mmc}$) by “metallothermic” reduction with alkali metals.
 La_2Br_5 can be partially reduced from LaBr_3 (black rods with copper-colored metallic luster; monoclinic, $\text{P}2_1/\text{m}$).

TASK 1.1: *in-situ, en-vacuo, variable temperature XRD* shows Br not lost during initial dehydration.

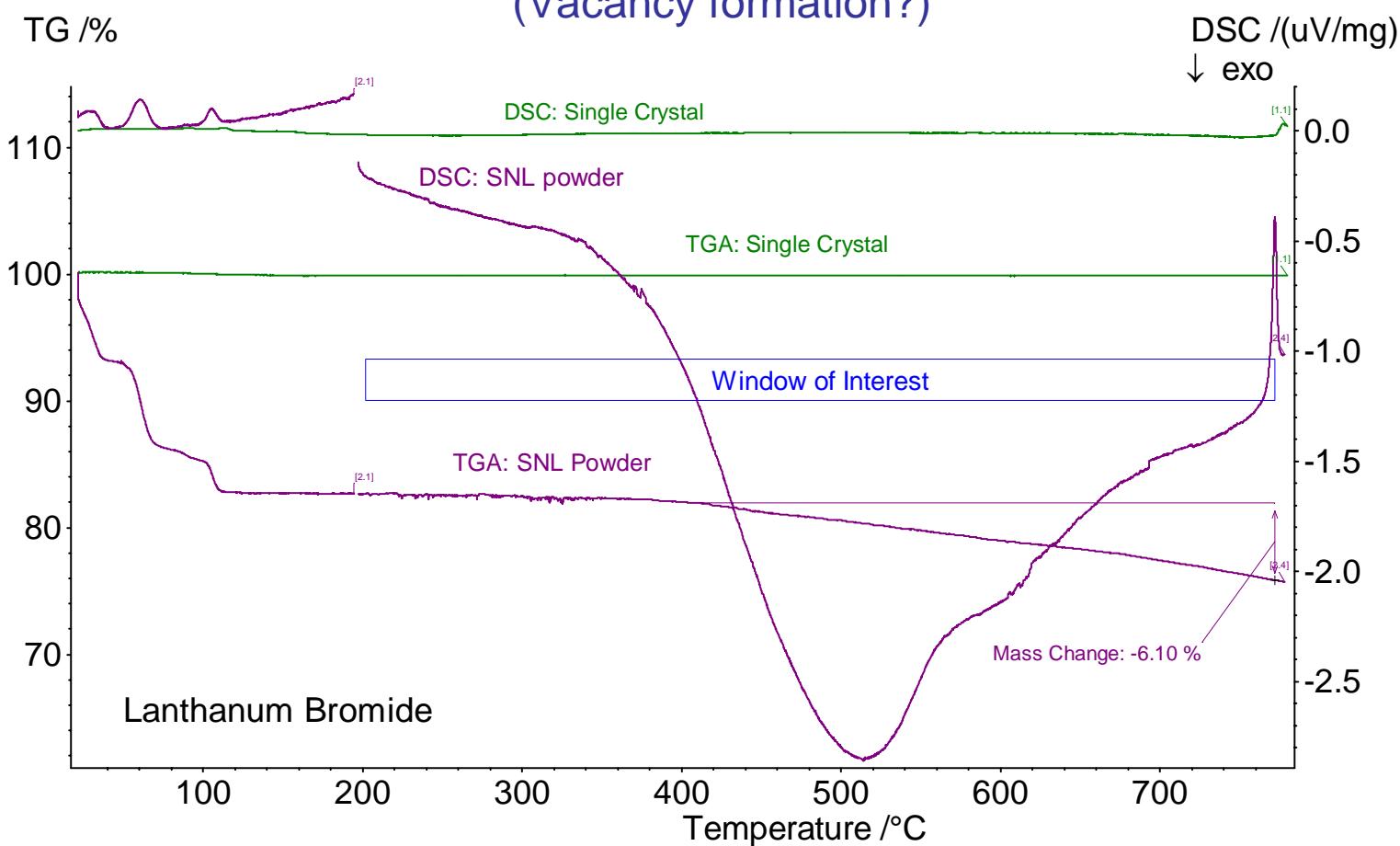


Conclusion: Dried LaBr₃ is stoichiometrically correct!
Processing conditions causing 'black' contamination?



Task 1.1 Weight loss and thermal events were observed during heating.

(Vacancy formation?)

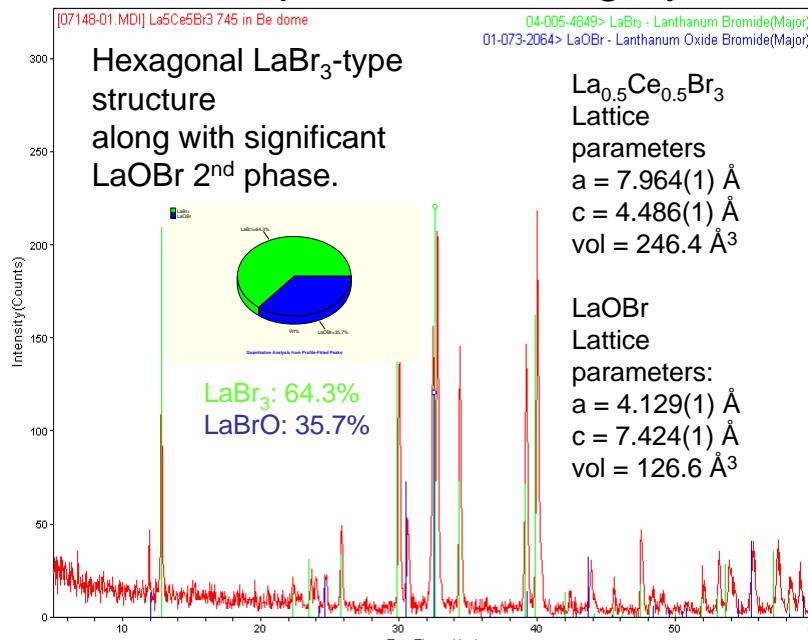


- Can weight loss be attributed to (1) vacancy formation, (2) decomposition of LaBr₃, or (3) chemical reactions?

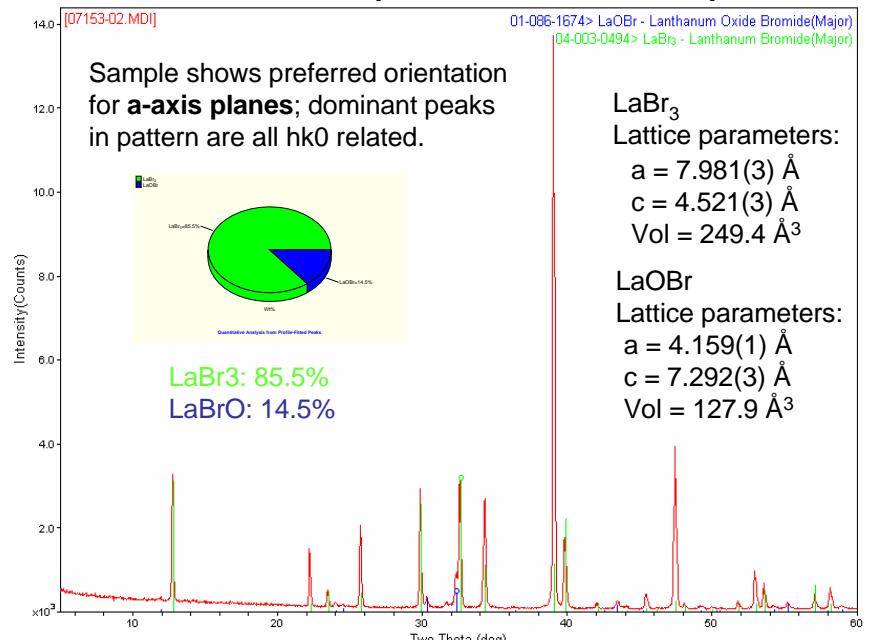


Task 1.1 XRD results show heating up to 720°C under a flow argon condition La_2Br_5 formed!

SNL powder – dark gray



Commercial powder – “transparent”



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[s877989]marodn\j\XRD_data\theta2theta\2007> Tuesday, June 19, 2007 04:57p (MDI\JADE8)

Hypothesis: $\text{LaBr}_3\text{H}_2\text{O} \rightarrow \text{LaBrO} + 2\text{HBr}$

- Wet powder under the same condition created La_2Br_5 powder (by color)
- Need to be verified by gas chromatography.

Potential source of $\text{LaBr}_3\text{H}_2\text{O}$

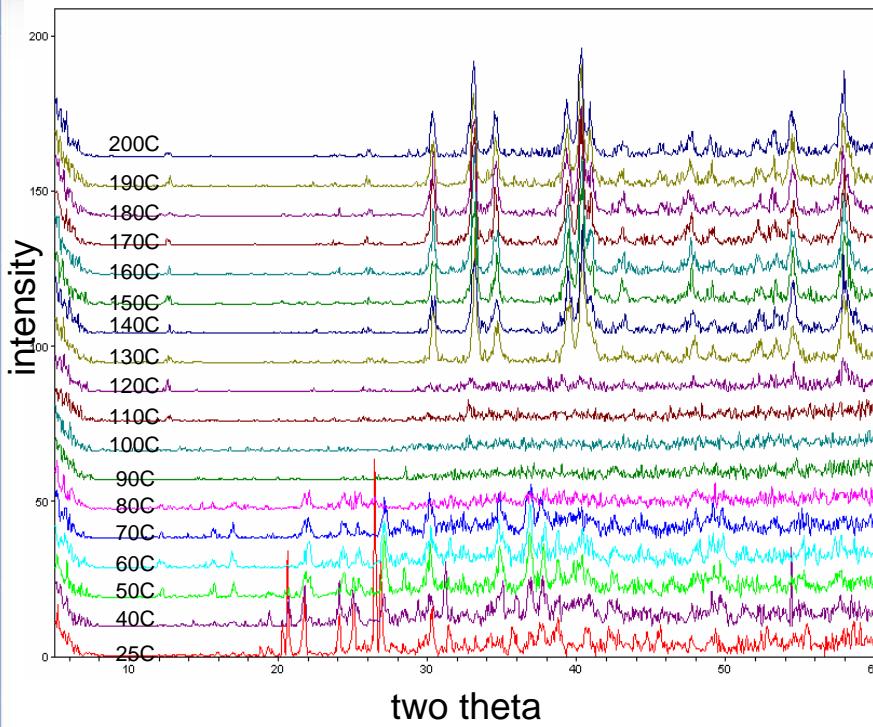
- Incomplete dehydration process (vacuum dry)
- High surface area of chemically prepared powder



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TASK 1.1: Removal of water by heat and solvent exchange, demonstrated.

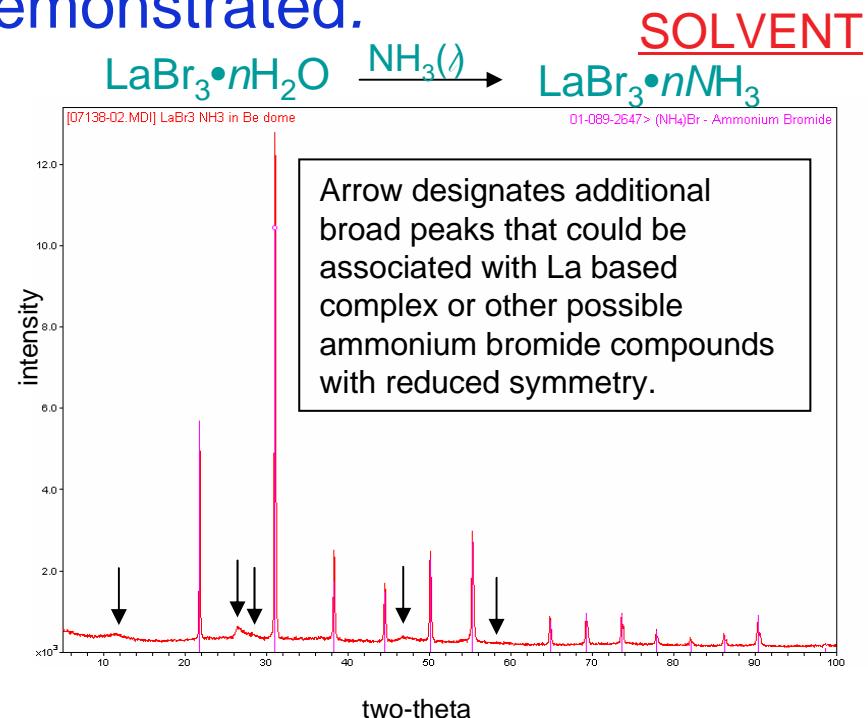
HEAT!



$\text{CeBr}_3 \bullet \text{H}_2\text{O}$ to CeBr_3 tracked by *in-situ*, *en-vacuo*, VT-PXRD shows similar pattern to La system - water lost as early as 140°C with no change in phase after initial crystallization.



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$\text{LaBr}_3 \bullet \text{H}_2\text{O}$ successfully converted using ammonia. Forms NH_4Br phase.

Conclusion:
Water can be removed by heat or solvent exchange. Completely?

TASK 1.1: Summary and Conclusion

Task 1.1:

Synthesis of large scale LaBr₃.

- (a) Transfer of synthesis accomplished,
- (b) **Organic solvents** ruled out as 'black' culprit,
- (c) **No** loss of Br during initial drying proven,
- (d) **Water** can be removed by **heat or solvents**.

Question: What is the source of the 'black'? Residual water in the material or processing issues?



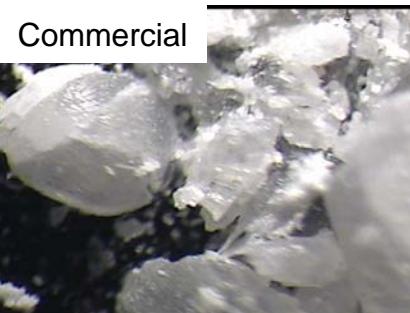
Size and morphology control and water removal – will be the main focus in the next quarter.



Recap (Seed Particle Preparation)

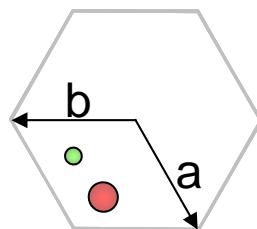
Precipitation of LaBr_3 Seed Particles

Available materials do not have the desired morphological properties needed.



Crystal Structure

Hexagonal; leads to faceted growth and anisotropic face growth rates.



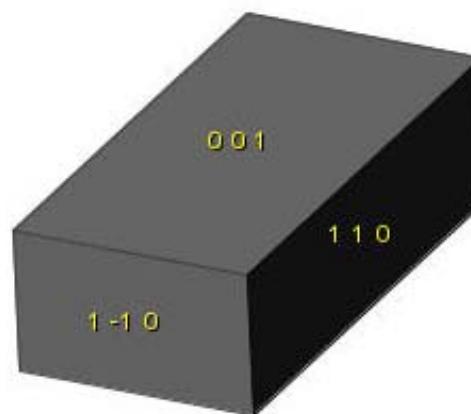
$P6_3/m$	x/a	y/b	z/c
La	1/3	2/3	1/4
Br	0.38506	0.29878	1/4
$a = b$	c	La^{3+}	Br^-
7.97 Å	4.92 Å	1.15 Å	1.95

Seed Particle Characteristics

- large particle size (i.e. several microns)
- anisotropic shape (platelet or needle)

Morphological Development

- control nuclei development
- exploit crystal structure for anisotropic growth
- Individual facets will exhibit differential diffusion and integration properties.



Very rapid growth eliminates facets which add material preferentially.



Recap (Seed Particle Preparation) Seed Particle Production Routes

- **Approach 1 – Hot Solution Route:** use thermal differential in salt solubility to create supersaturation and precipitation of template particles

Solubility must be temperature dependant, and non-linear solubility is required for high yields. Continuous production can be achieved.

Industrial Example: sugar refining

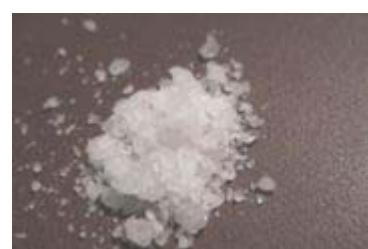


- **Approach 2 – Solvent Removal Route:** use evaporation of solvent to induce precipitation of anisotropic particles

Difficult to control supersaturation, and reproducibility is not expected to be good.

Potentially high yield can be achieved.

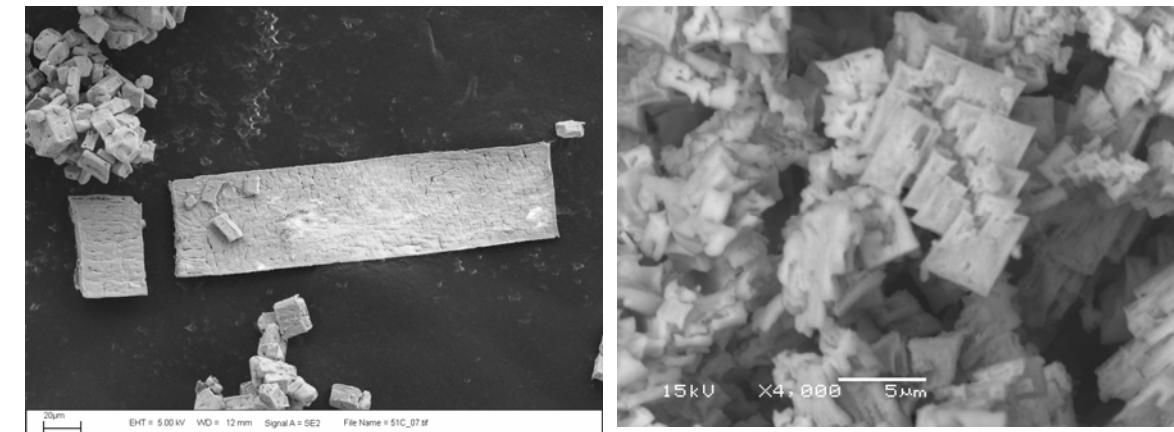
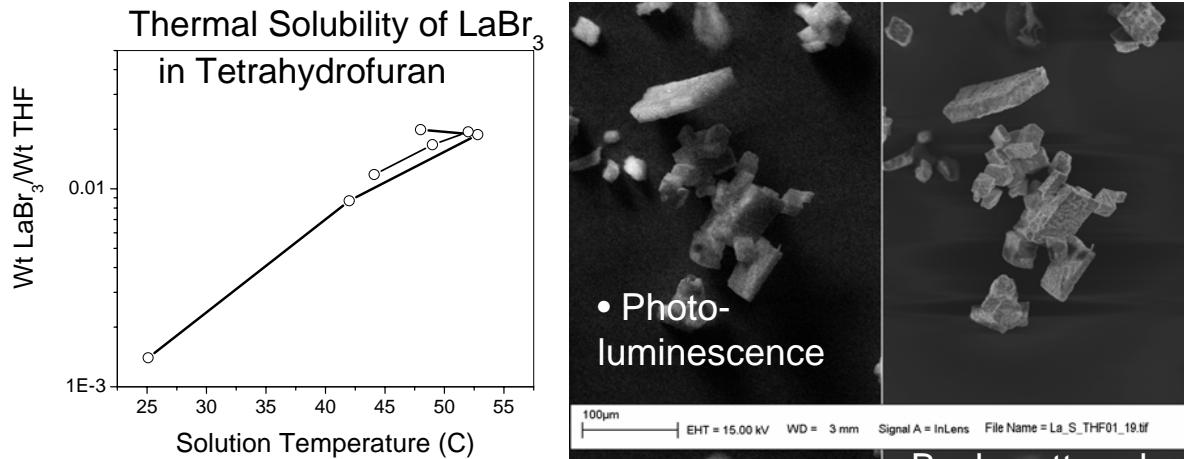
Industrial Example: table salt production
- brine solutions are dried sequentially



Recap (Seed Particle Preparation)

Seed Particles by Hot Solution Recrystallization

- Solubility measurements of LaBr_3 bead materials were tested in tetrahydrofuran (THF) as a function of temperature.
- Plates are formed which exhibit photoluminescence.



- Morphology investigated vs. heating rate.
- A large thermal differential leads to large crystals
- Rapid cooling with a non-solvent leads to heteronucleation.

Reaction in THF with
 $\Delta T = 25^\circ\text{C}$

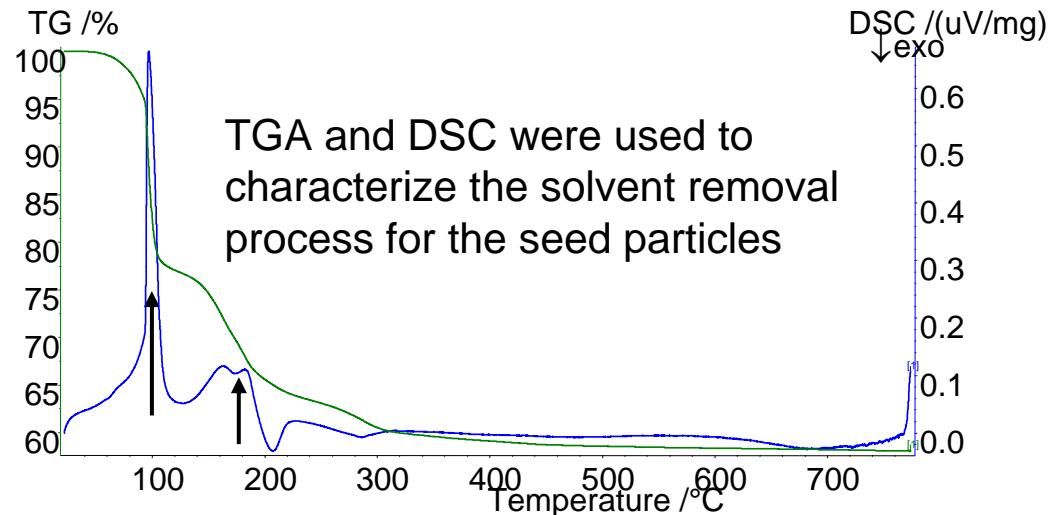
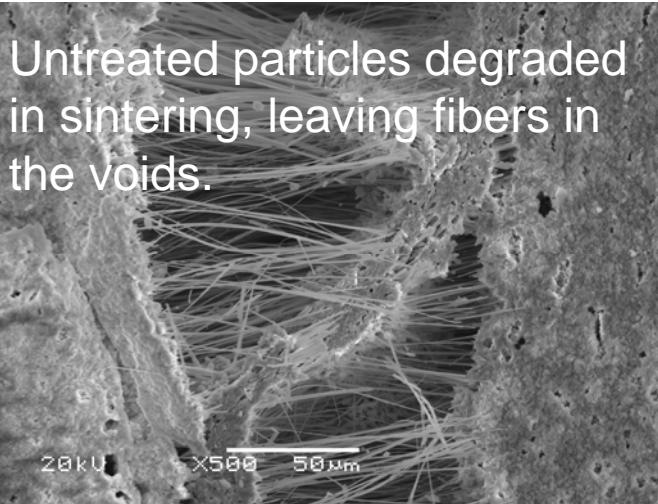
Rapid cooling using
hexanes non-solvent.



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Recap (Seed Particle Preparation)

Seed Particle Thermal Stability



There is a significant weight loss before temperature reaches 300°C.

- 100°C (endothermic reaction) – expected removal of adsorbed THF solvent
- 200°C (endothermic reaction) – there is another event, proposed as water removal
- Post ~300°C, seed particles appear stable up to melting point.

- A bake out procedure at 200 °C overnight was used to generate stable seed crystals. Particles maintain their integrity after processing.

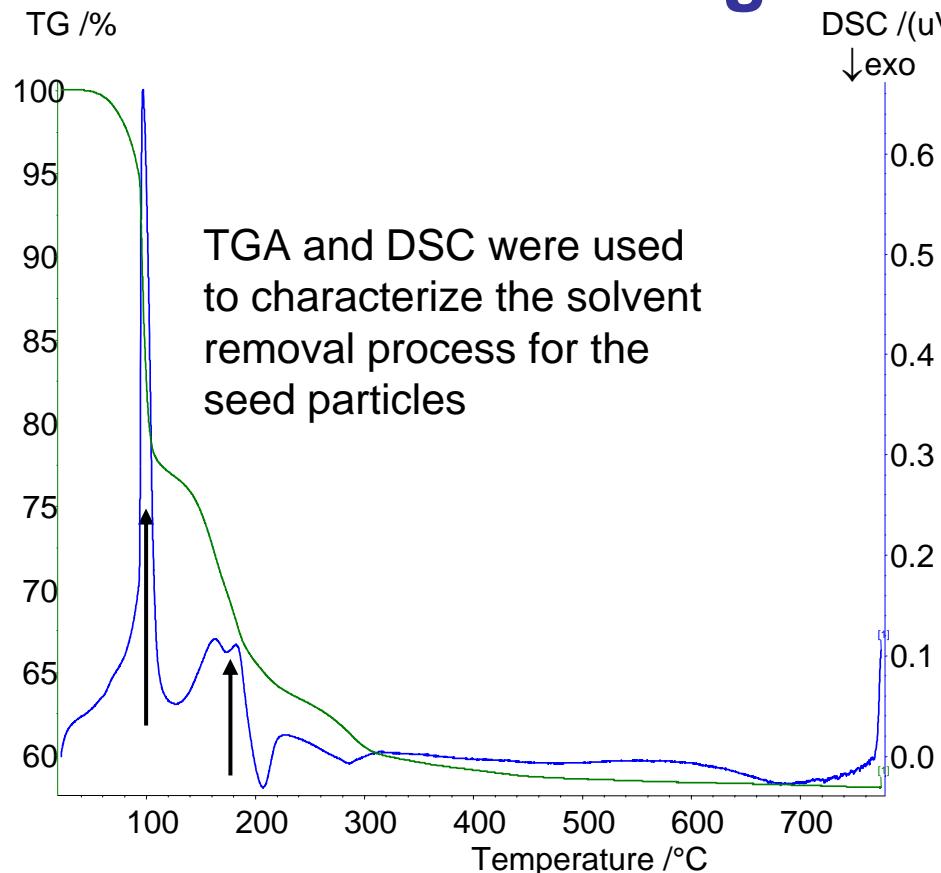


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Recap (Seed Particle Preparation)

Remaining Issues: Task 1.2

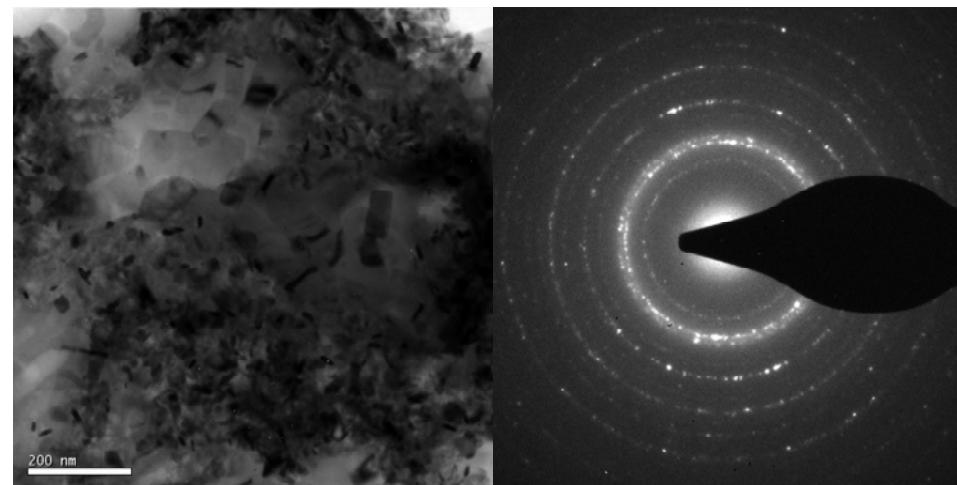
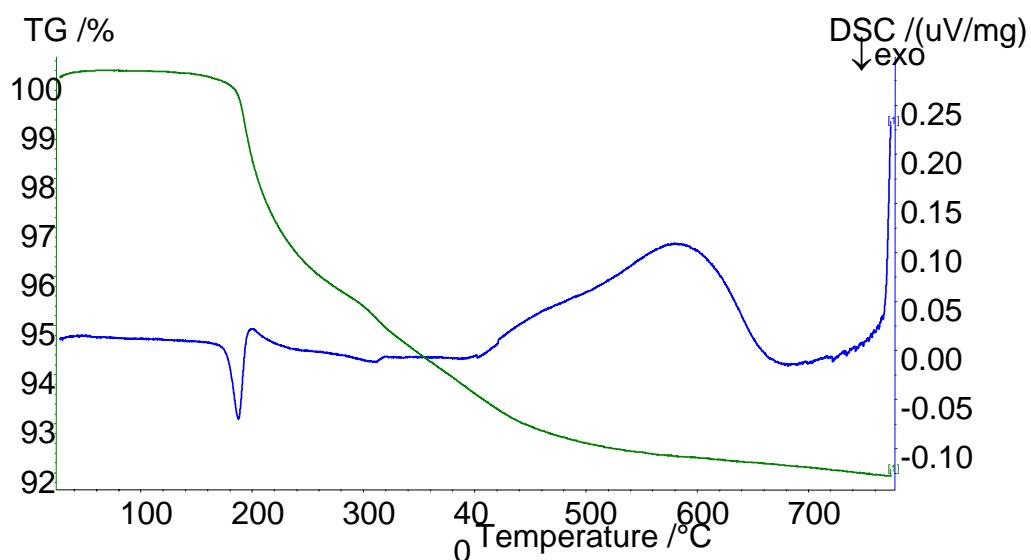
DSC / (mV/mg)
↓exo

- After thermal analysis, material seems to partially sintered together but particles remain their physical integrity
- Seed particles survive after densification.

What is the crystalline structure for seed particles after thermal treatment?

Task 1.2: Annealed Seed Particle Crystal Structure

- Sintered specimens show that seed particles do not maintain crystallographic orientation, even after the anneal treatment.
- Samples are coated with an amorphous C layer, and the interior structure shows an unoriented polycrystalline structure.
- New endothermic event from 400 - 650°C – perhaps related to THF carbonization contaminants or recrystallization.
- The adsorbed THF must cause a volume loss and recrystallization upon heating.



Large seed particle becomes unoriented noncrystalline aggregates after thermal treatment.



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Task 1.2: Alternative Seed Particle Synthesis Route – Seeding during Dehydration

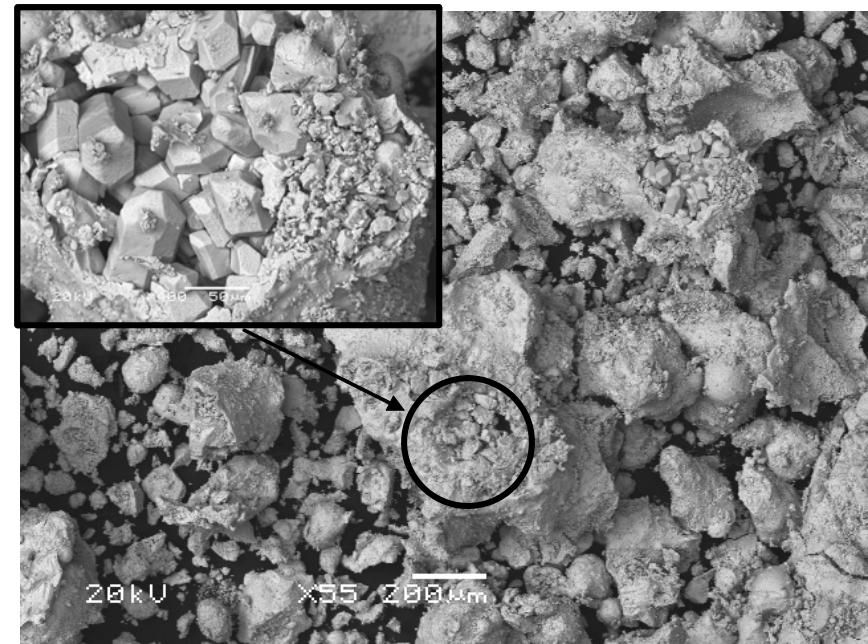
Objective: Assist the conversion of lanthanum halide hydrates into morphologically defined lanthanum halide particles during dehydration process, using anhydrous seeds.

Seeding processes:

- (1) Seeding during dehydration
- (2) Freeze drying, using liquid nitrogen (immediately form hydrates crystals)



Neither experiments yielded desirable results.



SEM microphotograph of partially dehydrated LaBr_3 powder. Insert shows a cluster of lanthanum bromide hydrate crystals.

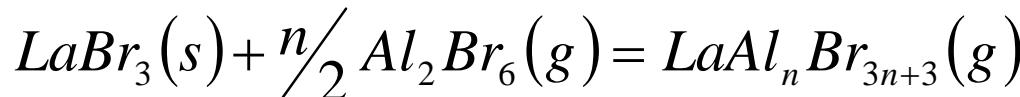


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Task 1.2: Alternative Seed Particle Synthesis Route – Vapor Phase Synthesis

- Literature review shows that vapor phase transport leads to LaBr_3 crystals
- AlBr_3 is a gasous complexing agent, allowing for low temperature material transport and precipitation
- Either the oxide or bromide can be explored for template particle synthesis.
- Advantage: No solvent incorporation to affect seed orientation
- Risk: crystal orientation unknown

J. Jiang, T. Ozaki, K. Machida, G. Adachi, *J. Alloys Compounds* **264** (1998) 157-163.
 G. Adachi, K. Murase, K. Shinozaki, and K. Machida, *Chem. Lett.* (1992) 511-514.
 F. P. Emmenegger, *J. Cryst. Growth* **17** (1972) 31-37.
 K. Kramer, T. Schleid, M. Schulze, W. Urland, and G. Meyer, *Z. anorg. allg. Chem.* **575** (1989) 61-70.
 M. Schulze and W. Urland, *Eur. J. Solid State Inorg. Chem.* (1991) 571-574.



This reaction is stated to be fully reversible. i.e. the product is LaBr_3 and the AlBr_3 is not consumed.



The AlBr_3 is reacted and lost in this reaction.
 from Kramer et al. (1989)

mixed with commercial La_2O_3 and sealed in a Duran tube under vacuum. After the reaction (eq. 1; at 360°C) is complete, the ampoule is transferred to a furnace with two temperature zones (400 and 500°C). Within 24 hours, the LaBr_3 product is transported to the lower temperature end, deposited there as colourless, transparent small single crystals of hexagonal columnar shape.

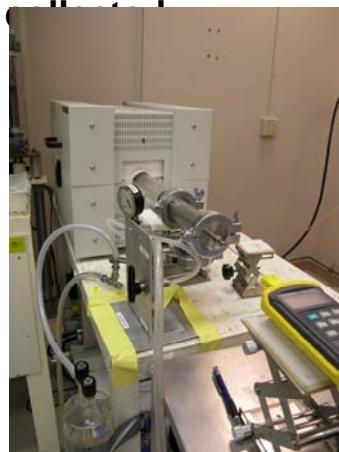
growth of single crystals of LaBr_3 can hardly be avoided. These are of good quality, perfectly suitable for single-crystal X-ray structure determination.



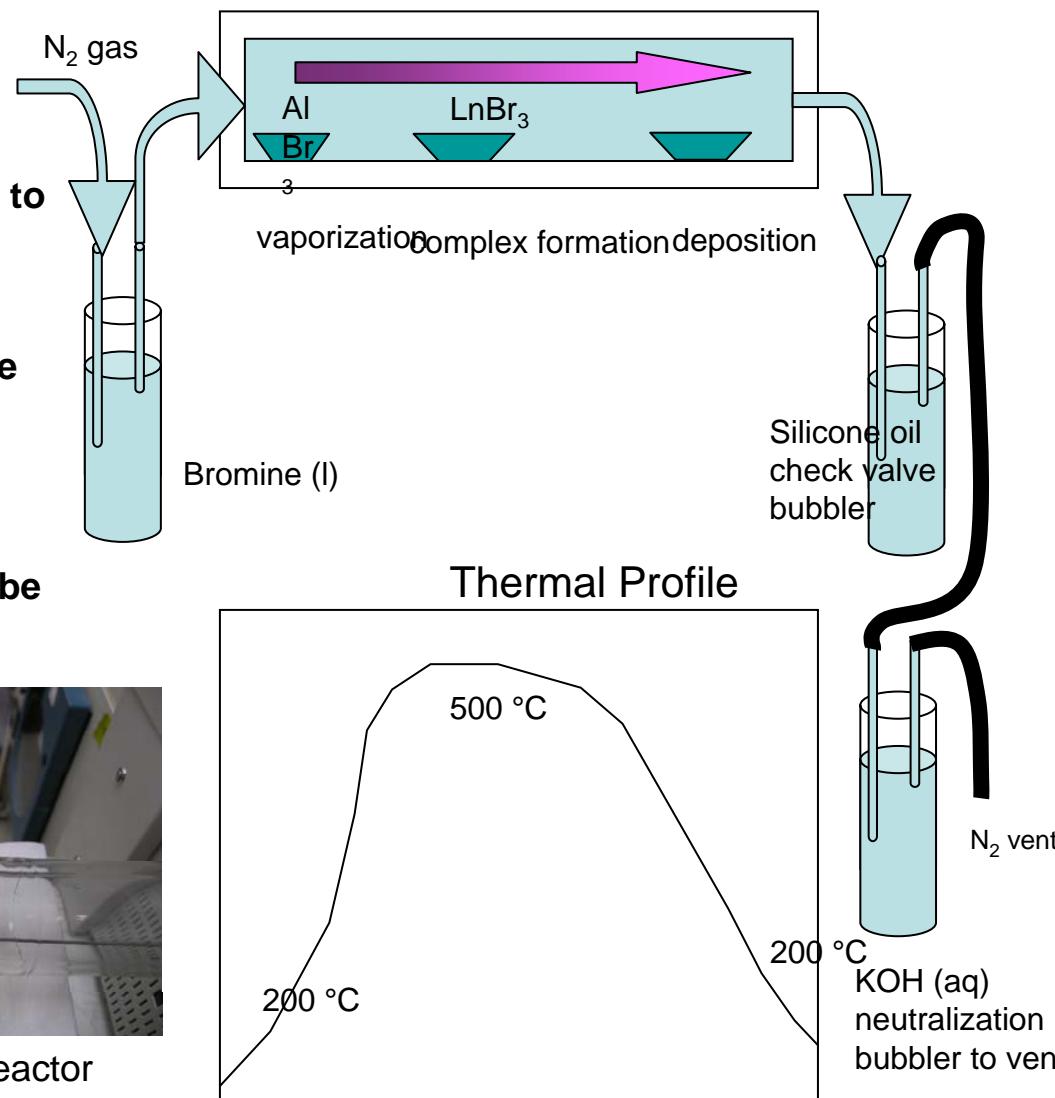
Task 1.2: Vapor Synthesis Route to Seed Particles

Vapor Synthesis Equipment

- Operations to date relate to construction of the equipment needed to form seed particles using vapor synthesis
- A sealed tube furnace will bubble nitrogen through Bromine to create the bromine atmosphere.
- $AlBr_3$ will volatize at 200 C, and flow over $LnBr_3$ or Ln_2O_3 at process temperature.
- Seeds will deposit upon cooling, and be collected.

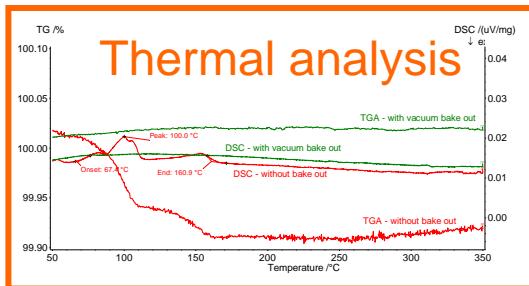


Double-tube reactor



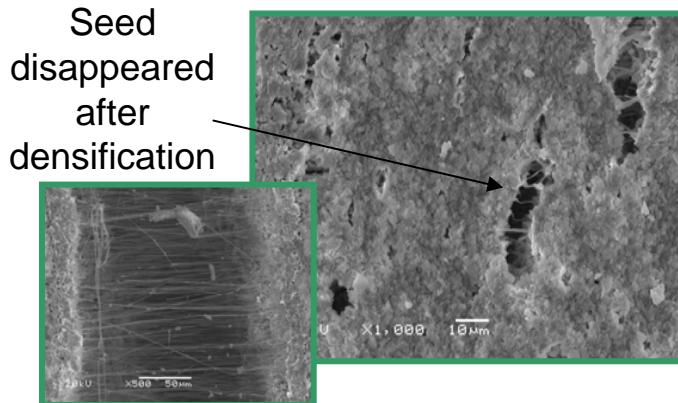
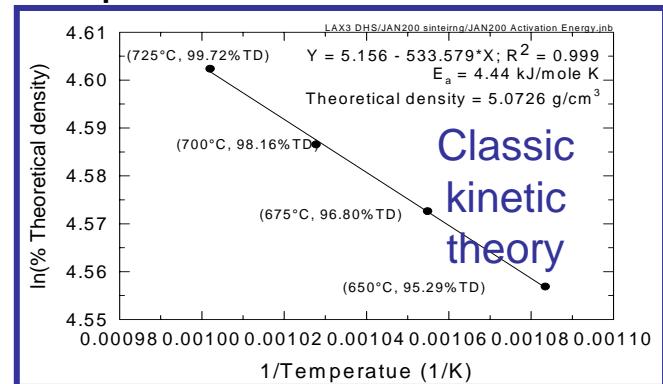
Recap (Textured Ceramics)

Task 1.3 Textured Ceramics

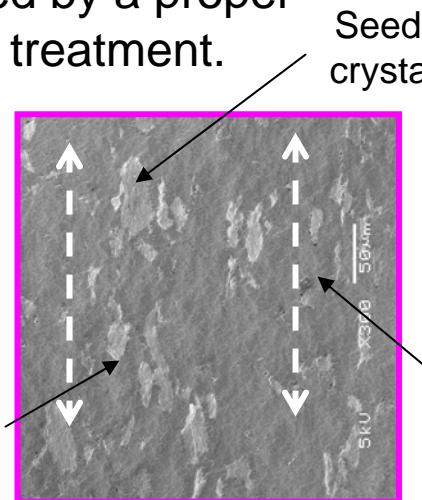


- Proper procedures for handling and processing hygroscopic materials have been developed.

- The kinetics of sintering has been investigated. A process window for densification of LaBr_3 ceramics has been identified.



- The structural integrity of seed crystals has been stabilized by a proper thermal treatment.



- Seed crystals have been successfully aligned in the densified ceramics by a rotation shear forming process.



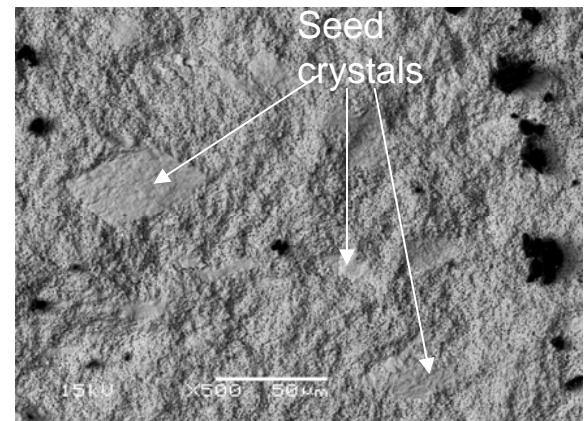
Task 1.3 Characterization of Ceramic/Seed

- Characterize the ceramic/seed interface to control and enhance solid state conversion.

Observations:

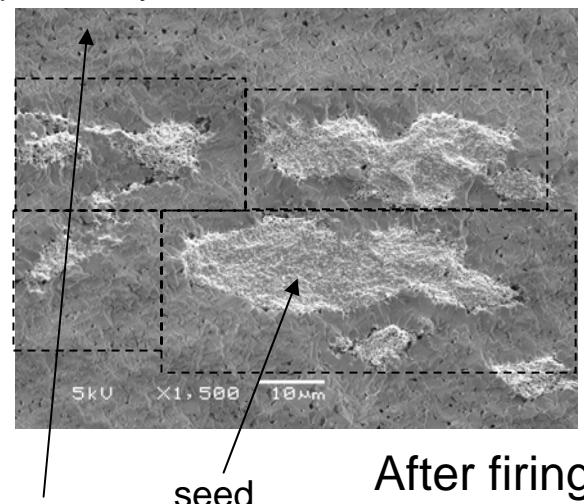
After thermal treatment, seed particles are no longer remain in single crystal form.

Densification seems to be preferentially located near the “seed” particles; therefore, the phenomenon is not a solid-state conversion process.



Green state

A preliminary result for solid state conversion

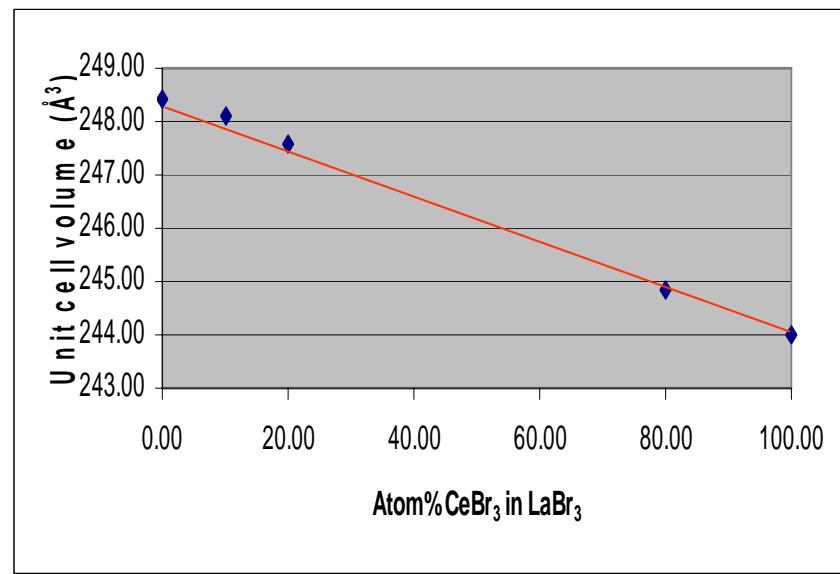
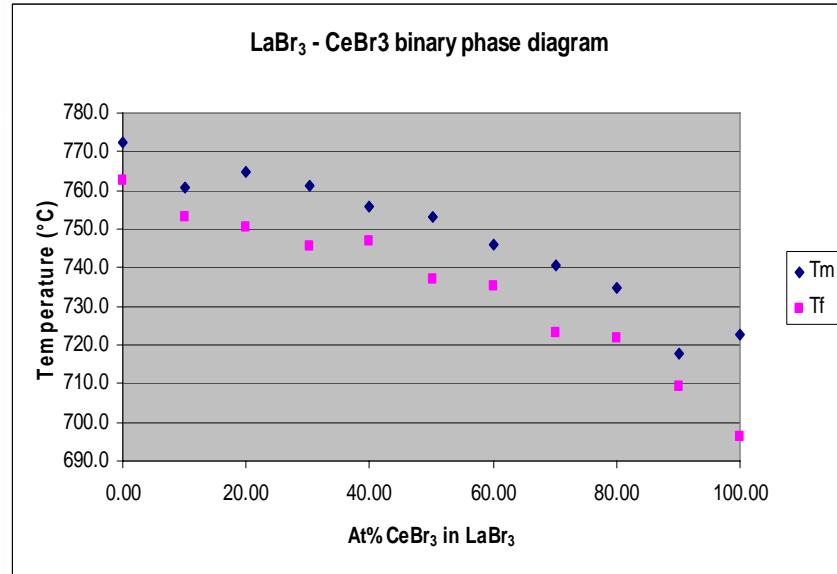


After firing



Task 2.1: Optimization of Dopant Level ($\text{LaBr}_3:\text{Ce}$)

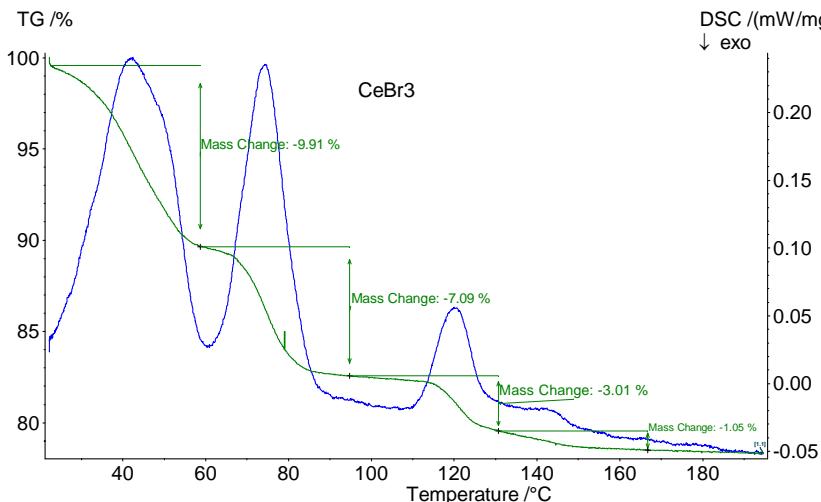
- Optimize the dopant level for maximum luminosity.
 - Establish $\text{LaBr}_3\text{-CeBr}_3$ phase diagram
 - Characterization scintillation properties



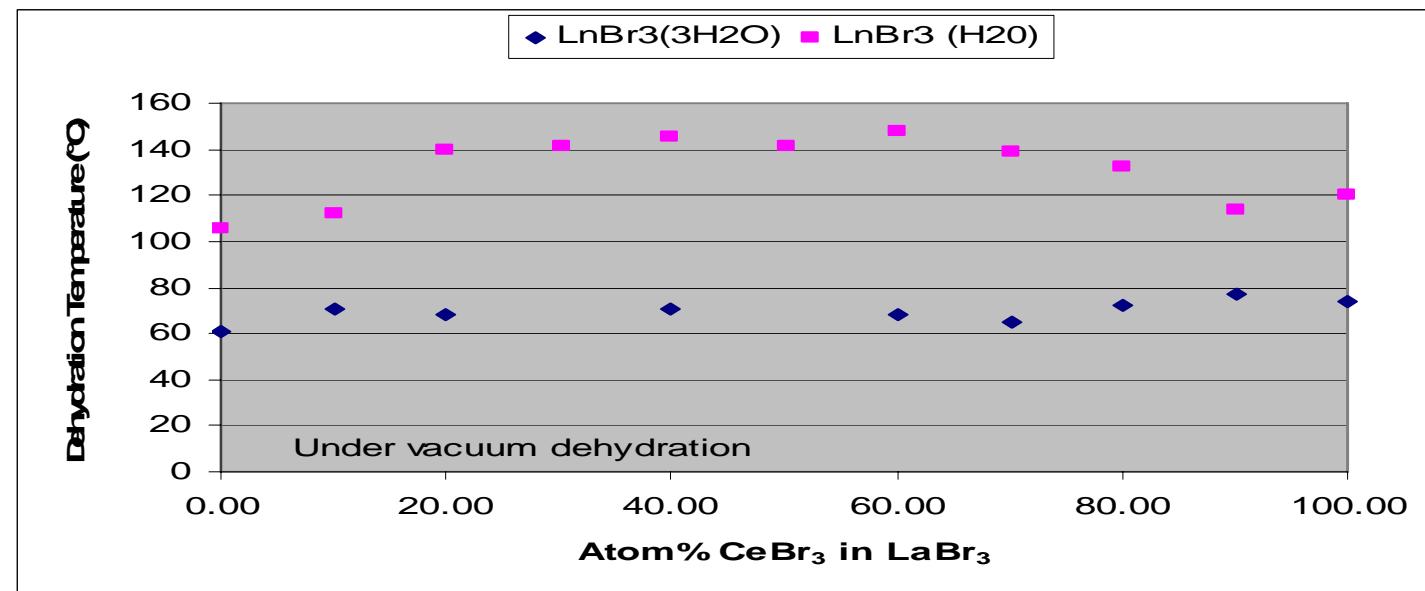
- Continue XRD investigation for the solid solution series of $\text{LaBr}_3\text{-CeBr}_3$
- Characterize the scintillation performance



Task 2.1: Dehydration Behavior for the $\text{LaBr}_3\text{-CeBr}_3$ System



Proper dehydration is crucial to avoid the formation of oxyhalides.



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Future Work and Contingent Plan

Pin Yang, Timothy J. Boyle, Nelson S. Bell,
Mark A. Rodriguez, Margaret R. Sanchez,
Leigh Anna M. Ottley, and Richard P. Grant



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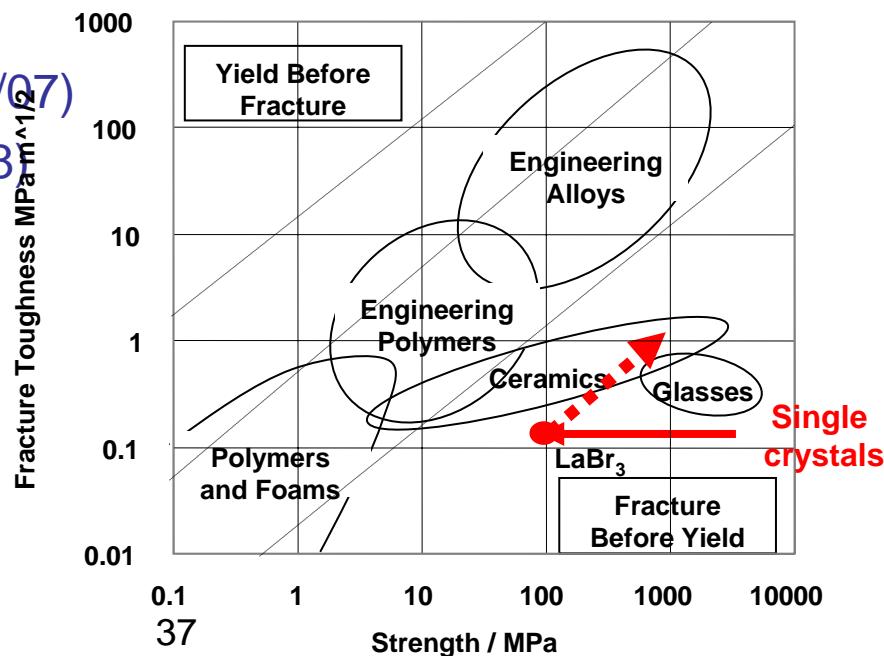
Future Work – Task 1: Material and Process Development

- (1.1) Chemical synthesis of ultrafine, high purity lanthanum halide powders
 - Identify “black” source, and develop an effective solution (07/07)
 - Size/morphology control (09/07)
 - Elimination of water (08/07).
- (1.2) Seed crystal preparation
 - Vapor phase synthesis (08/07)
 - Morphology control (07/07).
- (1.3) Densification of textured ceramics
 - Optimization of solid state conversion and densification processes (10/07)
 - Development of highly textured, optical quality ceramics (11/07)
 - Fabrication of large size ceramic scintillator for property evaluation (01/08).



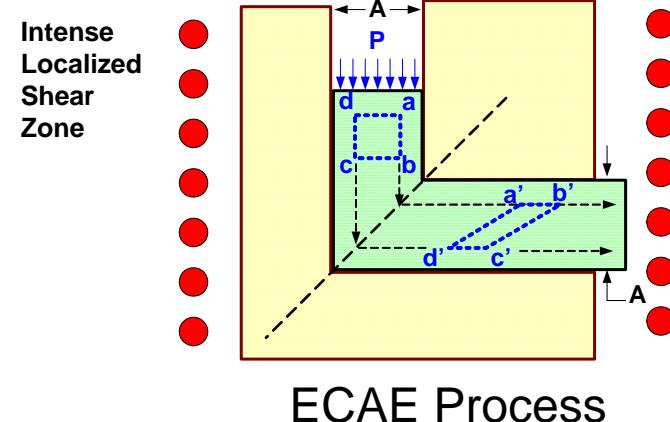
Future Work - Task 2: Investigation of Composition-Microstructure-Property Relationship

- Optimize the dopant level for maximum luminosity.
 - Establish $\text{LaBr}_3\text{-CeBr}_3$ phase diagram (07/07)
 - Characterization scintillation properties (09/07)
- Evaluate the effect of microstructure on mechanical and optical properties of textured ceramics.
 - Grain size (09/07)
 - Degree of texture (11/07)
 - Light scattering (01/08)

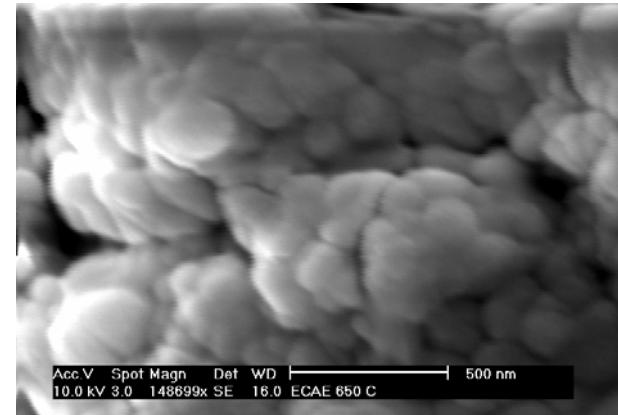


Contingent Plan – Ultra-fine Grained Lanthanum Halides (I)

- Equal Channel Angular Extrusion
 - Effective densification through high stress
 - Microstructure refinement through severe shear deformation
 - Large size production is feasible (Honeywell 16" X 16" X3")



Courtesy of C. Chen (LANL)



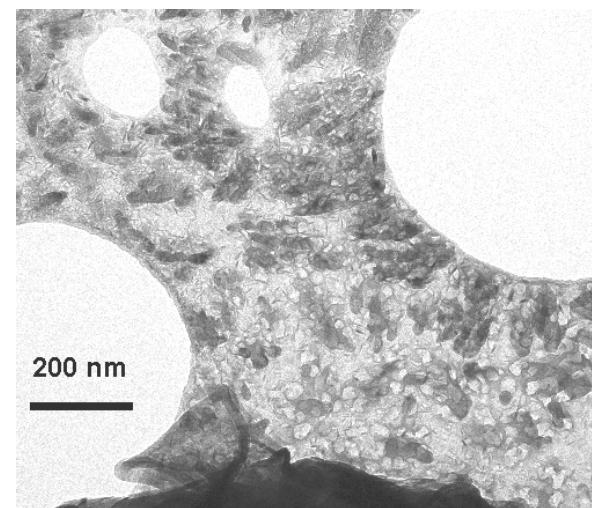
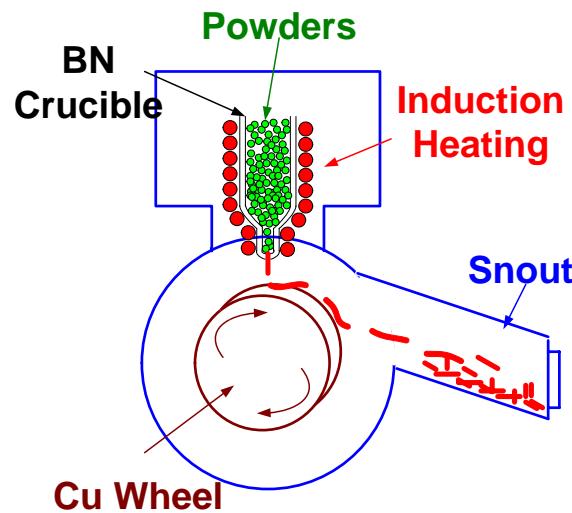
Courtesy of C. Chen (LANL)



Contingent Plan – Ultra-fine Grained Lanthanum Halides (II)

Objective: Use the complementary strengths of SNL (densification) and LANL (oxyhalide free nano-powder produced by melt spinner technique) to fabricate low-cost, large size lanthanum halide scintillators for γ ray spectroscopy.

Additional benefit: verification the source of “black” during high temperature processes.



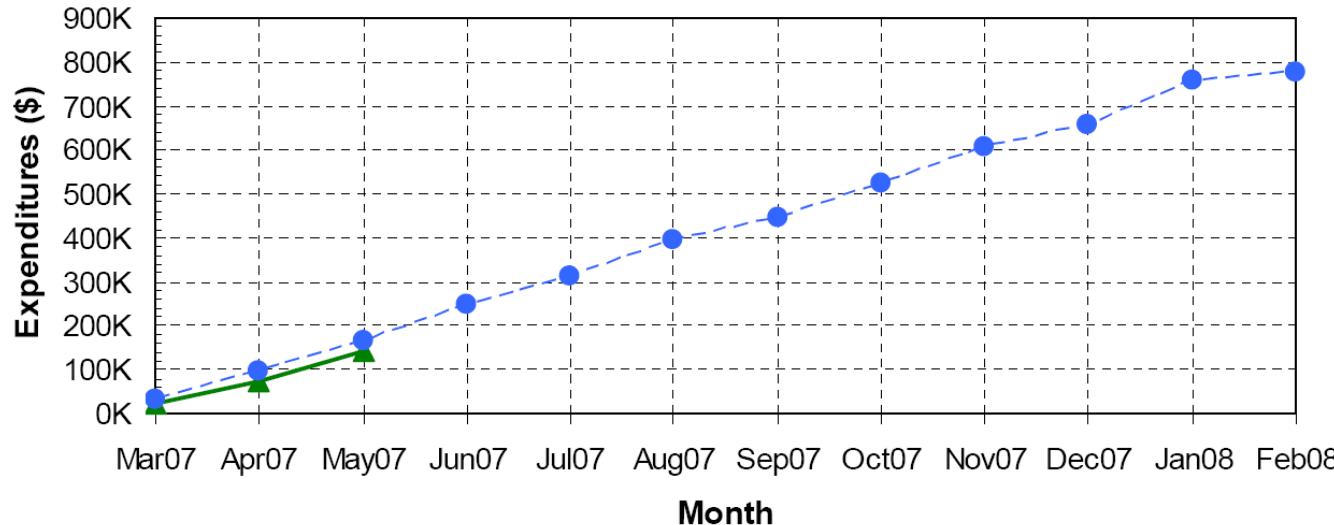
Courtesy of C. Chen (LANL)



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Cumulative Funding Profile and Project Status

Cumulative Actual and Planned Expenditures



Task Name	Finish	Timeline
Fabrication of Large-Volume, Low-Cost Ceramic Lanthanum Halide Scintillators (FY07)	Tue 1/29/08	Mar '07 - Feb '08
Task 1 Material and Process Development	Thu 7/26/07	Mar '07 - Jul '07
1.1 Chemical Synthesis of powders	Tue 5/15/07	Mar '07 - 5/15
1.2 Seed-particle preparation	Wed 6/20/07	5/15 - 6/20
1.3 Densification of textured ceramics	Thu 7/26/07	6/20 - 7/26
Prepare powder batch > 100g	Tue 5/15/07	Mar '07 - 5/15
Synthesize contamination free high aspect seed particles	Wed 6/20/07	5/15 - 6/20
Fabricate > 2" optical quality ceramics	Thu 7/26/07	6/20 - 7/26
Task 2 Investigate Composition-Microstructure-Property Relationship	Tue 1/15/08	Mar '07 - Jan '08
2.1 Optimize dopant level	Thu 8/30/07	Mar '07 - 8/30
2.2 Investigate interplay between grain size, texture, & scattering	Tue 1/8/08	8/30 - 1/8
2.3 Evaluate effect of microstructure	Tue 1/15/08	1/8 - 1/15
Establish optimum composition	Fri 9/14/07	Mar '07 - 9/14
Determine amount of light scattering as function of microstructure	Fri 9/28/07	9/14 - 9/28
Compare mechanical properties with single crystal values	Wed 1/2/08	9/28 - 1/2
Task 3 Prepare Final Report	Tue 1/29/08	1/2 - 1/29
Draft final report	Tue 1/29/08	1/29
Submit final phase 2 report	Tue 1/29/08	1/29

Remarks:

- Training new technologists, re-adjusting work load, and establishing new capabilities (including ES&H) consumes a significant amount of resource.

- The team is at ready to accelerate our progress in the 2nd quarter.



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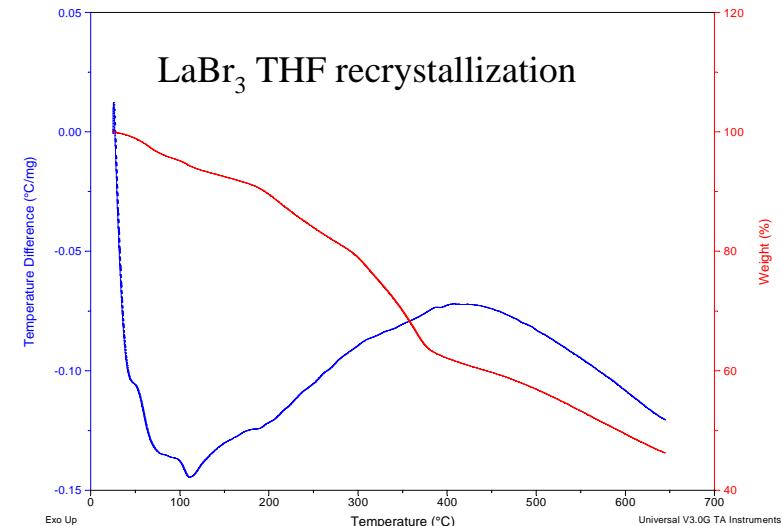
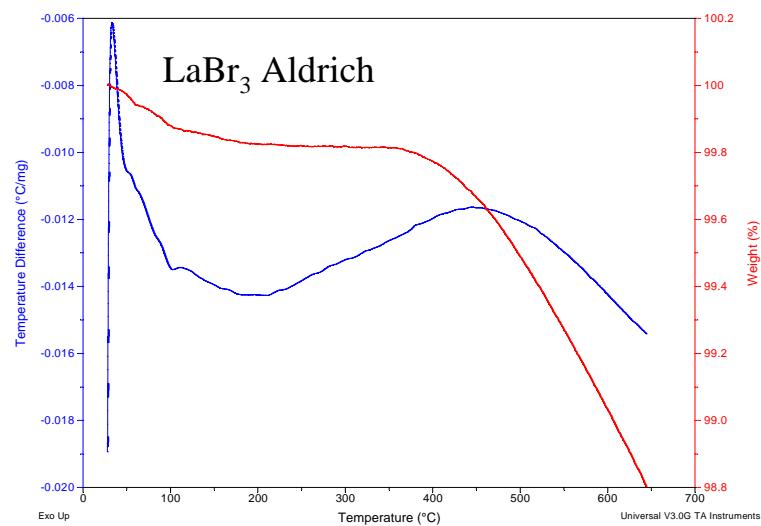
Pin Yang*, Timothy J. Boyle, Nelson S. Bell,
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Sandia National Laboratories

June 27, 2007
(Quarterly Review – DHS Headquarters)

Seed Particle Thermal Stability

The LaBr_3 powder both as received and after recrystallization in THF were examined using DTA/TGA. The products were tested by SEM and EDS. THF is a coordinating solvent, and may form a complex with the salt.



At 300 $^{\circ}\text{C}$, there is $\sim 20\%$ weight loss from the recrystallized material, but not from the commercial material. These results suggest that THF is coordinated with the recrystallized material. Further examination is required to understand optimal methods to remove the material.

