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Crystal Growth and Scintillation Properties of $Cs_2NaGdBr_6:Ce^{3+}$

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Introduction:

Single crystals of $Cs_2NaGdBr_6$ with different Ce^{+3} activator concentrations were grown by a two-zone Bridgman method. This new compound belongs to a large elpasolite halide (A_2BLnX_6) family. Many of these compounds, including Cs_2LiYCl_6 and $Cs_2LiLaBr_6$, have shown high luminosity, good energy resolution and excellent proportionality in comparison to traditional scintillators such as CsI and NaI; therefore, they are particularly attractive for gamma-ray spectroscopy applications. Because the trivalent gadolinium ion has only a few 4f energy levels with large energy gaps between sublevels (Fig. 1), it is expected that after excitation gadolinium based compounds should have less nonradiative interactions and be more suitable as host materials for Ce^{+3} activators. This study investigated the scintillator properties of $Cs_2NaGdBr_6:Ce^{+3}$ crystals as a new material for radiation detection. Special focus has been placed on the effects of activator concentration (0 to 7.5 atom.%) and stoichiometry of cesium in the compound on the photoluminescence responses. Results of structural refinement, photoluminescence, radioluminescence, lifetime and proportionality measurements for this new compound will be reported.

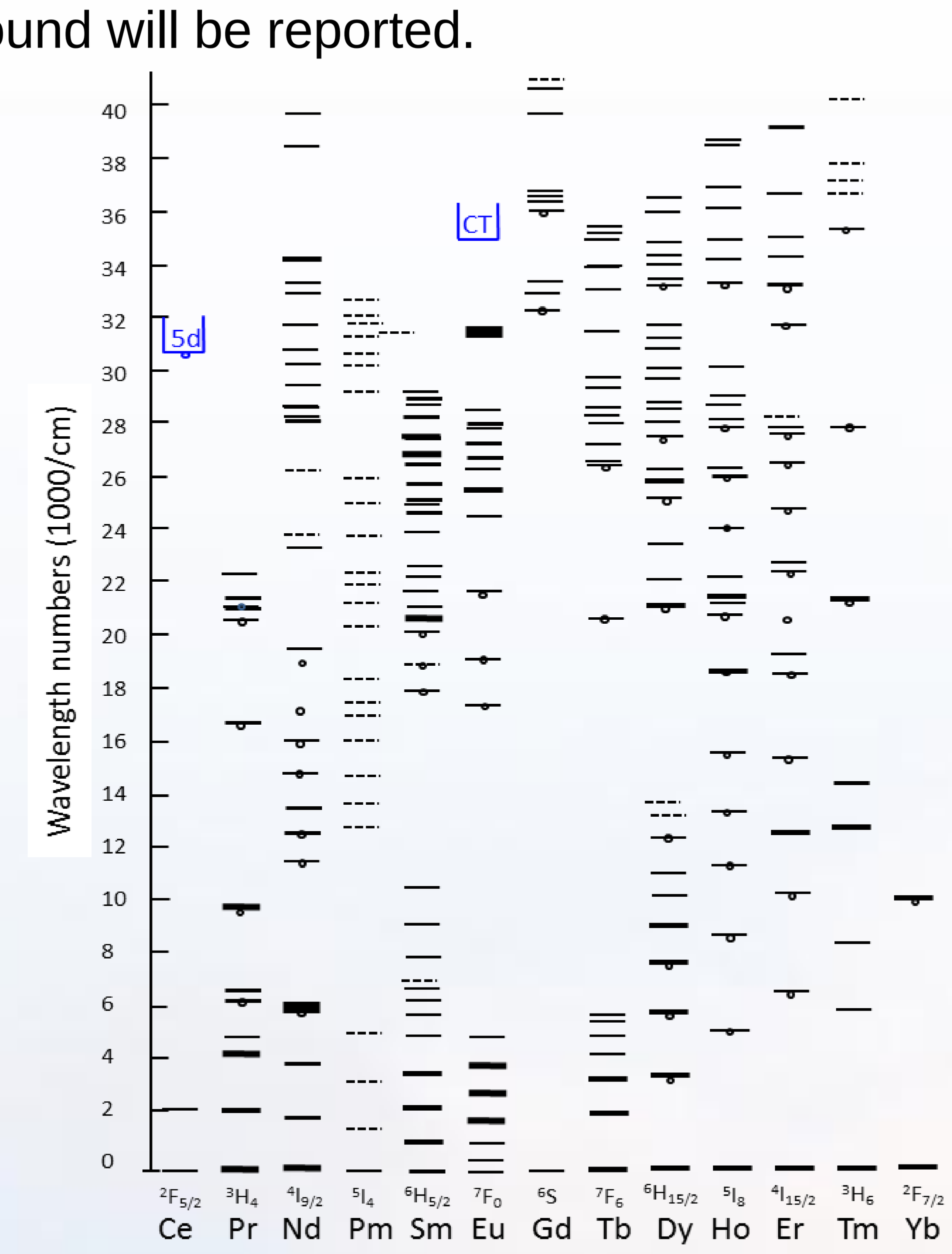


Fig. 1 Spectra and energy levels of rare earth ions in crystals

Elpasolite Halide Compounds (A_2BLnX_6) :

- Structural model:
- – A,B : Alkali metals (Li-Cs) = 5
- – Ln: Rare earth (La-Yb + Sc-Lu) =17
- – X: Halogen group (F-I) = 4
- 5 x 4 x 4 x 17 = 1360 different compounds
- Cubic compounds enable the manufacturing of transparent ceramics and alleviate manufacturing challenges.

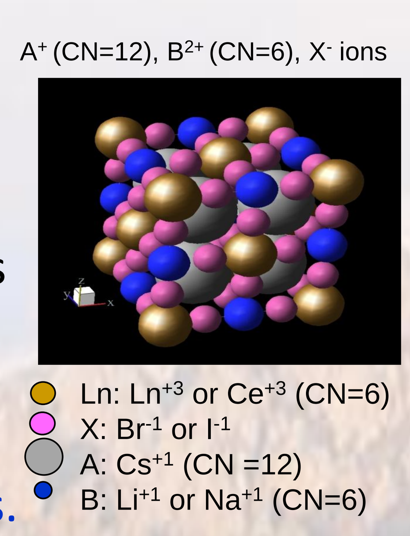


Fig. 2 Structural model of elpasolite halides.

Structure Prediction and Analysis :

- Embedded-ion Method – cubic elpasolite (Fm-3m)
- Shannon tolerance factor – 0.9239
- Bond valence potential tolerance factor - 0.9386
- SPuDs: G' = 0.2564 > 0.2 - deviated from cubic
- Density: 3.785 g/cm^3, Average Z = 39.5
- All Ce^{3+} activated $Cs_2NaGd_{1-x}Ce_xBr_6$ crystals are cubic elpasolites

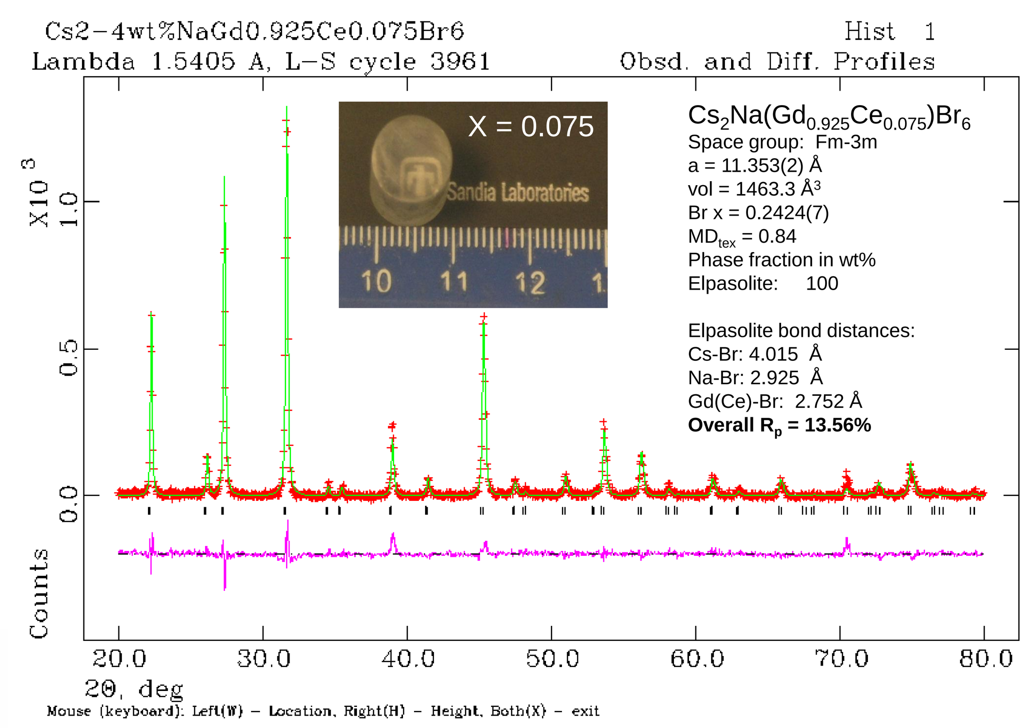


Fig. 3 X-ray structure refinement for $Cs_2NaGdBr_6:Ce^{3+}$.

Thermal Properties and Single Crystal Growth:

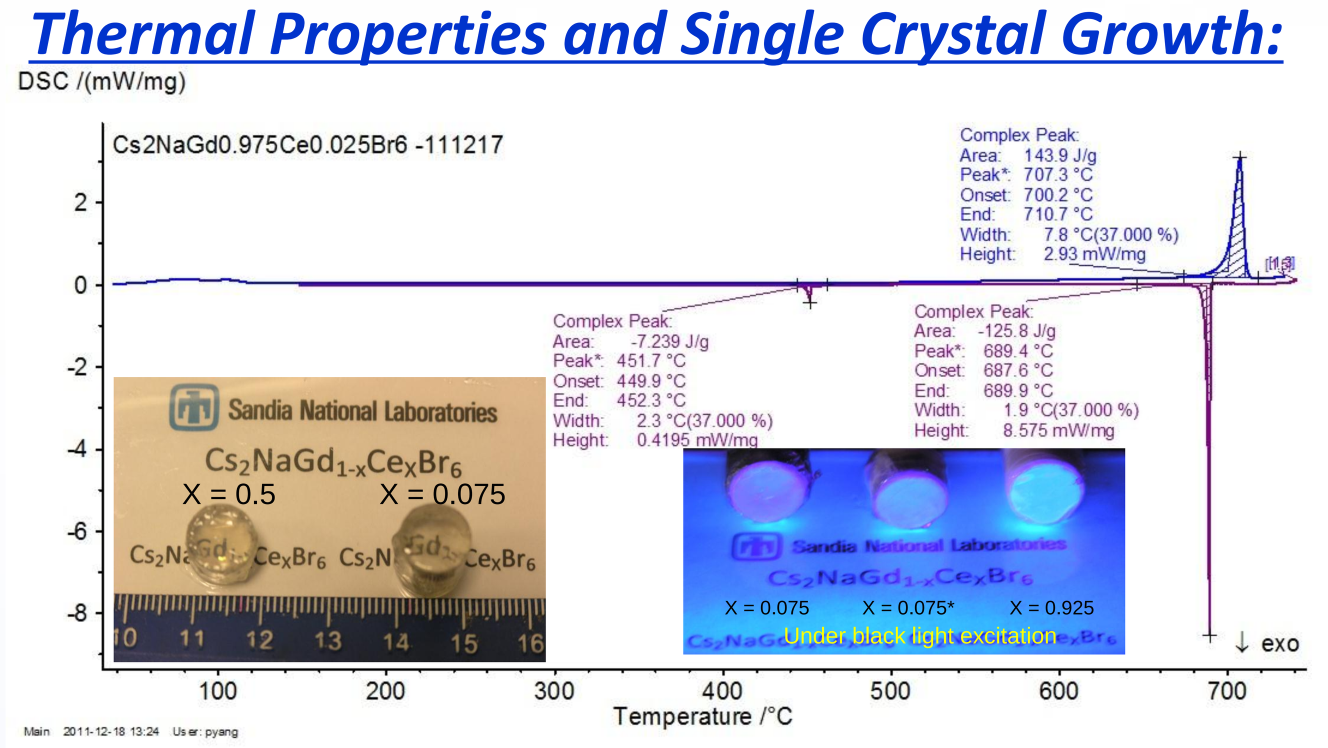
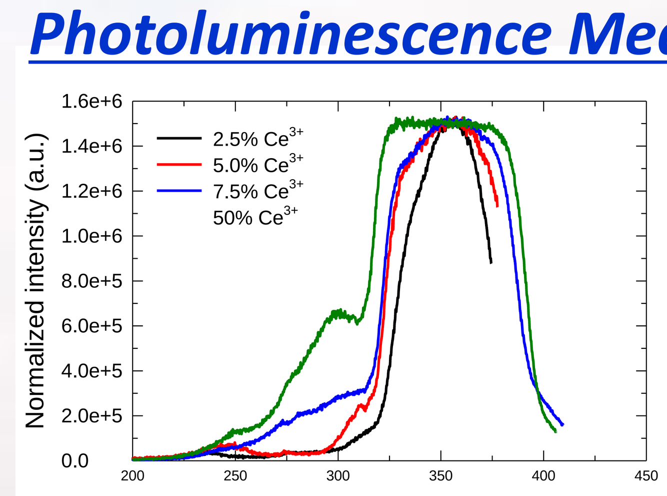
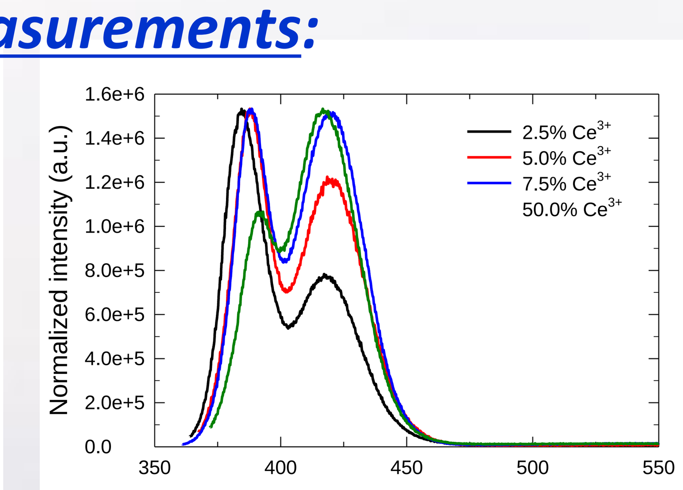


Fig. 4 DSC results and single crystals of $Cs_2NaGdBr_6:Ce^{3+}$.

- Single phase, optically transparent single crystals of $Cs_2NaGd_{1-x}Ce_xBr_6$ have been successfully grown by a Bridgman method (x = 0, 0.025, 0.5, 0.075, 0.5 0.925, 1).
- Enthalpy change and melting point of these Ce^{3+} activated $Cs_2NaGd_{1-x}Ce_xBr_6$ were measured by DSC.

Photoluminescence Measurements:





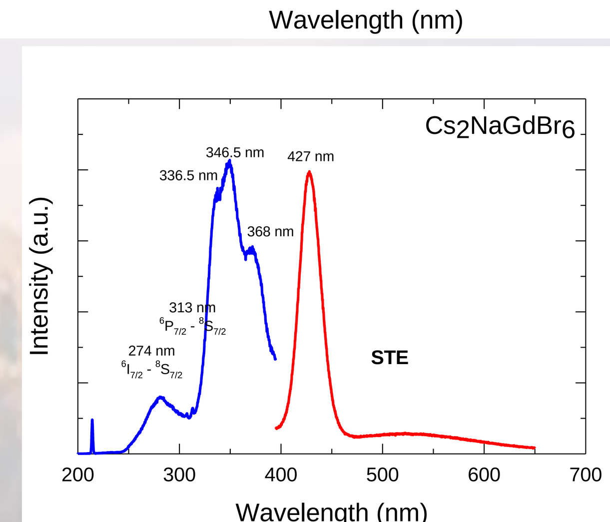
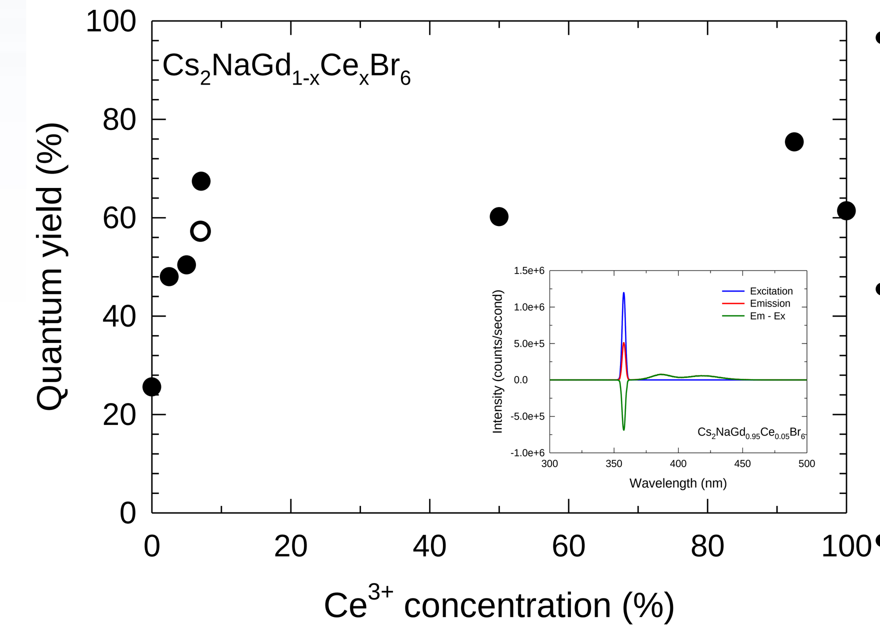


Fig.5 Photoluminescence responses for $Cs_2NaGdBr_6:Ce^{3+}$.

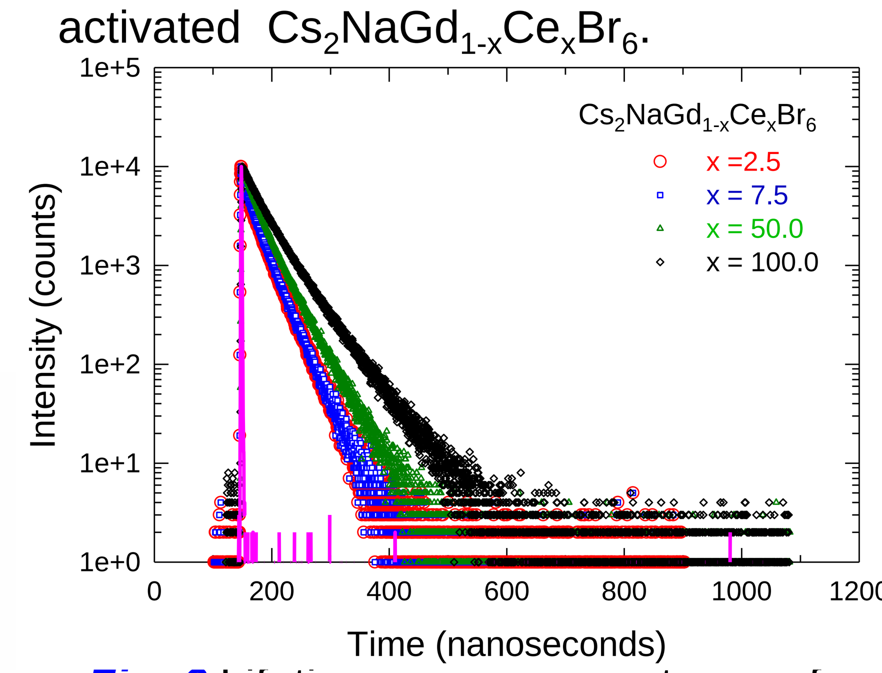
- Intrinsic compound shows STE excitation and emission.
- A double peaked emission band is observed, which corresponds to the 5d-to-4f cerium emission.
- As Ce^{3+} increases, the 5d-to-$4f^1\,{}^2F_{7/2}$ intensity increases at the expense of 5d-to-$4f^1\,{}^2F_{5/2}$ emission.

Optical Quantum Yields and lifetime:



- Optical quantum yield increases as Ce^{3+} concentration increases.
- Non-stoichiometric compound (unfilled circle) has a lower quantum yield.
- Light yield starts to level of ~ 0.75% Ce^{3+}.

Fig. 5 Optical quantum yield for cerium activated $Cs_2NaGd_{1-x}Ce_xBr_6$.

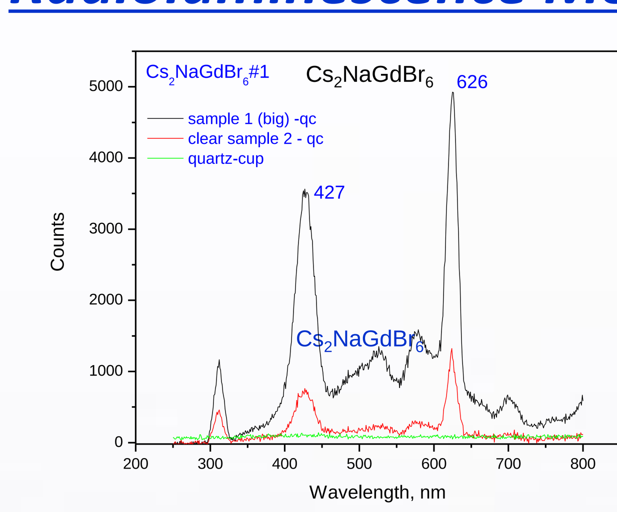


Ce3+ conc. (At.%)	Lifetime (ns) Fast	Intermediate	Slow
2.5	32.5 (33%)	30.8 (83.7)	
5.0	19.9 (74.3%)	38.3% (25.7%)	
7.5	35.2 (98.6%)		266.6 (1.4%)
50.0	18.17 (40.7%)	38.55 (59.0%)	606.9 (0.3%)
92.5	15.7 (7.4%)	39.5 (31.9%)	55.2 (60.7%)
100.0	24.7 (45.9%)	51.8 (54.1%)	

- Lifetime decreases as Ce^{3+} concentration increases.

Fig. 6 Lifetime measurements as a function of Ce^{3+} concentration in $Cs_2NaGdBr_6$.

Radioluminescence Measurements:



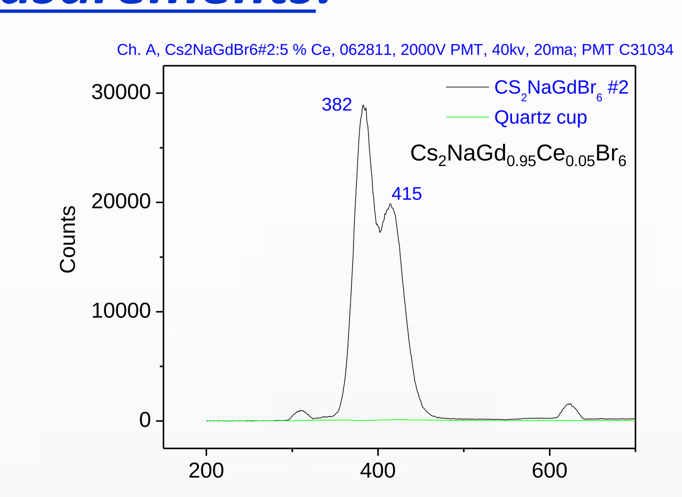
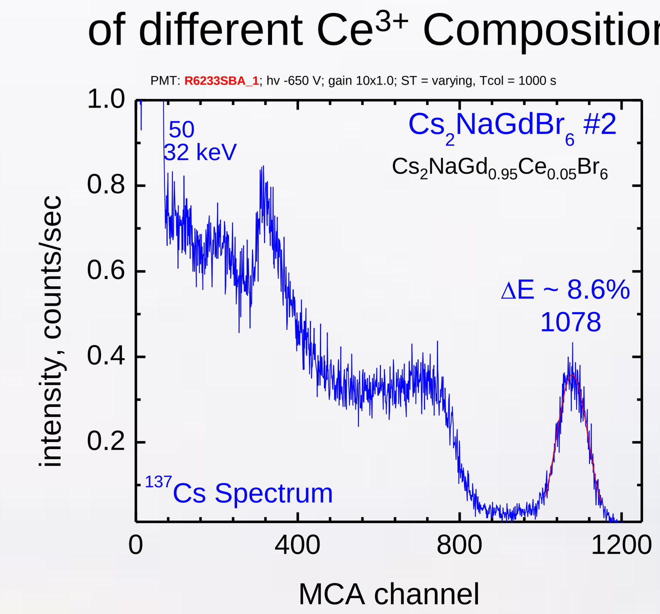


Fig. 7 X-ray induced emission spectra for $Cs_2NaGdBr_6$ crystals of different Ce^{3+} Compositions.



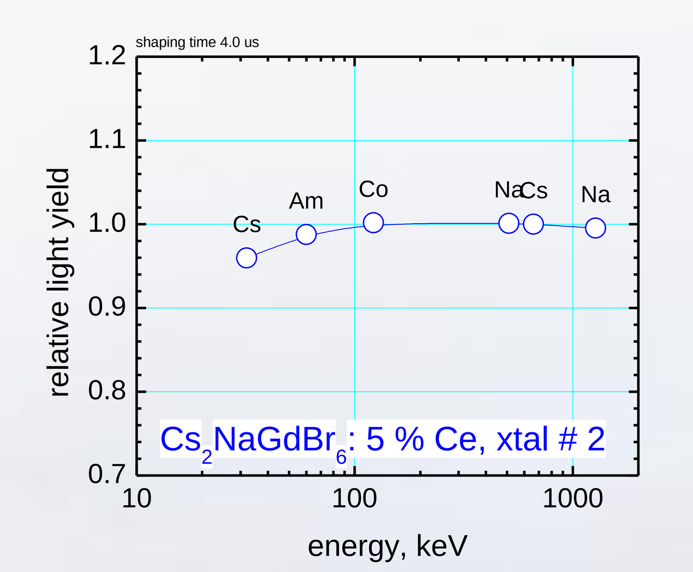


Fig. 8 Pulse height spectrum and non-proportionality curve for $Cs_2NaGd_{0.95}Ce_{0.05}Br_6$ crystal.

- Enhance crystal quality might help to increase the energy resolution.

Summary:

- A series of cubic cerium activated $Cs_2NaGdBr_6$:Ce single crystals were grown and characterized for their scintillation performance.
- Cerium concentration plays an important role for optical emission, quantum yield, and lifetime responses.
- Stoichiometric crystals perform better than the Cs deficiency crystals.

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