Eu^{2+}-doped Ba_2CsI_5 a new high-performance scintillator

Chemical Technology of Materials

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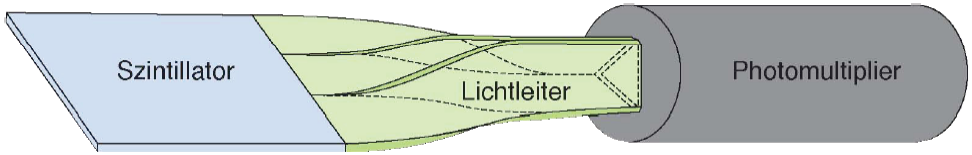
Contents

- What is a scintillator?
- Properties of $Ba_2CsI_5:Eu^{2+}$
- Preparation of iodides
- Preparation of $Ba_2CsI_5:Eu^{2+}$
- Summary

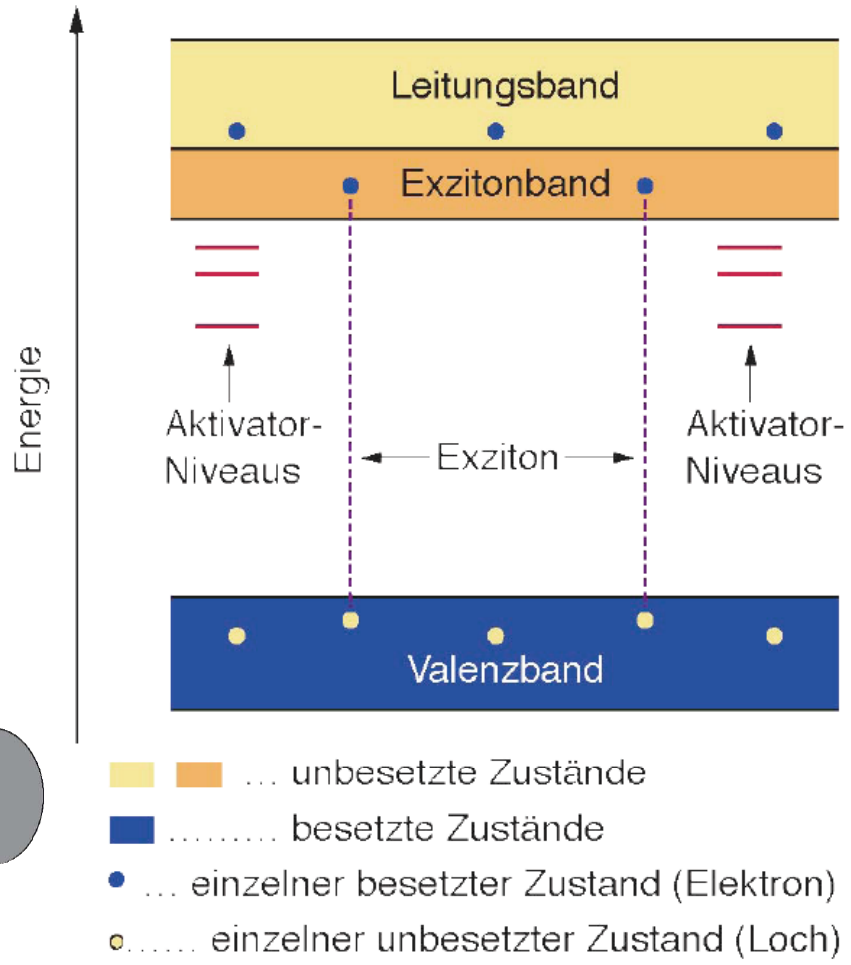
What is a scintillator?

Functional principle

- Generating of electron-hole pairs
- Excitation of luminescent centers
- Returning to the ground state by emitting a photon
- Typical band gaps 5-10 eV



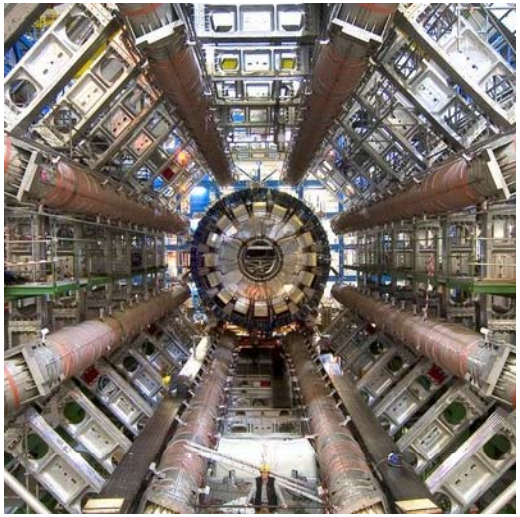
Functional principle of a scintillator



What is a scintillator?

Application fields

Computed tomography scanner (CT).



High-energy physics calorimetry.

Deep drilling.

Body scanner.

Properties of $Ba_2CsI_5:Eu^{2+}$

Structure

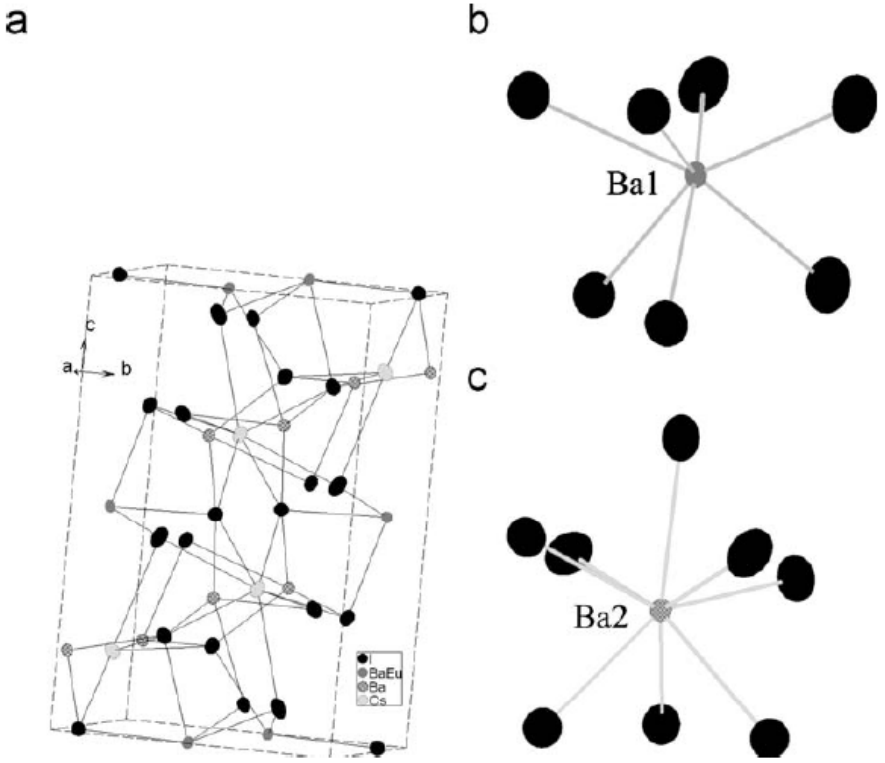
Profile of Ba_2CsI_5

- $NH_4Pb_2Cl_5$ structure
- Monoclinic
- Space group: $P2_1/C$
- Cell parameters:

  a = 1054.1 pm

  b = 925.6 pm

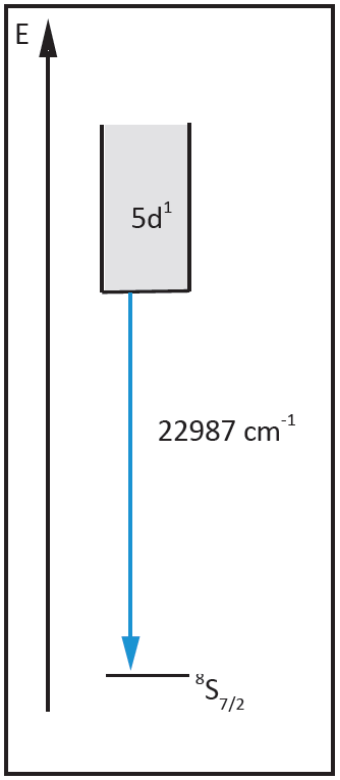
  c = 1463,7 pm



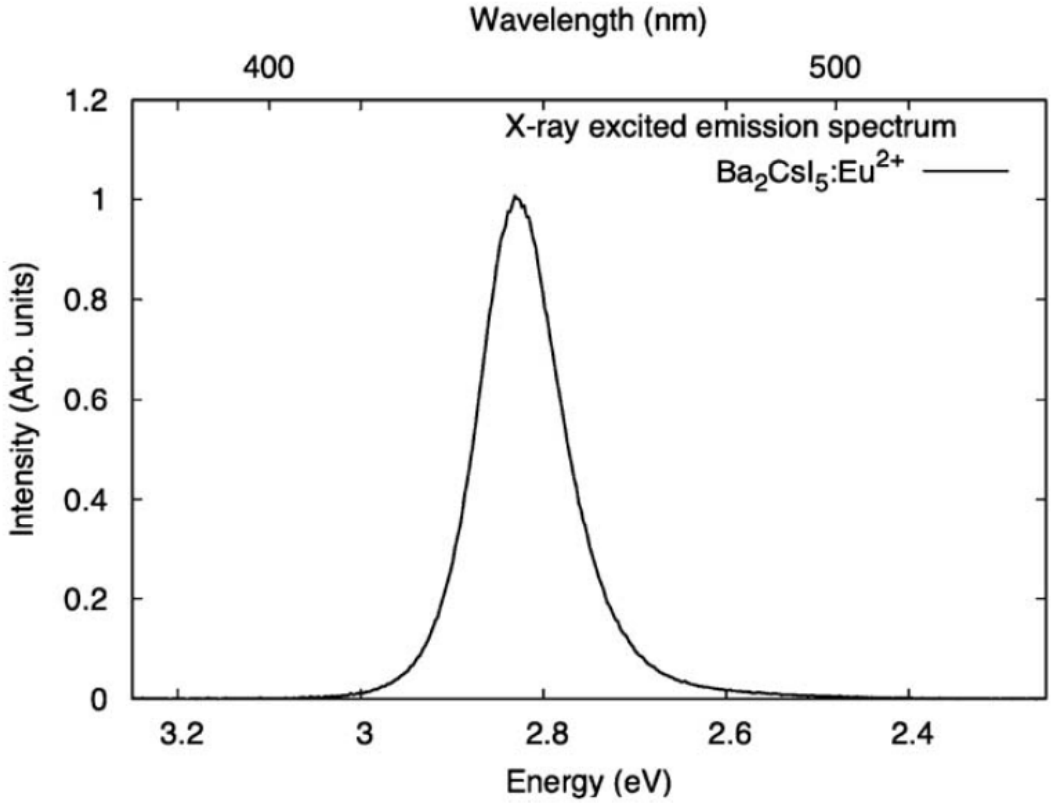
Representation of the$P2_1/C$-type structure (a) containing two Ba sites of different coordination: Ba1, coordinated by 7 I (b) and Ba2 coordinated by 8 I (c).

Properties of $Ba_2CsI_5:Eu^{2+}$

Optical properties



Schematic of emission transition in Eu^{2+} -doped Ba_2CsI_5



Normalized X-ray excited emission spectrum of $Ba_2CsI_5:Eu^{2+}$ at room temperature.

Preparation of iodides

Preparation of barium iodide

$$BaCO_3 + 2\,HI \longrightarrow BaI_2 + H_2O + CO_2$$

or

$$Ba(OH)_2 + 2\,I^- + 2\,H^+ \longrightarrow BaI_2 + H_2O$$

Crystallised barium iodide loses HI when heated in nitrogen, but can be obtained anhydrous by heating it in a dry HI-flow.

Preparation of iodides

Preparation of barium iodide

Reported by E. Duval, G. Zoltobroda, Y. Langlois (1999)

$$Ba_{(THF)} + I\text{-}CH_2\text{-}CH_2\text{-}I_{(THF)} \longrightarrow BaI_2 + CH_2{=}CH_2$$

(- 10 °C / 36 h styring / Ar-atmosphere)

Reported by M. D. Taylor, L. R. Grant (1955)

$$BaH_2 + 2\ NH_4I \xrightarrow{C_6H_5N} BaI_2 + 2\ NH_{3(g)} + H_{2(g)}$$

(150°-160° drying step)

Preparation of iodides

Preparation of Caesium iodide

$$2\ Cs_{(s)} + I_{2(s)} \longrightarrow 2\ CsI_{(s)}$$

or

$$CsOH_{(aq)} + HI_{(aq)} \longrightarrow CsI_{(aq)} + H_2O_{(l)}$$

Removing water from the product is important, but not reported.

It has to be proven how the commercial companies obtain an anhydrous product.

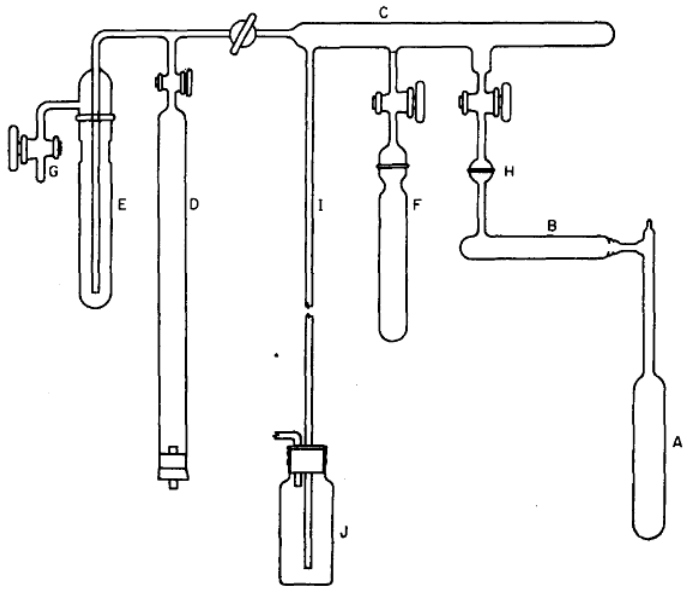
Preparation of iodides

Preparation of Europium iodide

Reported by M. D. Taylor and C. P. Carter (1961)

$$Eu_2O_3 + 6\ HI \longrightarrow 2\ EuI_2 + I_2 + 3\ H_2O$$

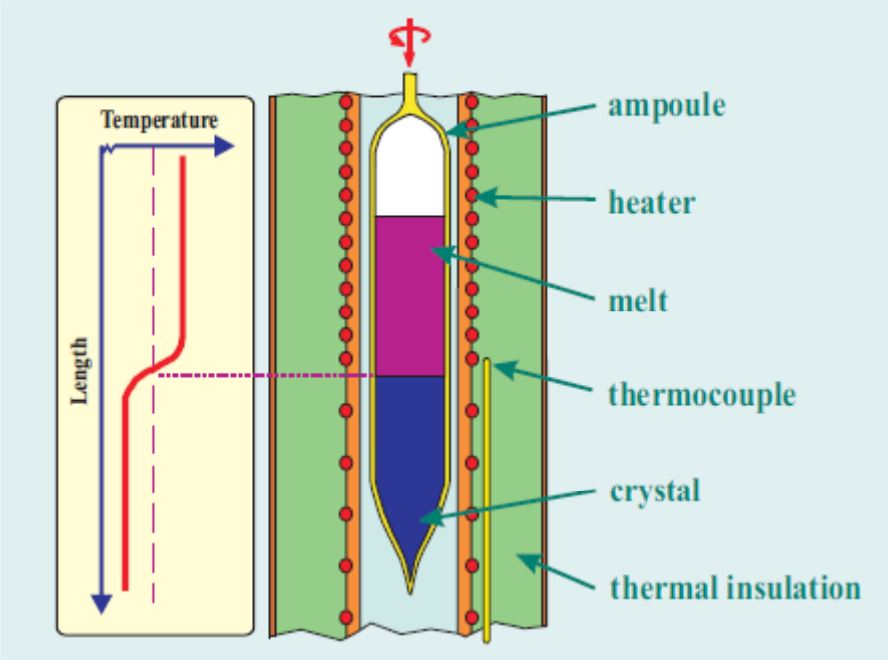
- NH_4I has to be added to prevent hydrolysis of EuI_2
- Evaporate mixture till dryness



Apparatus to remove water and NH_4I. Pyrex reaction vessel (A), sublimation tube (B, vacuum line manifold (C), ball and socket joint, (H), manometer (I), drying tube (D), trap (E), and outlet to the pump (G).

Preparation of $Ba_2CsI_5:Eu^{2+}$

Bridgman-Stockbarger method



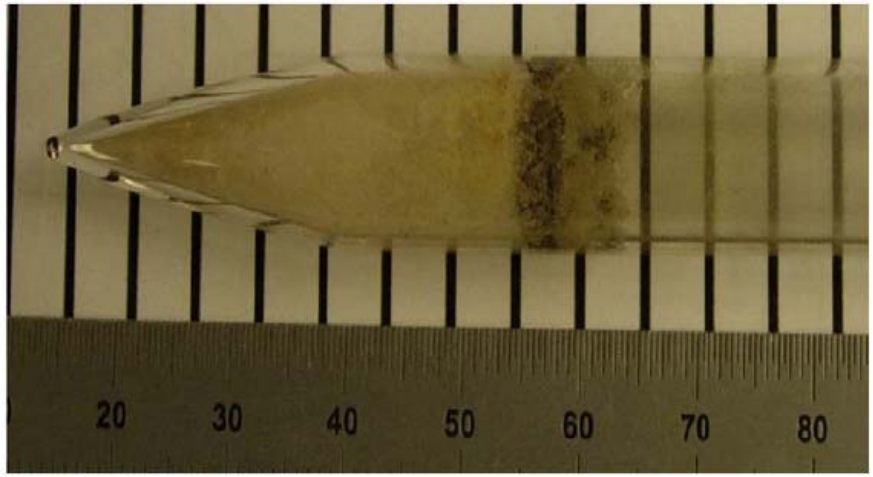
Briggman-Stockbarger technique.

- Melting of starting materials
- Crystal growth by moving the crucible through the furnace

Preparation of $Ba_2CsI_5:Eu^{2+}$

Crystal Growth

- Reported by E.D. Bourret-Courchesne et al.
- BaI_2, CsI, EuI_2 are filled into an evacuated sealed quartz ampule
- T_m of mixture 575 ± 25 °C
- Temperature gradient: 30 °C/cm
- Growth rate: 1 mm/h



A 1 cm in diameter $Ba_2CsI_5:Eu^{2+}$ shown as-grown in a sealed quartz ampoule.

Preparation of $Ba_2CsI_5:Eu^{2+}$

Powder Preparation

- No method for powder Preparation published yet!
- Maybe two processes possible:
  - Open process (HI-atmosphere)
  - Closed process (Quartz-Ampule)
- Estimated reaction temperature: 200-400 ° C

Summary

- Emission maximum at 435 nm (2,85 eV)
- Difficult to obtain anhydrous iodides
- Preparation via Bridgman-Stockbarger method
- Powder preparation has to be tested
- Risk of iodine loss in case of open-system-reactions or due to high temperatures

Quellen

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