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VACUUM DEHYDRATION OF LANTHANIDE BROMIDE HYDRATES

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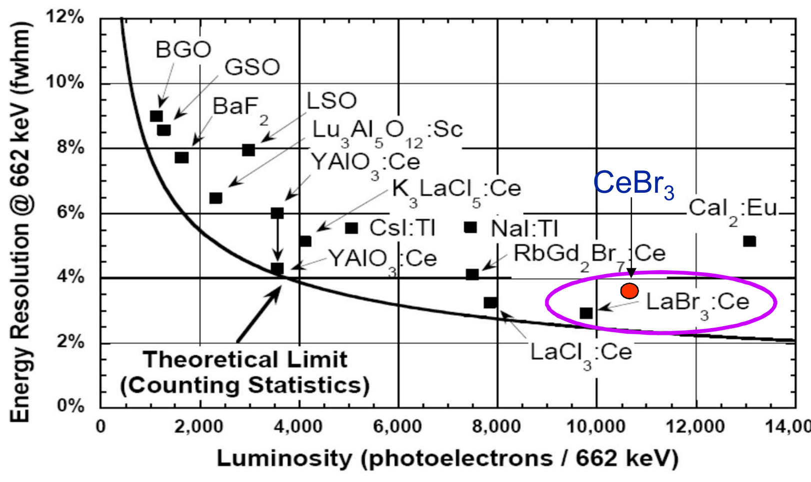
Motivation:



Lanthanide bromides ($LaBr_3$:Ce* and $CeBr_3$) scintillators show superior performance for γ-ray detection over other advanced materials.

Objective:

(A) To develop an effective dehydration method to produce anhydrous lanthanum-cerium bromide powders

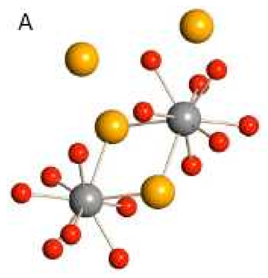
(B) To understand the thermal events and structural evaluation during the dehydration process

Approach:

(A) Using a scalable chemical synthesis route to fabricate low-cost hydrates

$$Ln^o + HX(aq) = LnX_3{\bullet}nH_2O + H_2(g)$$

(B) Applying vacuum to assist the dehydration process



$\{[La(\mu\text{-}Br)(H_2O)_7][Br]_2\}_2$

Characterization:

(1) Thermal analysis : TGA and DSC (Netzsch STA449C)

- Identify thermal events
- Measure the weight loss and determine the amount of bound water in hydrates

(2) Be-dome X-ray diffraction (XRD)

- Identify phases and structures
- Determine structural evolution

Vacuum Dehydration

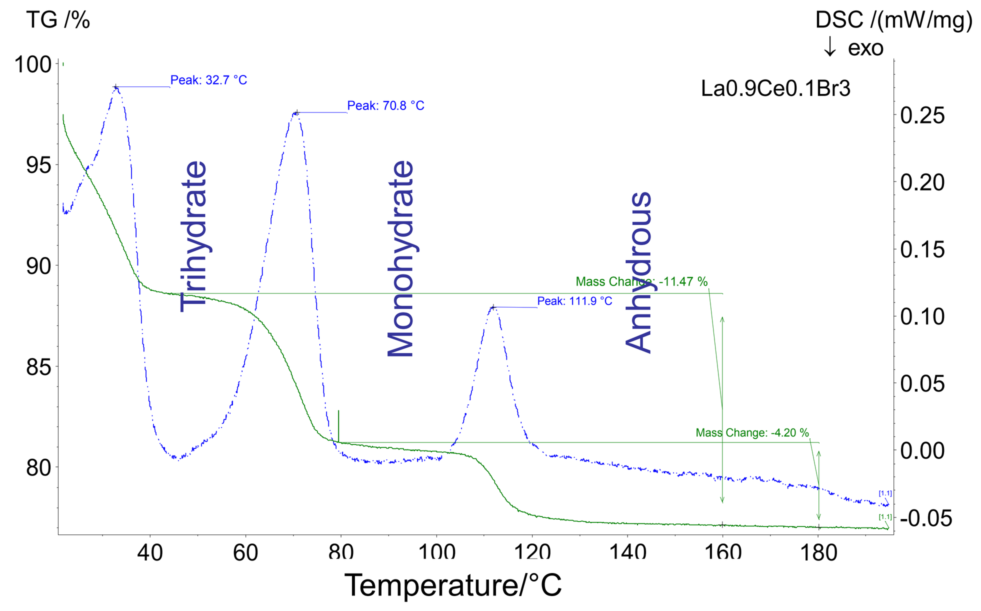


Fig. 1. The vacuum dehydration behavior of lanthanide bromide hydrate.

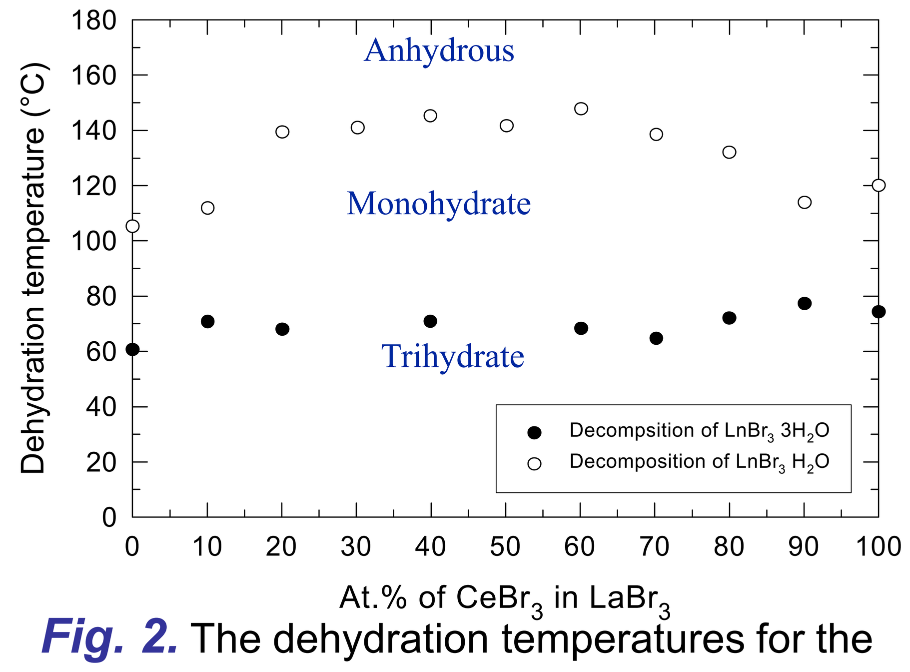


Fig. 2. The dehydration temperatures for the $(La_{1-x}Ce_x)Br_3$ solid solution.

- The dehydration process involves multiple steps and several intermediate hydrates.
- The application of vacuum lowers the dehydration temperature.

Structural Evolution and Solid Solution Formation

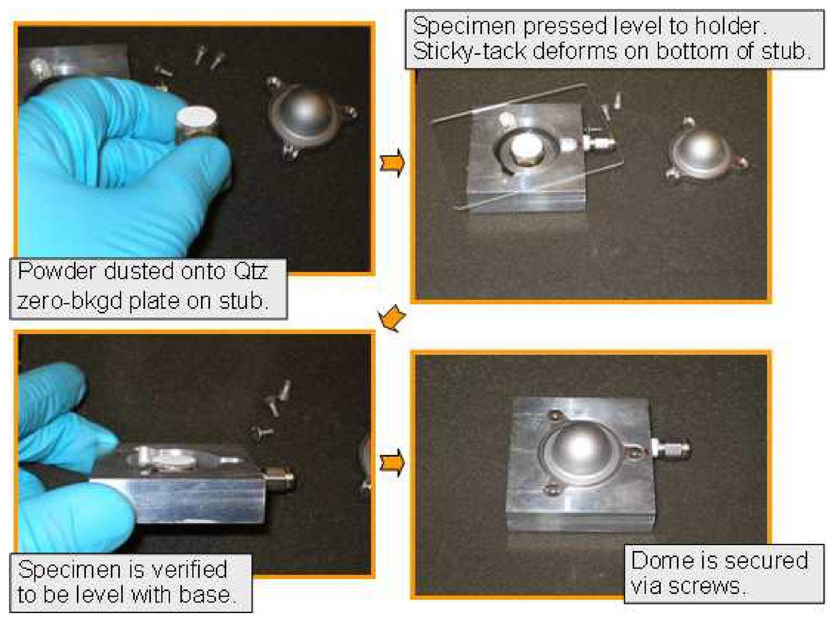


Fig. 3. Beryllium dome XRD analysis for hygroscopic lanthanum halides.

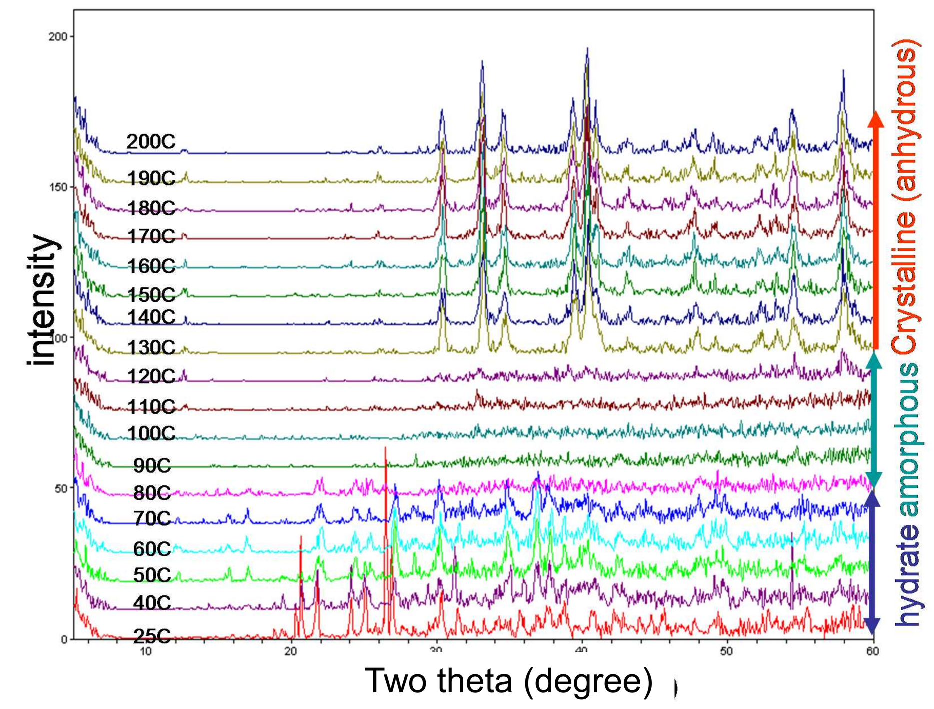


Fig. 4. Structural evolution during the vacuum dehydration process.

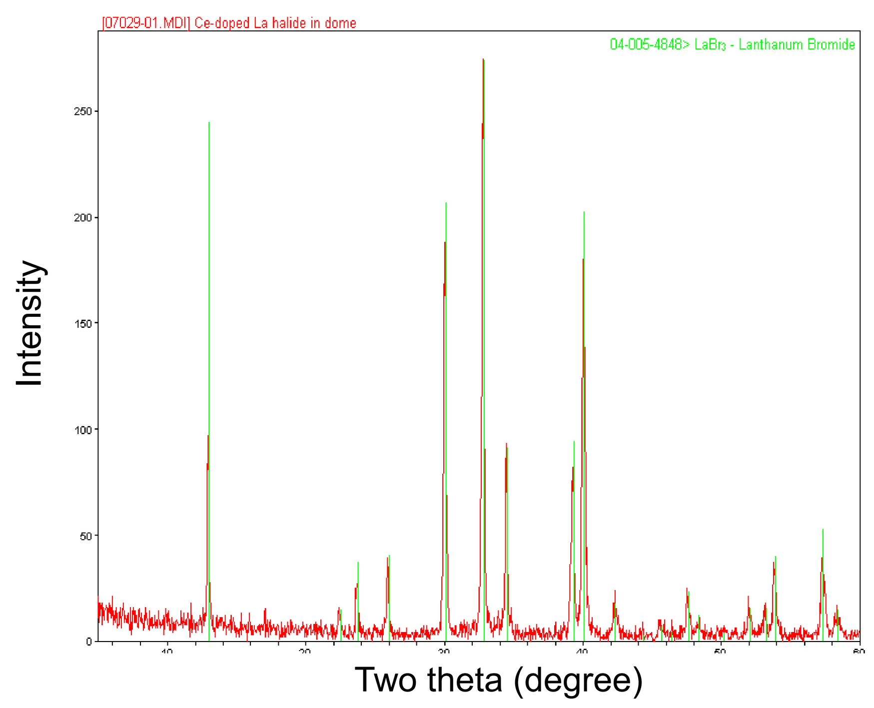


Fig. 5. A complete solid solution formed after a low temperature dehydration process.

- Dehydration goes through three separate phases (a) crystalline hydrates ($LnBr_3$ nH_2O, n≥3), (b) amorphous (LnBr3 *n*H2O, n<3), and (c) crystalline anhydrous $LnBr_3$ as temperature increases.
- A complete solid solution forms between $LaBr_3$ and $CeBr_3$ below 200°C.

Processing Challenges

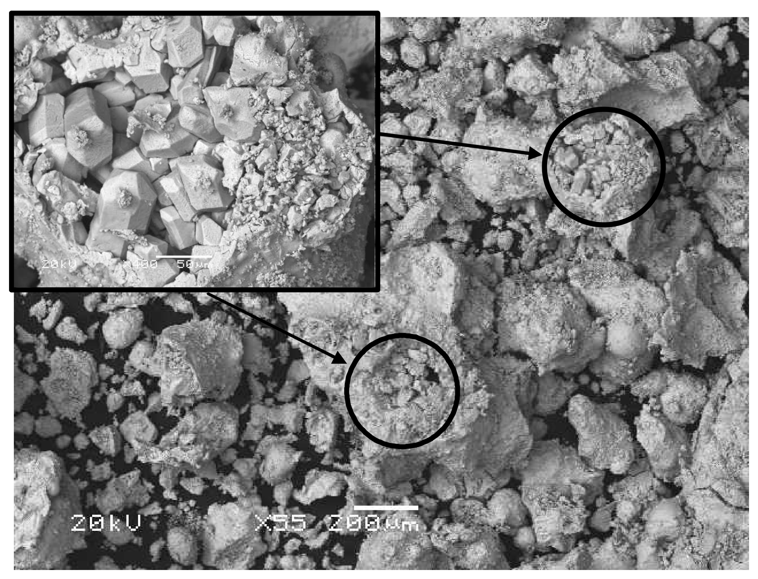


Fig. 6. SEM microphotographs show that dehydration starts from the outside. Partially dehydrated lanthanum bromide heptahydrate crystals can be found in side of powder agglomerate.

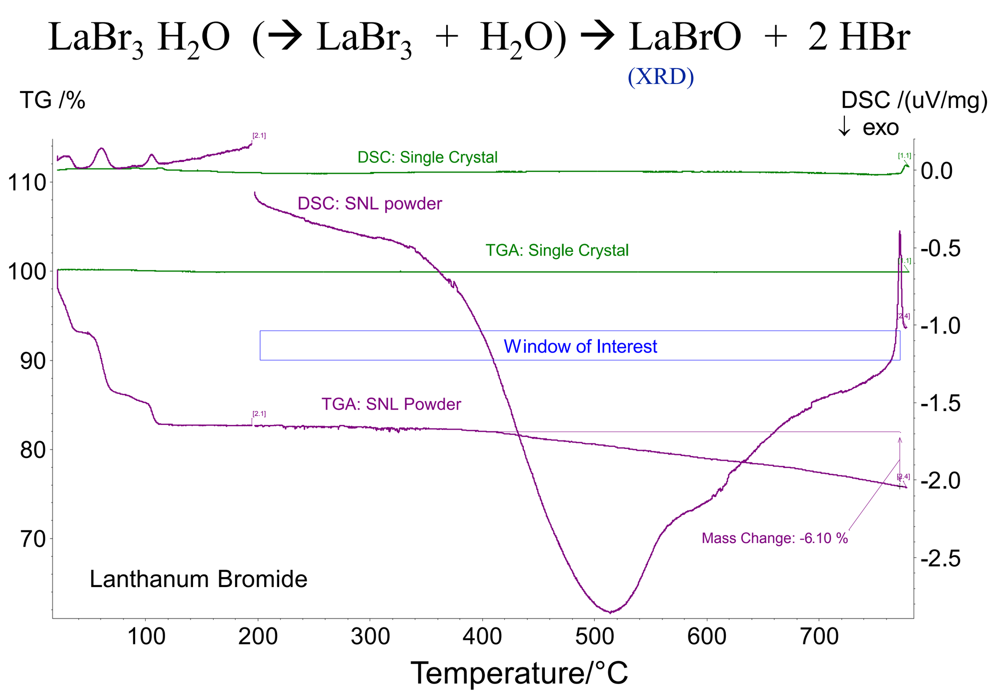


Fig. 7. A comparison of the thermal behavior of a single crystal and vacuum dehydrated lanthanum bromide powder.

- Poor heat transfer during vacuum dehydration could leave residual amorphous hydrates.
- Incomplete dehydration can lead the formation of oxyhalide at high temperature in an inert atmosphere.

Conclusion:

(1) The application of vacuum lowers the processing temperature, improves the dehydration efficiency, and assists the solid solution formation.
(2) The dehydration involves a reconstructive crystalline-amorphous-crystalline phase change as bonded water is progressively removed.
(3) Incomplete dehydration can lead to the formation of oxybromide which has been shown to negatively impact scintillation performance.

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