U.S. DEPARTMENT OF ENERGY

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National Nuclear Security Administration
Defense Nuclear Nonproliferation

Office of Defense Nuclear Nonproliferation Research & Development

# Nuclear Weapons and Material Security (WMS) Team Program Review

***WMS2013***

# Accelerated Discovery of Elpasolite Scintillators

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**Sandia National Laboratories**

April 9, 2013

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# Elpasolite Scintillators

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**Participating laboratories, PIs and Co-investigators**


| | | |
|---|---|---|
| F. P. Doty, PI | SNL/CA | Luminescence and scintillation properties |
| Xiaowang Zhou | SNL/CA | Modeling and simulations |
| Pin Yang | SNL/NM | Crystal growth, structure, and properties |


**Project overview, goals, technical approach**

Our goal is efficient discovery of producible elpasolite crystals and alloys for gamma spectroscopy, and exploit their isotropic nature for ceramic scintillators. Our approach is to eliminate unstable or highly distorted candidate structures using the embedded ion model, and produce cubic elpasolite crystals for test and evaluation.

<u>Major proposed tasks include:</u>

✓ FY12: Extend EIM data base, investigate effect of Ce(III) loading on host stability

✓ FY13: Extend database, investigate cationic substituents for alloy stabilization

__FY14: Complete data base, investigate anionic substituents for alloy stabilization

Results on structure, phase stability, luminescence intensity, emission wavelength, linearity, and decay characteristics, etc., will be used to rank candidates for further development.

# Elpasolite Scintillators



**Deliverables**

- Technical reports to NA22 on the findings of these studies
- Journal publication of results

**Description of capability improvement to be addressed by project success**

Success of this work will be optimal materials, and strategies for low cost, large volume scintillator fabrication.

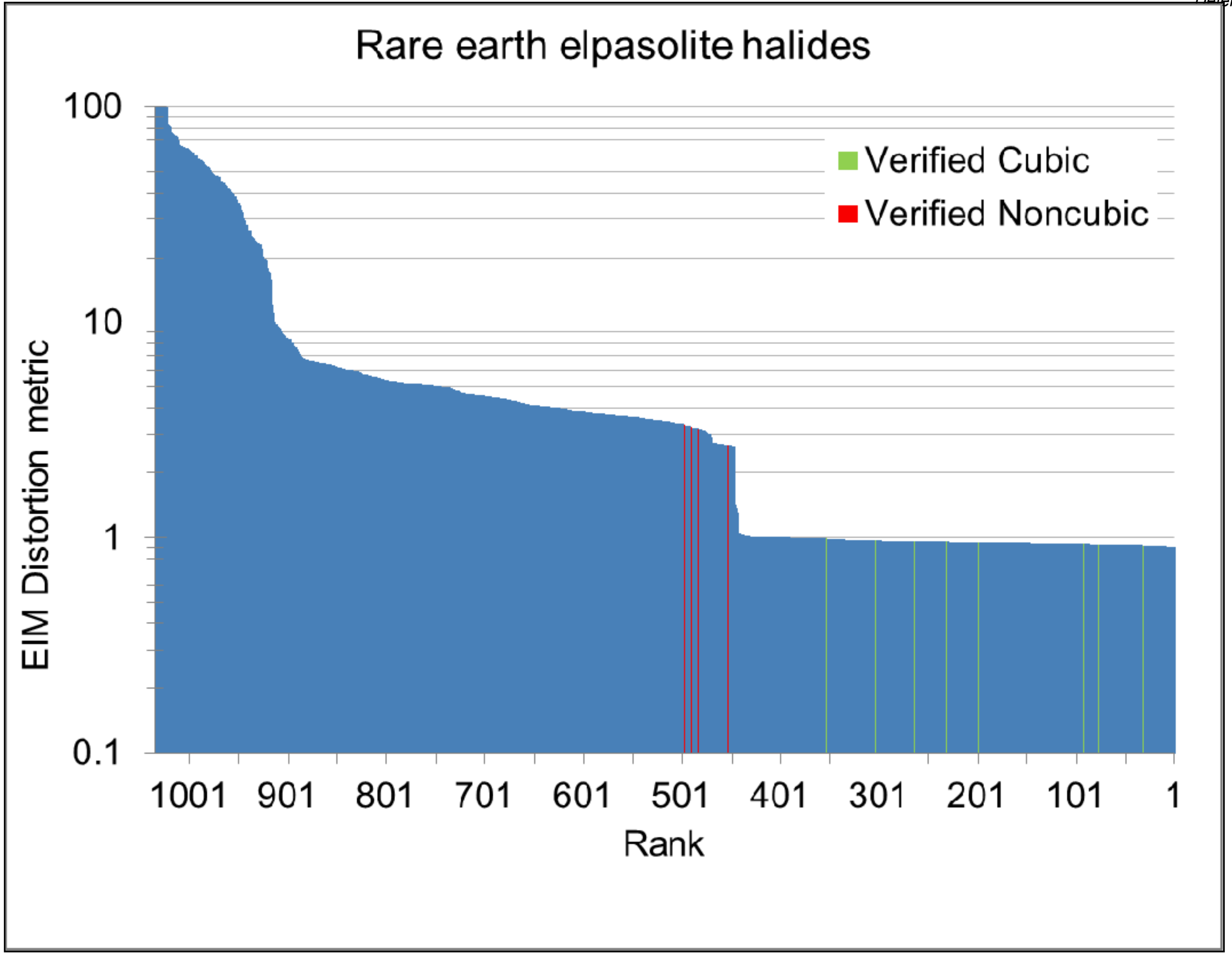
**Technical challenges**

- Segregation
- Phase instability
- Polymorphism
- Transparency

**Future work for the remainder of the project**

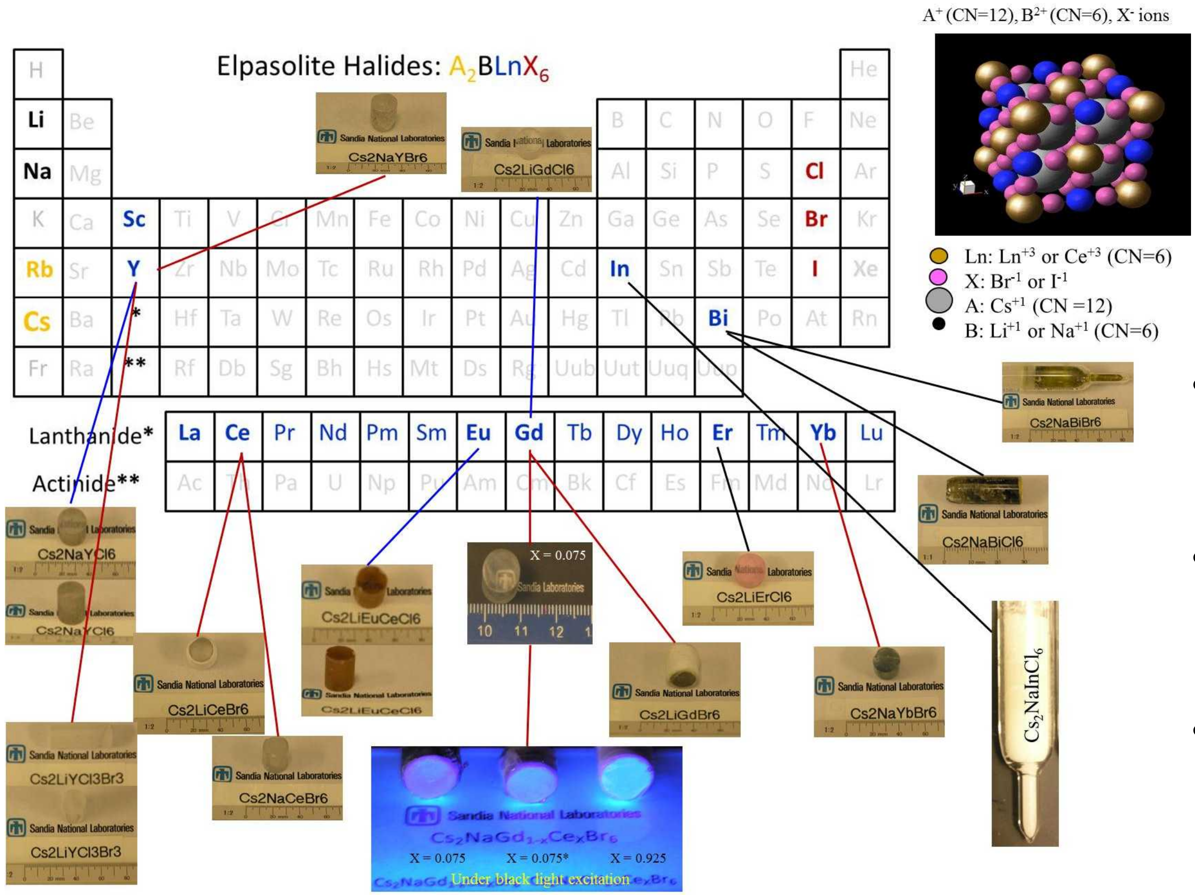
1. Complete EIM data base
2. Perform Monte Carlo simulations of alloy short range ordering for solid solutions
3. Investigate anionic substituents for alloy optimization
4. Focus on host stabilization and luminosity of CLLB and iodides with lowest distortion
5. Explore ceramic scintillator using best selected system

# EIM data base



# Single crystal growth

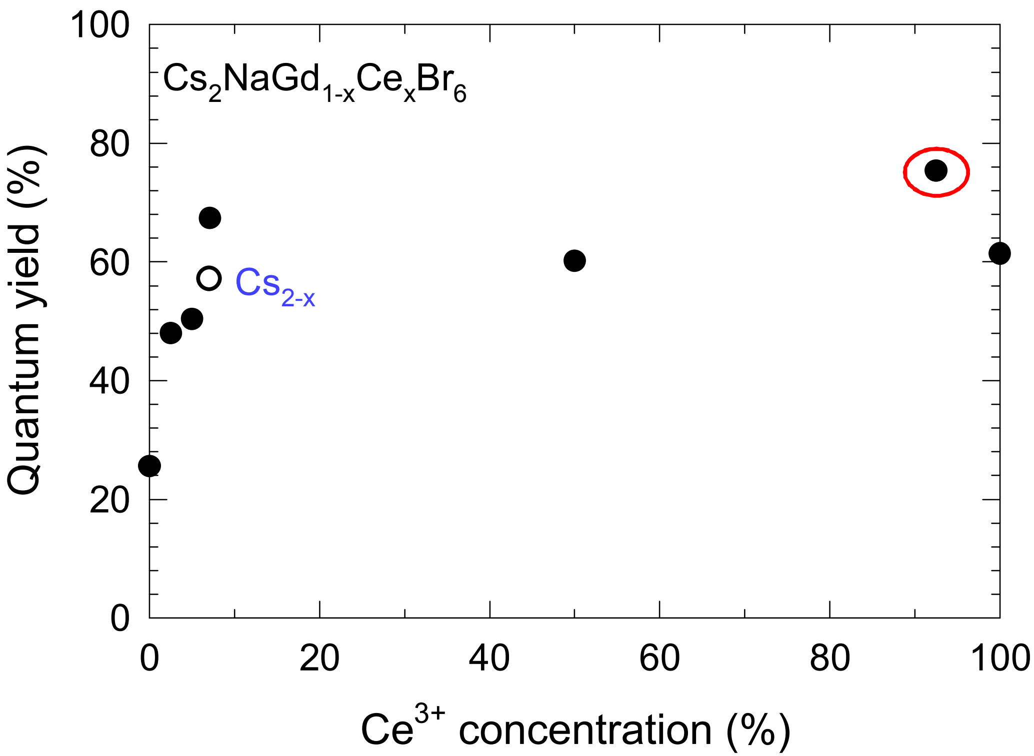
Laboratory-scale single crystals
structure and properties

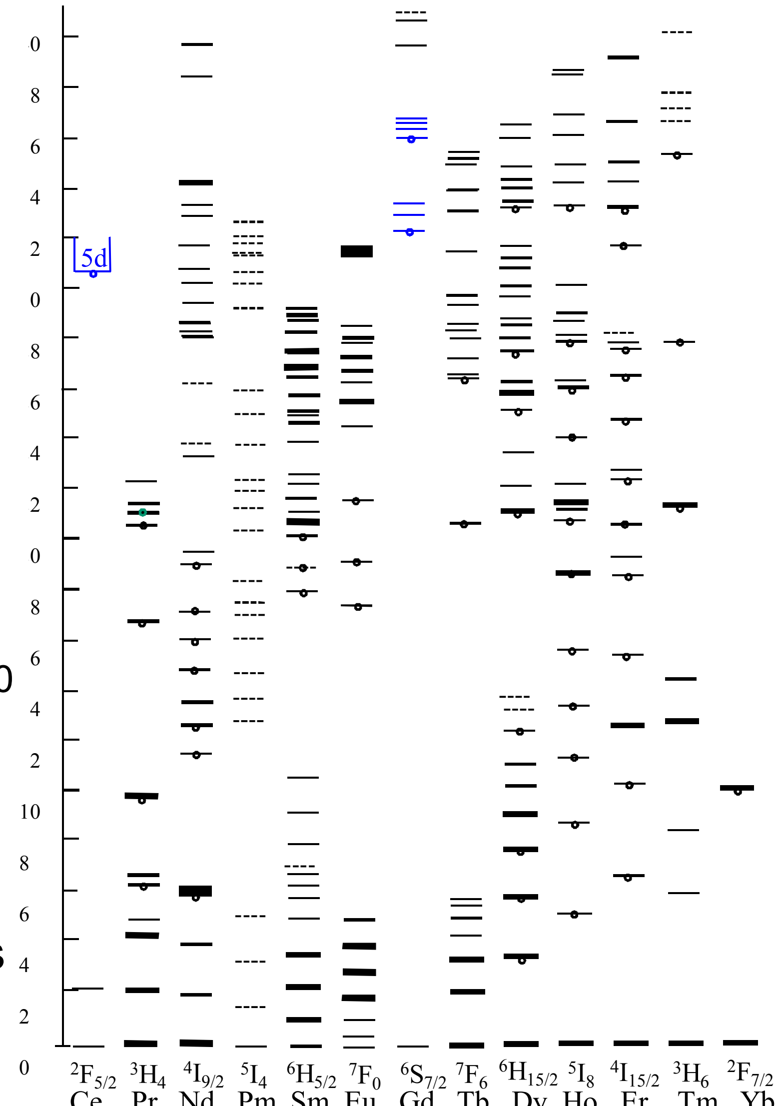



- 21 different single crystal compounds
- 7 cation-mixing alloy crystals ($Ln^{3+}$ site)
- 4 anion-mixing alloy crystals ($Cl^-$, $Br^-$)

# Cation mixing

I. Improve light yield through sensitizing




- Study the effect of sensitizing by energy transfer (i.e. $Gd^{3+}$ 4f to $Ce^{3+}$ 5d) through co-doping of $Gd^{3+}$ and $Ce^{3+}$ in elpasolite halides to improve their luminosity

# Cation mixing

II. Tune emission spectra

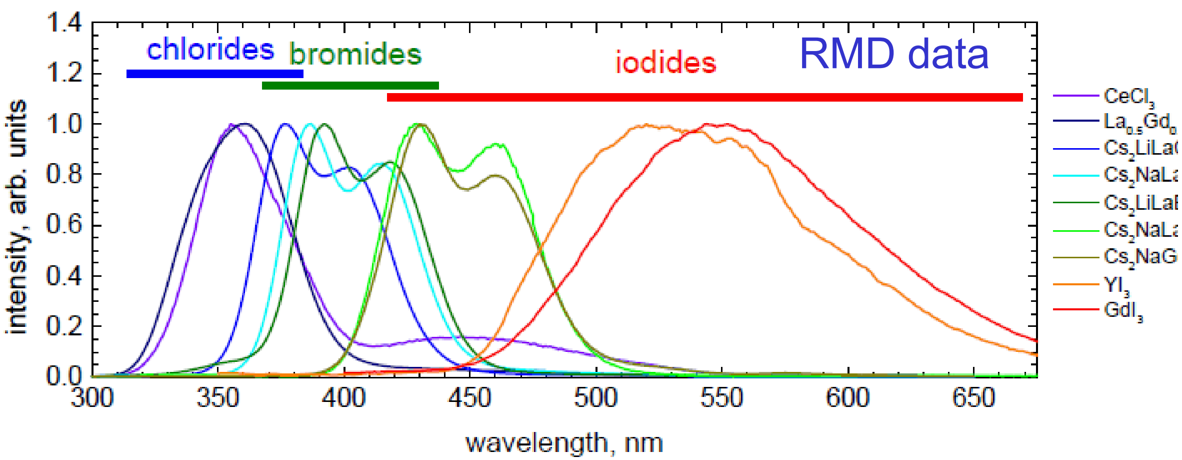
## Crystal-field and emission spectra

The size of crystal field splitting has a profound effect on optical emission, which generally follows the electrochemical series

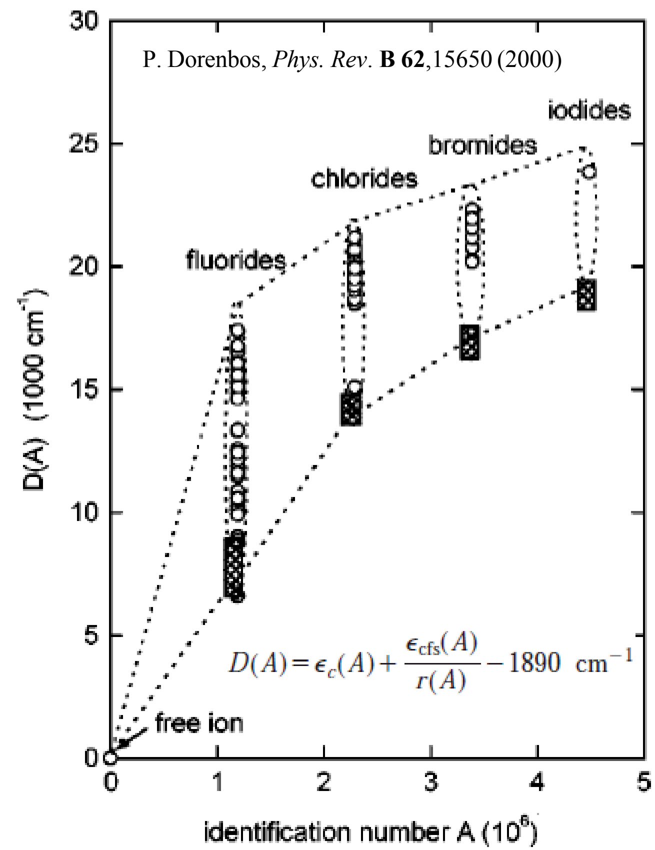
$I^- < Br^- < Cl^- < F^- < OH^- < NH_3 < NO_2^- < CN^-$

The larger the splitting, the greater the redshift.

## Emission spectra of selected tri-halides and elpasolites



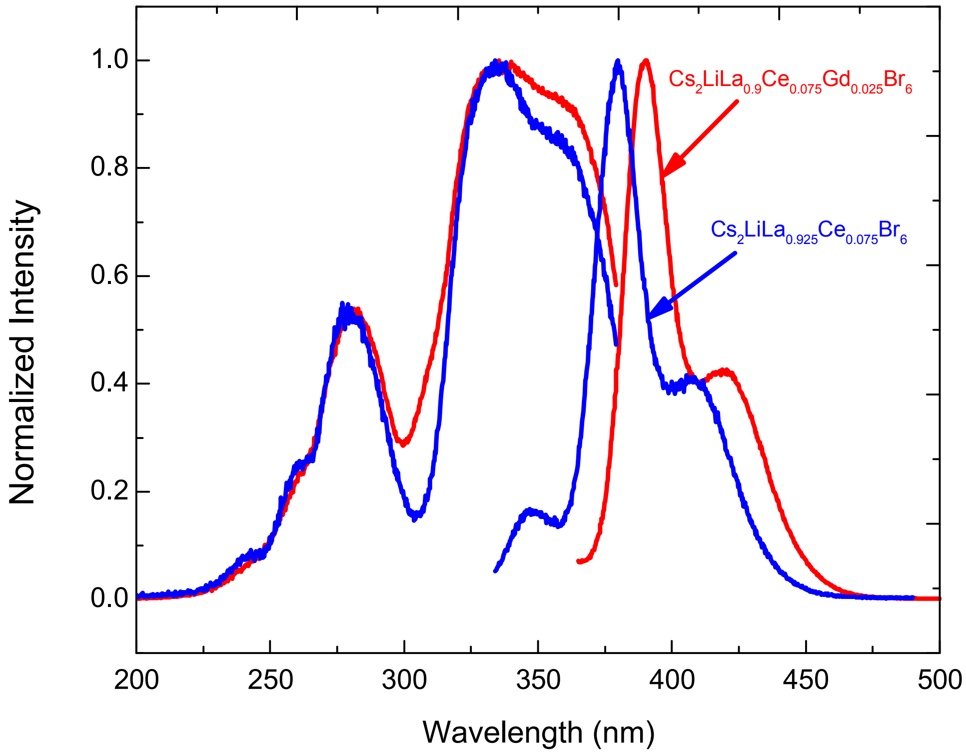

*5d*-level energies of $Ce^{3+}$ in the halogenide compounds




Investigate the spectrum broadening by anion-mixing in elpasolite halide scintillators

# Cation mixing

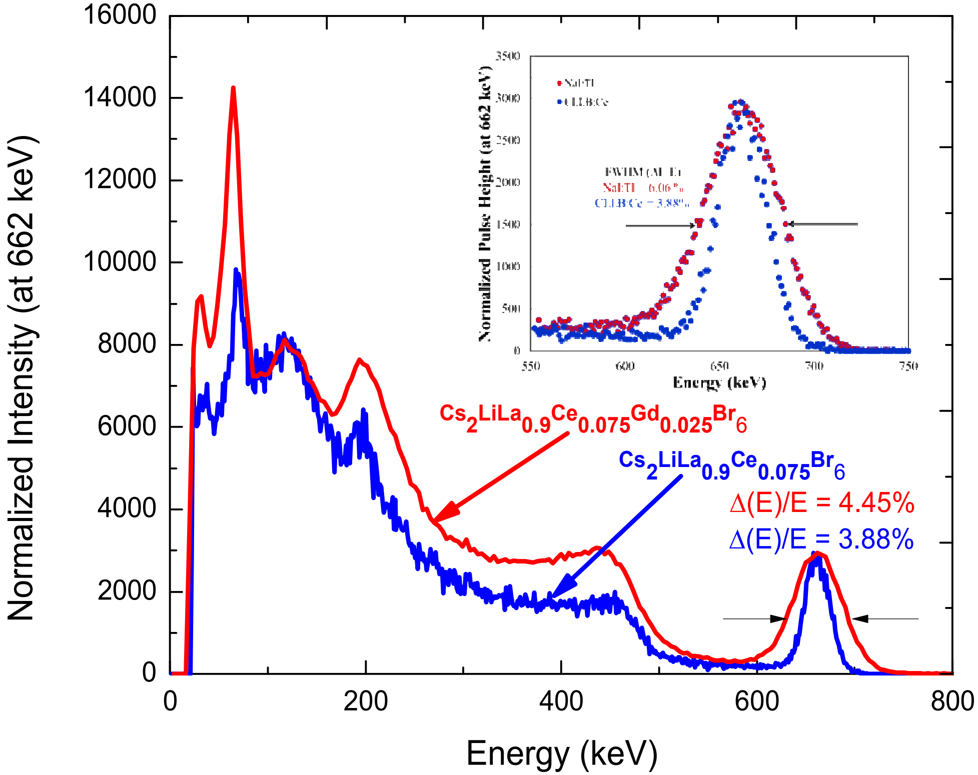
The effect of co-doping on the optical quantum yield of CLLB




- Co-doping of $Gd^{3+}$ and $Ce^{3+}$ can shift the emission spectrum of $Cs_2LiLaBr_6$ (CLLB).
- Co-doping effectively improves the optical quantum yield from 63.4% to 86.5%.

# Cation mixing

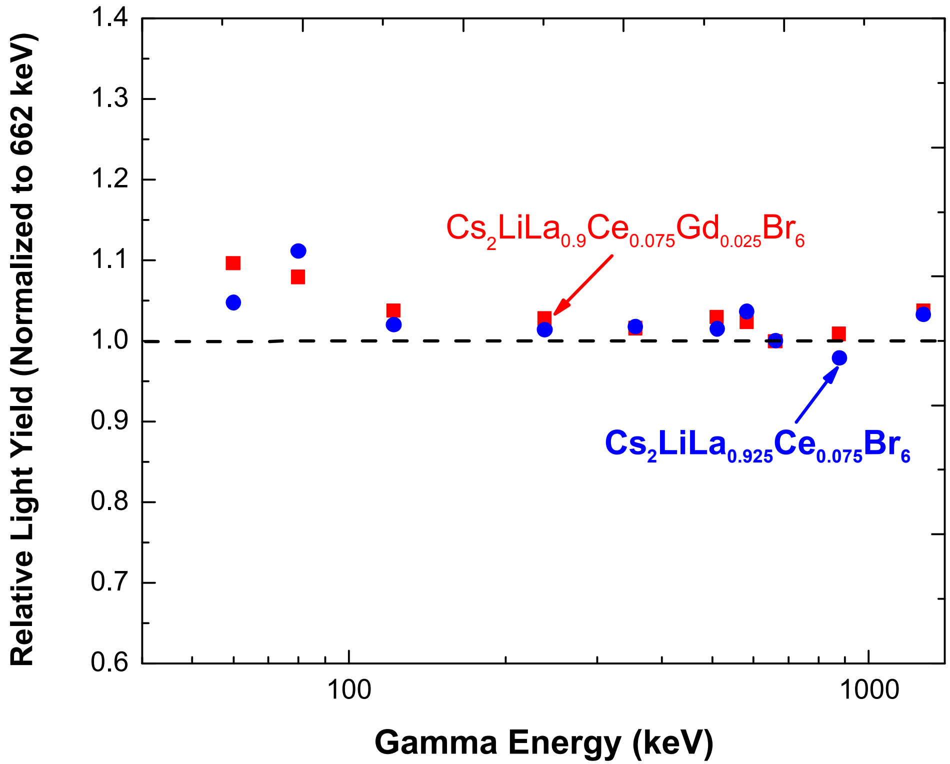
The effect of co-doping on the energy resolution of CLLB




- Energy resolution decreases when additional $Gd^{3+}$ is added to the $Ce^{3+}$ activated $Cs_2LiLaBr_6$.

# Cation mixing

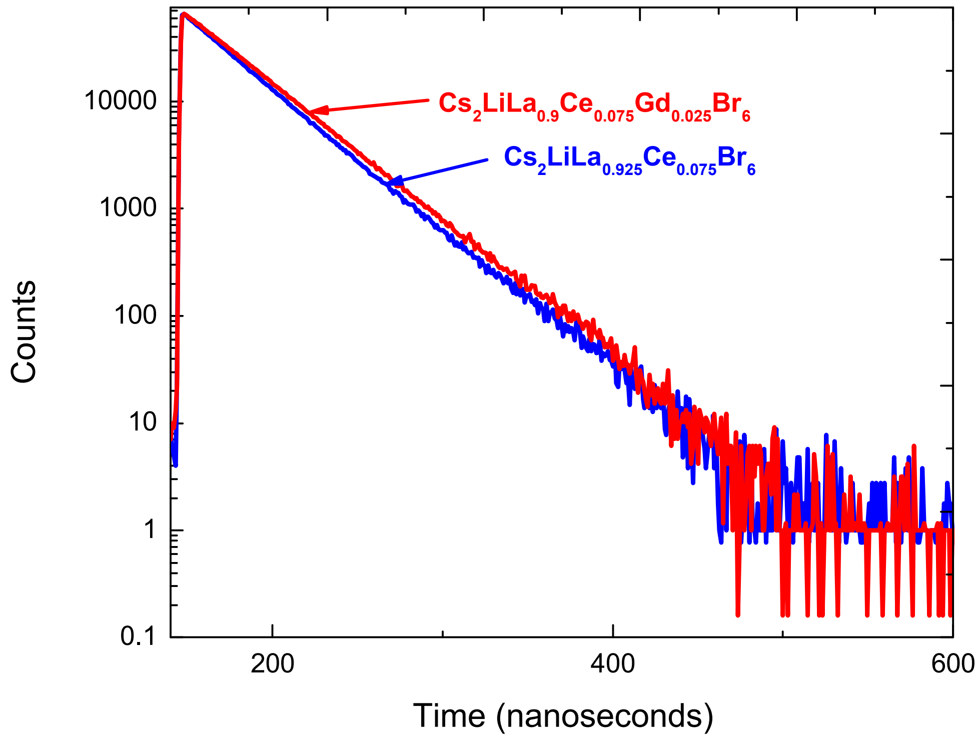
The effect of co-doping on the proportionality of CLLB




- No significant change in proportionality for co-doped CLLB.

# Cation mixing

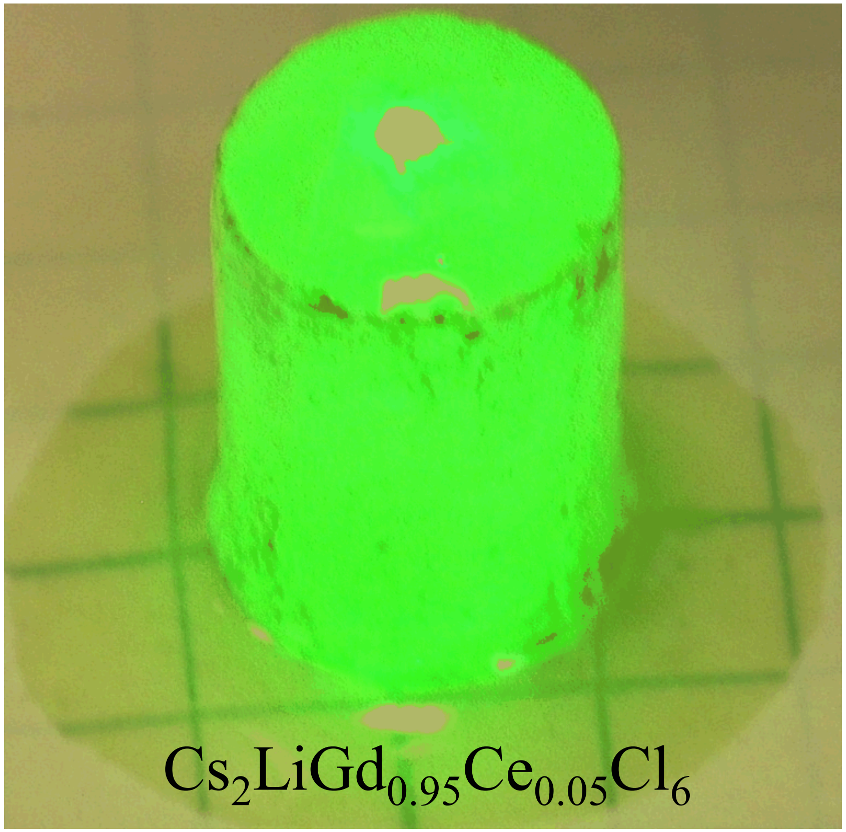
The effect of co-doping on the lifetime of CLLB




- The lifetime for the $Gd^{3+}$ doped CLLB increases slightly presumably due to the energy transfer process.

Lifetime:
CLLB:$Ce^{3+}$: 31.86±1.91 ns (98%)
CLLB:$Ce^{3+}$/$Gd^{3+}$: 33.68±2.04 ns (92%)

# Phase impurities



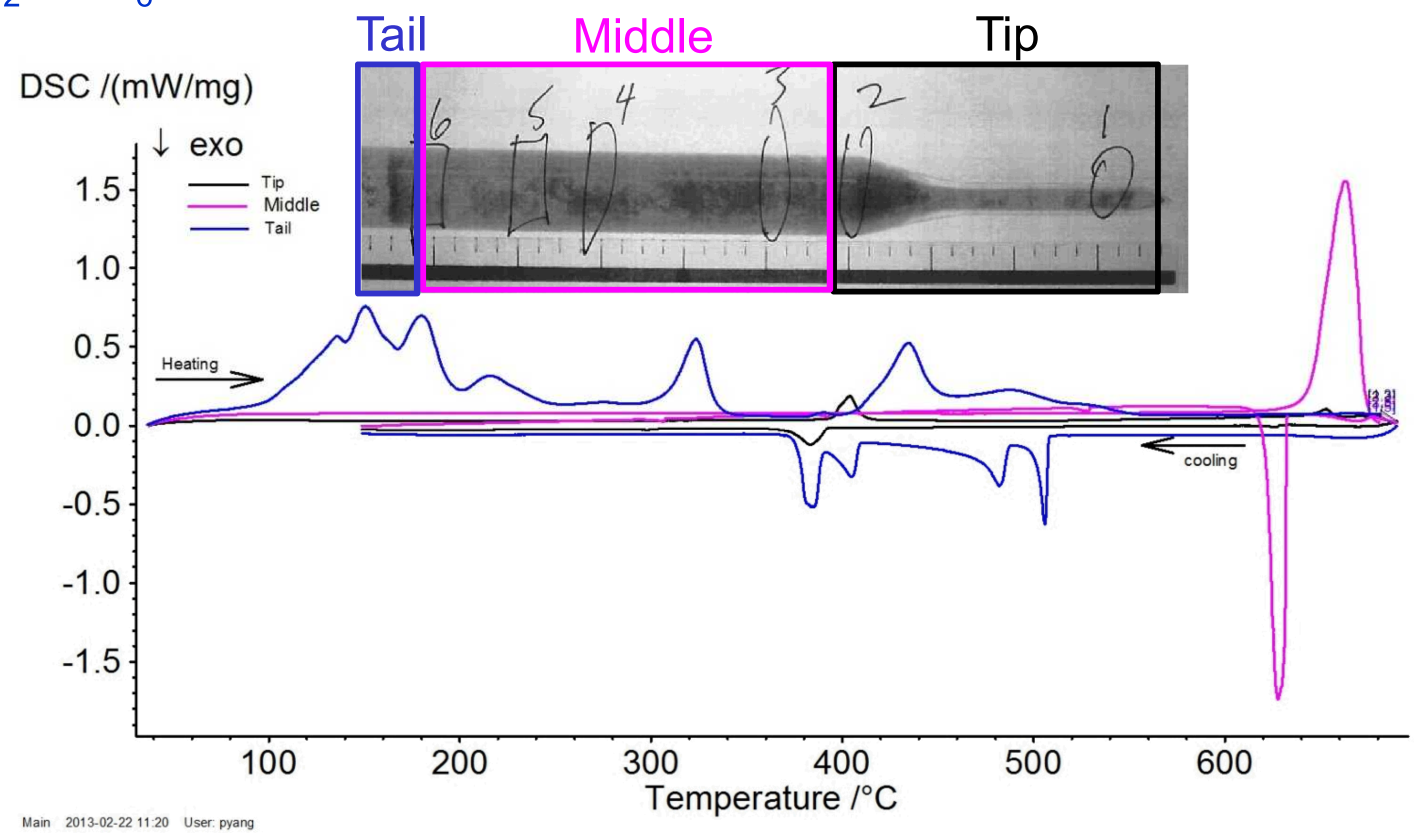

This sample has $Cs_3GdCl_6$ impurity phase (XRD)

- Can cause significant scattering in large single crystals.
- Other intermetallics identified
  - Bi compounds (many)
  - $Cs_3CeBr_6$ phase in CLCB
  - $Cs_3YCl_6$ in CLYC
  - $Cs_2GdCl_6$ in $Cs_2LiGdCl_6$
  - $Cs_3Sc_2I_9$ in $Cs_2NaScI_6$
  - $Cs_3Gd_2Br_9$ in $Cs_2NaGdBr_6$
  - CsBr and LiBr in many systems
- Self-limiting process

# Phase impurities

## Phase separation during crystal growth

$Cs_2LiYCl_6:Ce^{3+}$




- Thermal analysis on different sections of the CLYC crystal reveals the formation and segregation of foreign phase.

# Phase impurities

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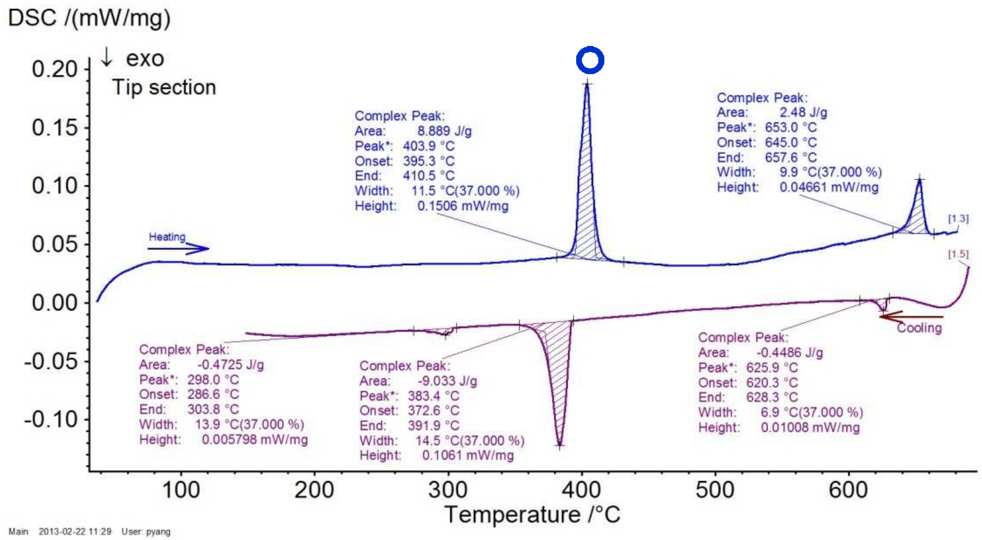
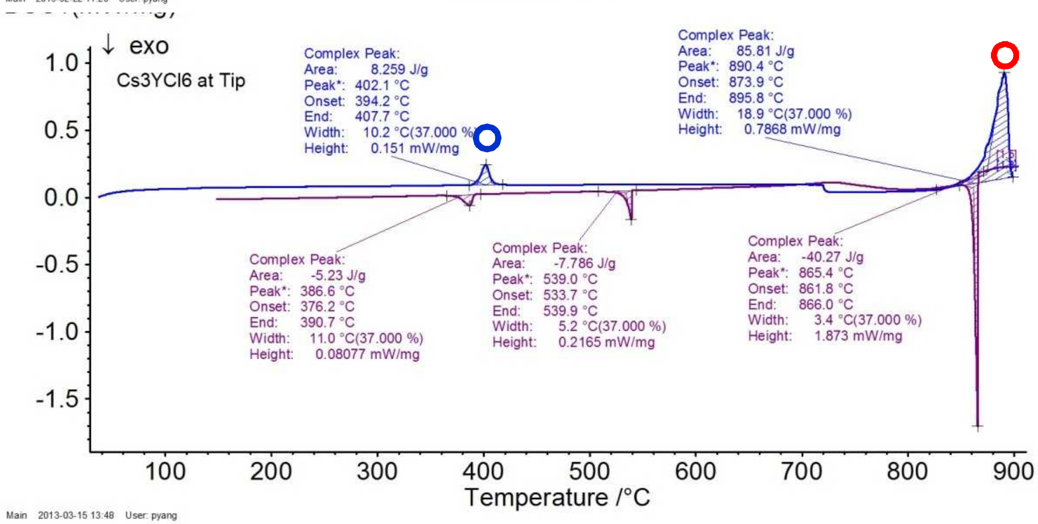
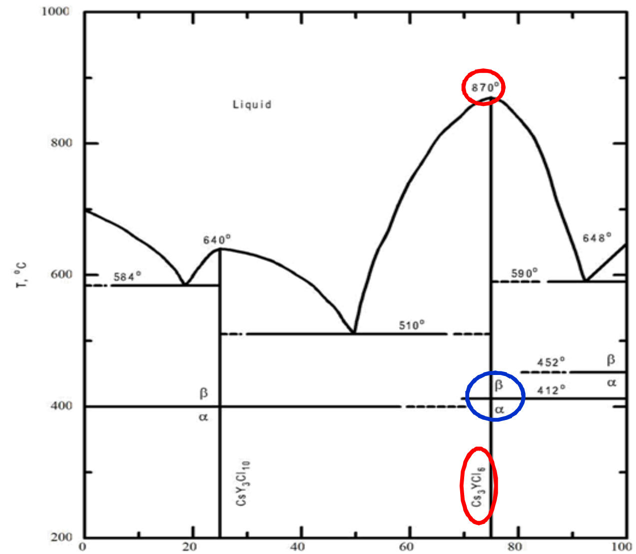
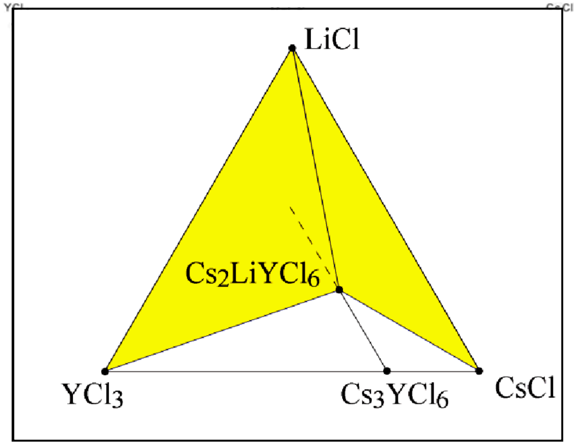
## $Cs_3YCl_6$ forms and segregates at the tip section

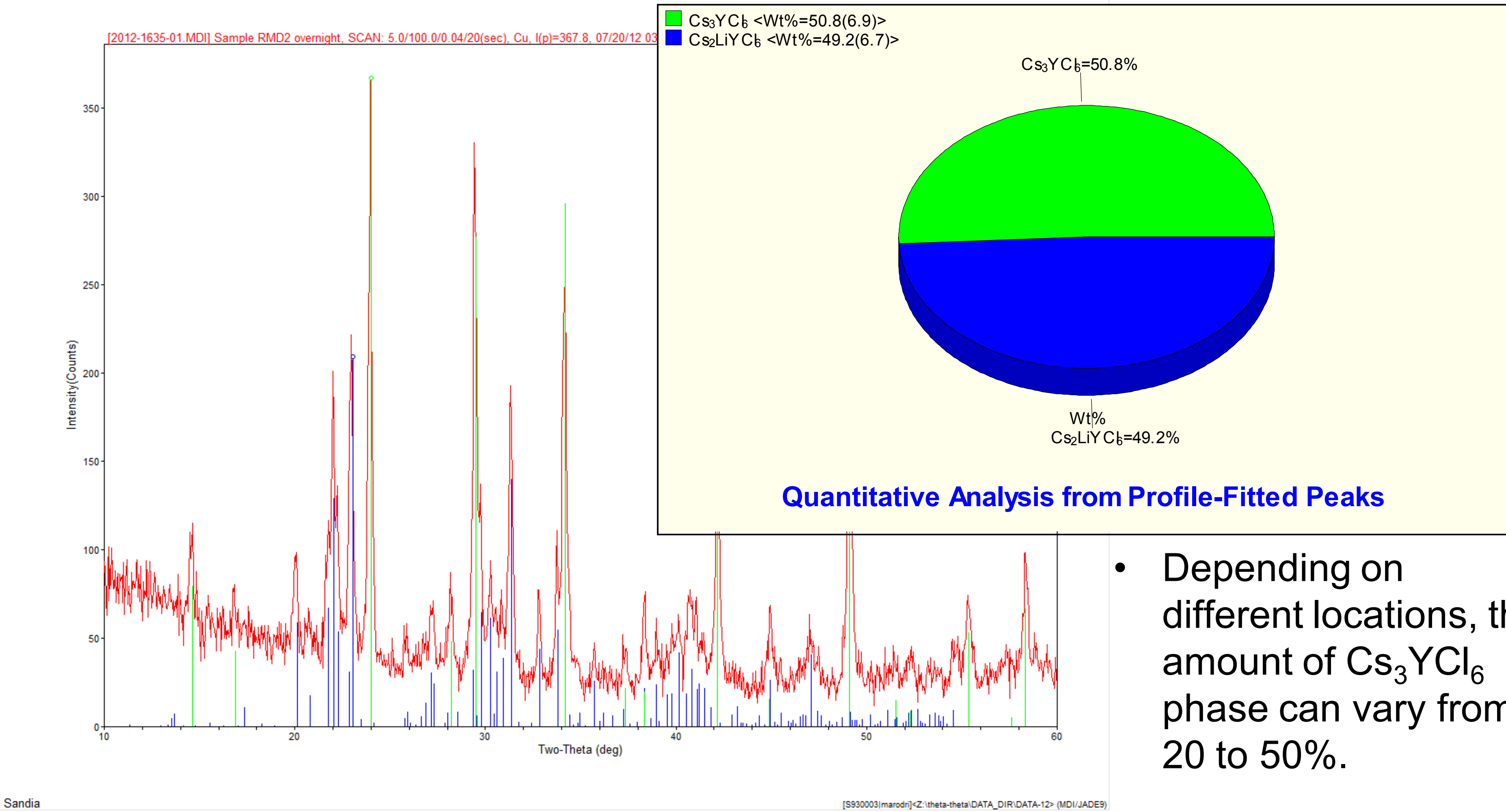


# Phase impurities




- Depending on different locations, the amount of $Cs_3YCl_6$ phase can vary from 20 to 50%.

- X-ray result confirms that the tip section has $Cs_2LiYCl_6$ elpasolite along with a 2nd phase of $Cs_3YCl_6$ phase.

# Phase impurities

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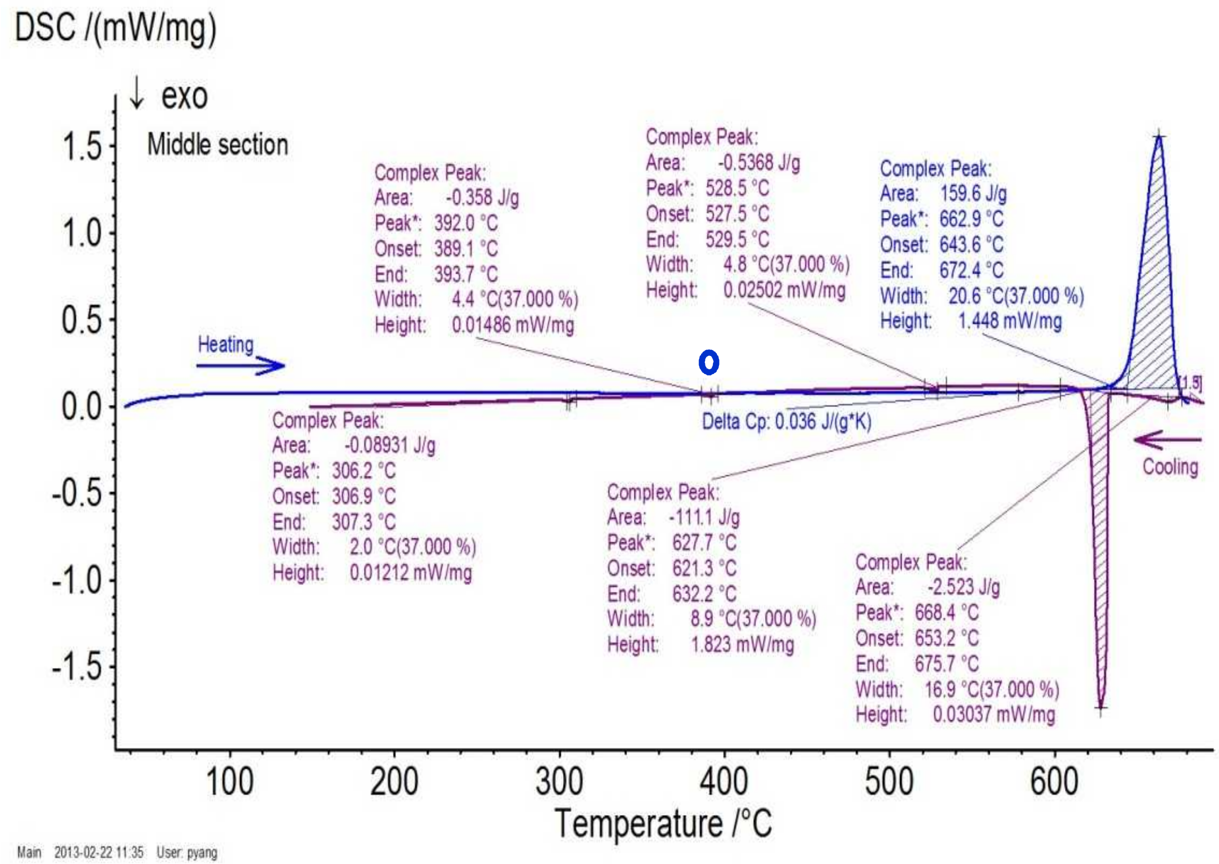
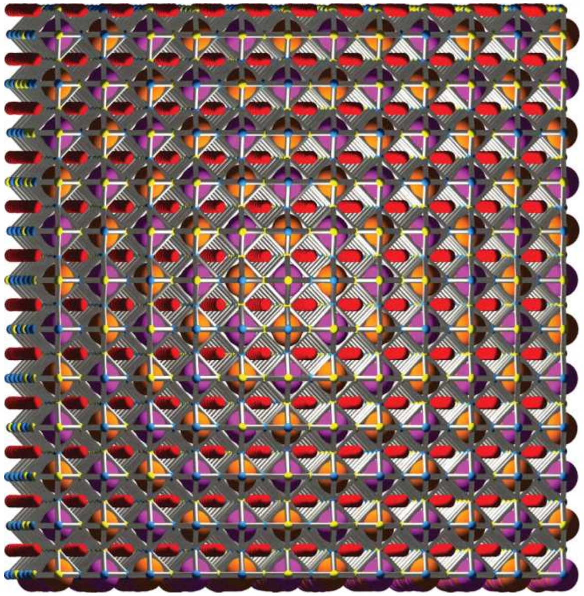
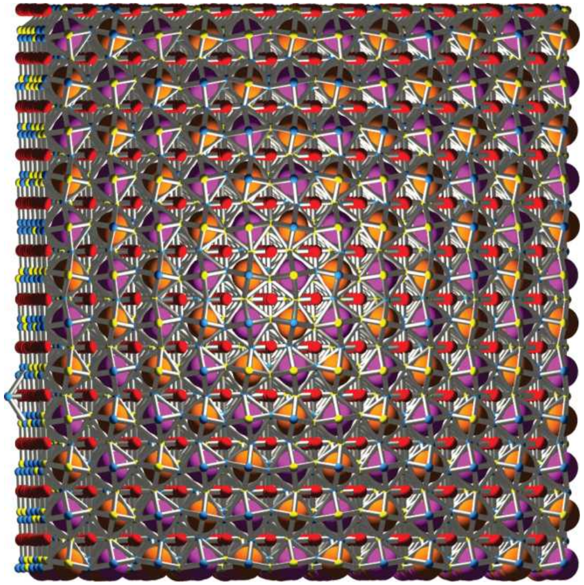



- A trace amount of $Cs_3YCl_6$ remains in middle transparent section
- Can induce significant light scattering in large single crystals and ceramic scintillators.

# Anion mixing: crystal structure

Even with a significant change in anion radii from 1.81Å ($Cl^-$) to 1.96Å ($Br^-$), mixed anion elpasolite retains cubic structure with octahedron tilting

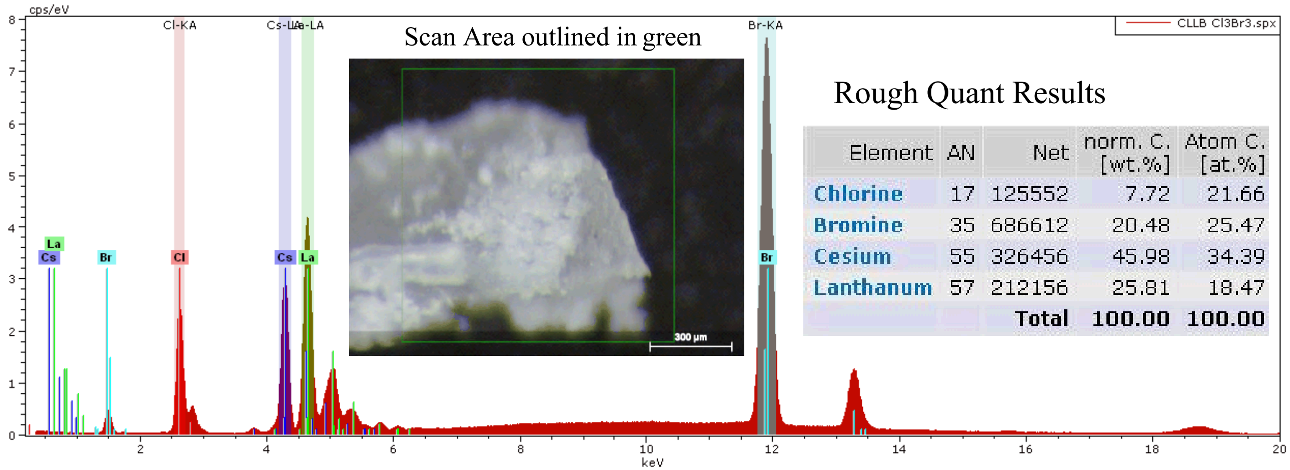




- IEM predicts that Cl and Br are randomly populating the anion mixed solid solution should remain well in the cubic structure
- Confirmed by the X-ray structural refinement

# Anion-mixing: homogeneity

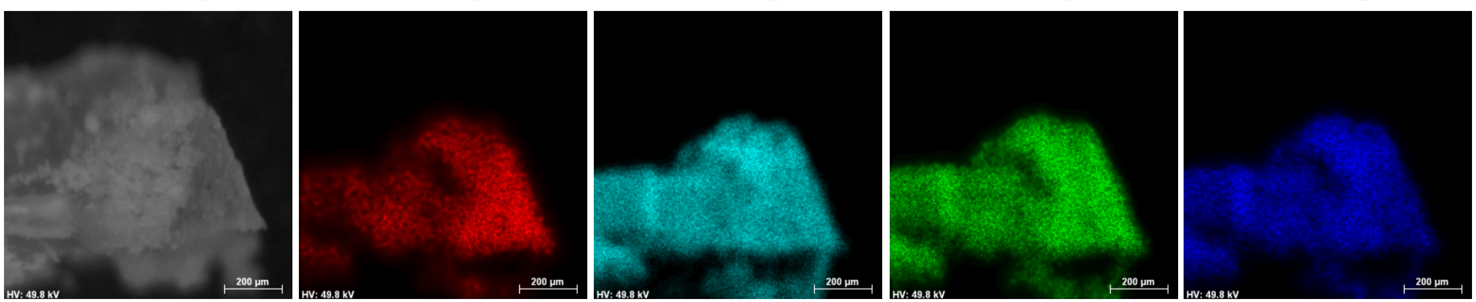
μ-XRF on sample: $Cs_2LiLaCl_3Br_3$




Rough Quant Results

| Element | AN | Net | norm. C. [wt.%] | Atom C. [at.%] |
|---|---|---|---|---|
| Chlorine | 17 | 125552 | 7.72 | 21.66 |
| Bromine | 35 | 686612 | 20.48 | 25.47 |
| Cesium | 55 | 326456 | 45.98 | 34.39 |
| Lanthanum | 57 | 212156 | 25.81 | 18.47 |
| | | Total | 100.00 | 100.00 |

Video Map Cl Map Br Map La Map Cs Map




Sample was selected from the most transparent section of the single crystal.

- μ-XRF analysis indicates the chemical species are uniformly distributed.

# Anion-mixing: structure

**$Cs_2LiLaCl_3Br_3$:**
Single crystal lattice parameter: a = 10.987 Å
Predicted Br in formula from Vegard's law:
$Cs_2LiLaCl_{3.1}Br_{2.9}$

XRF analysis for chemical formula
$Cs_{1.9}LiLaCl_{4.6}Br_{1.4}$ Br normalized to La (underestimates Br)
$Cs_2LiLaCl_{2.8}Br_{3.2}$ Cl/Br intensity ratio (~matches Vegard's law prediction)

| Atom | x | y | z | Occ | $B_{iso}$ (Å$^2$) |
|---|---|---|---|---|---|
| Cs | ¼ | ¼ | ¼ | 1 | 1.8 |
| Li | ½ | ½ | ½ | 1 | **4.7** |
| La | 0 | 0 | 0 | 1 | 0.88 |
| Cl | 0.2583(4) | 0 | 0 | 0.5 | 2.2 |
| Br | 0.2583(4) | 0 | 0 | 0.5 | 2.2 |

Refined formula : $Cs_2LiLaCl_3Br_3$
Space group: Fm3m (225)
a = 10.987(3) Å
vol = 1326.4 Å$^3$
MW = 757.75 x 4 = 3031.0 g/mol
$\rho_x$ = 3.794 Mg/m$^3$
temp: -80°C

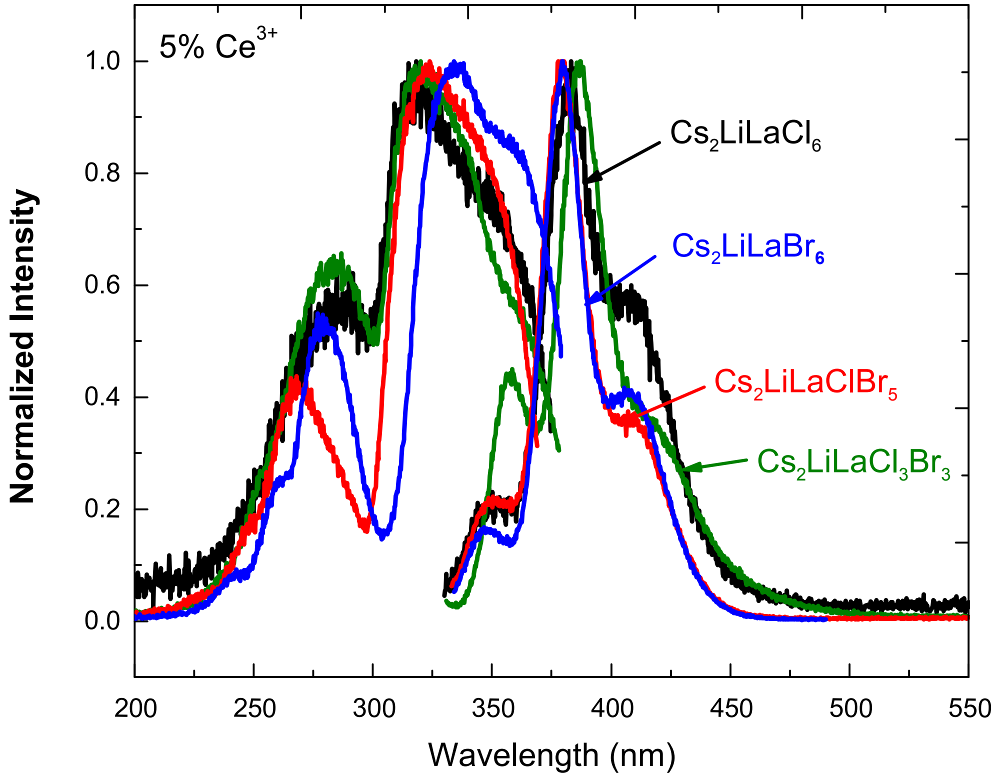
Elpasolite bond distances:
Cs-Cl/Br: 3.886 Å
Li-Cl/Br: 2.656 Å
La-Cl/Br: 2.838 Å
**Overall $R_p$ = 5.08%**

Note the enlarged Li $B_{iso}$ value. For this Br rich composition. This Li displacement parameter may be correlated with the uncertainty of a Li-Br vs. Li-Cl bond.

- The $Cs_2LiLaCl_3Br_3$ sample shows good agreement structurally (lattice parameter) and chemically (XRF) for the nominal composition ($Cl_3Br_3$).

# Anion mixing: PL

The effect of anion mixing on photoluminescence: $Cs_2LiLaCl_6$- $Cs_2LiLaBr_6$ solid solution

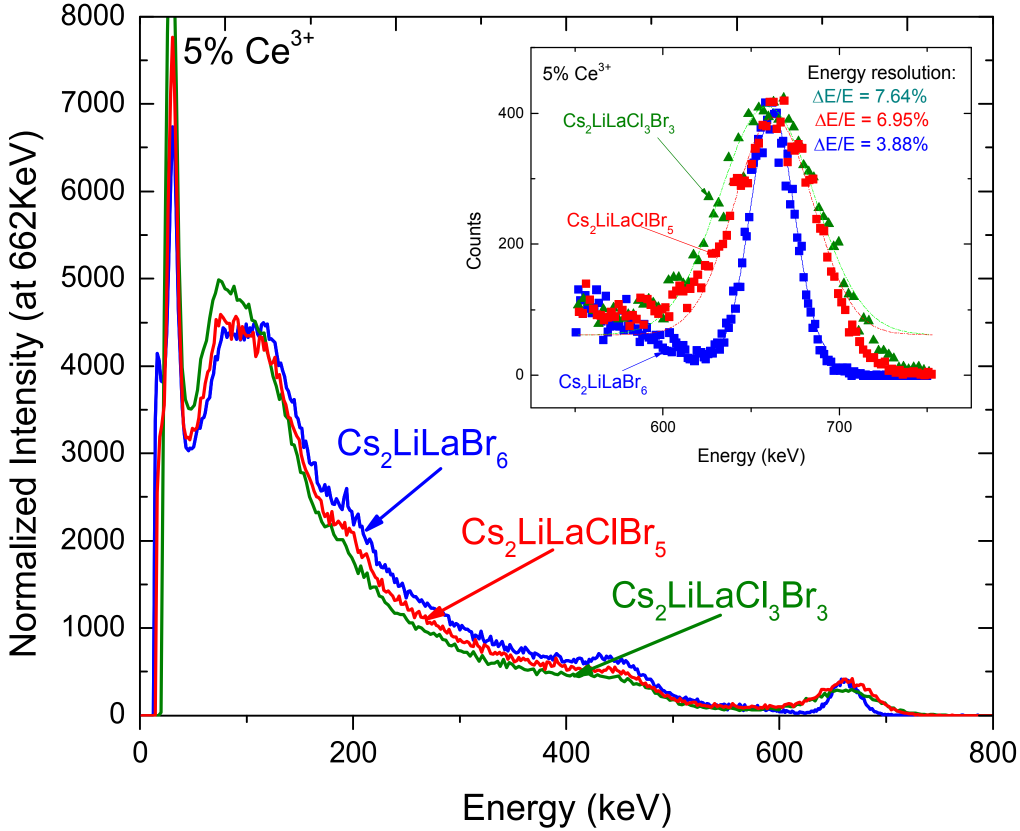



The effect of anion mixing on photoluminescence

- The mix of $Cl^-$ and $Br^-$ in CLLB lattice did not produce the expected broadening of emission spectrum.
- Optical quantum yield:
  - $Cs_2LiLaBr_6$: 63.4%
  - $Cs_2LiLaClBr_5$:49.74%
  - $Cs_2LiLaCl_3Br_3$: 43.25%
  - $Cs_2LiLaCl_6$: 54%

# Anion mixing: luminosity

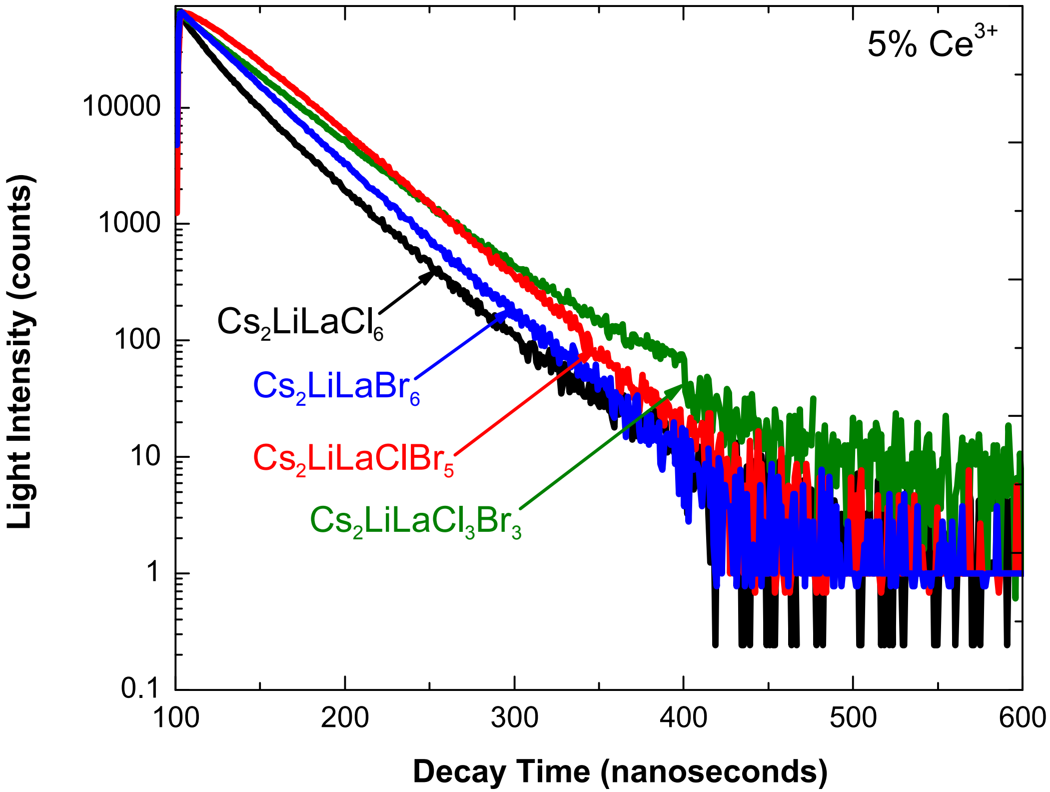
The effect of anion mixing on luminosity and energy resolution




- Relative light yield at 662 keV:
  - $Cs_2LiLaBr_6$: 100.0%
  - $Cs_2LiLaClBr_5$: 79.6%
  - $Cs_2LiLaCl_3Br_3$: 56.1%
- Light yield and energy resolution decease when more $Cl^-$ substitutes the $Br^-$ in the CLLB lattice

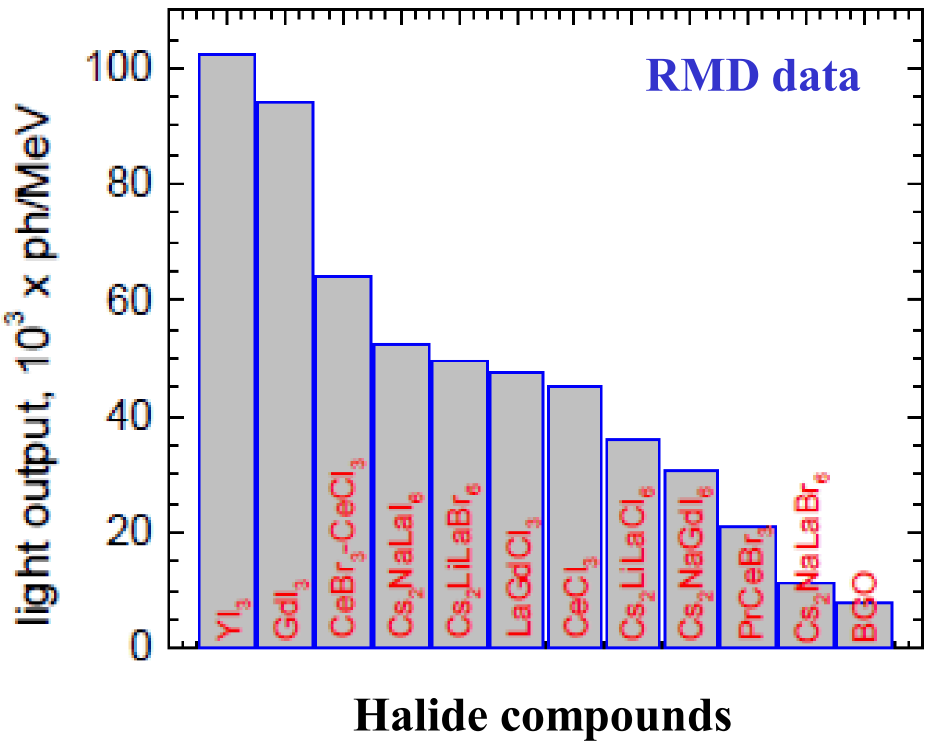
# Anion mixing: decay time

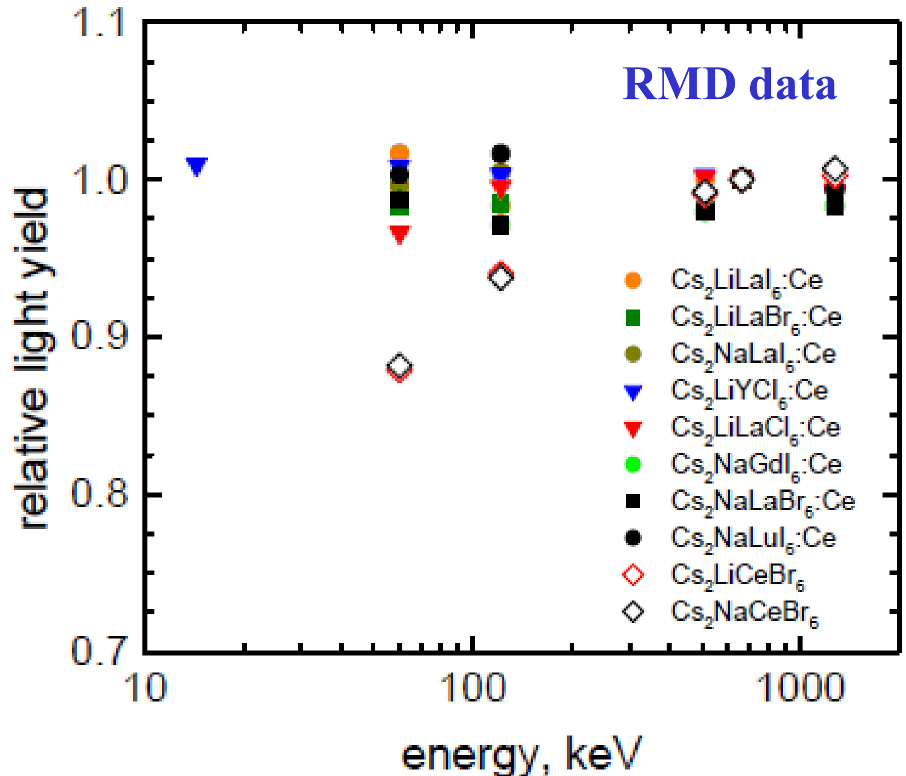
The effect of anion mixing on decay behavior




- The anion mixing increases the lifetime of CLLB and CLLC scintillators.

# Motivation for FY 14




- Higher Z anion increases light yield in Ce(III) activated halides through: 1.) reduced bandgap, 2.) local strain enhanced emission probability
- Elpasolite halides have good luminosity and excellent proportionality

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*Strong motivation to optimize elpasolite iodide compositions: $A_2BB'I_6$*

# Elpasolite Scintillators



**Interaction with the user community, and technology transfer opportunities**

Work for others:

1. Radiation Monitoring Devices, Watertown MA Develop CLYC polycrystalline ceramic (Gary Baldoni), and single crystals (Josh Tower),
2. CapeSym, Inc., Natick MA Develop alloy strengthening of SrI2 (SBIR Phase I award), and purification of CLYC and SrI (SBIR Phase II proposal)

**Technical challenges**

- Cubic polymorphs (local property variations)
- Phase impurities, especially for Li compounds (light scattering)
- Decomposition, especially for iodides

**Future work for the remainder of the project**

- Complete EIM data base
- Perform Monte Carlo simulations of alloy short range ordering for solid solutions
- Investigate anionic substituents for alloy optimization
- Focus on host stabilization and luminosity of CLLB and iodides with lowest distortion
- Explore ceramic scintillator using best selected system

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# Acknowledgement

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Note: (1) Hiring an undergraduate Nuclear Engineering student from UNM (Marlene Bencomo)

P. Yang, X. Zhou, H. Deng, M. A. Rodriguez, P. L. Feng, E. V. Van Loef, K. S. Shah and F. P. Doty, "Crystal Growth and Scintillation Properties of $Cs_2NaGdBr_6:Ce^{3+}$", IEEE Transactions on Nuclear Science, 60(2), 1-6, (2013).

# Anion- mixing

GE- Patent suggests anion mixing could enhance light yield.

US Patent No.: 7368719 (May 6, 2008)