Peculiarities of SrI_2(Eu) crystal growth

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History – invention of $SrI_2(Eu)$ scintillator

United States Patent Office

3,373,279

Patented Mar. 12, 1968

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3,373,279

EUROPIUM ACTIVATED STRONTIUM IODIDE SCINTILLATORS

Robert Hofstadter, Stanford, Calif., assignor, by mesne assignments, to Kewanee Oil Company, Bryn Mawr, Pa., a corporation of Delaware

No Drawing. Filed Jan. 29, 1965, Ser. No. 429,141

5 Claims. (Cl. 250—71.5)

ABSTRACT OF THE DISCLOSURE

This invention comprises a scintillation crystal composed of strontium iodide activated by europium. The invention also comprises a radiation detector having a detecting element and a chamber optically coupled to this detecting element, having within the chamber a scintillator consisting of strontium iodide activated with about 10–16,000 parts per million of europium.

TABLE IV.—RELATIVE RESPONSE FROM CESIUM 137 RADIATION

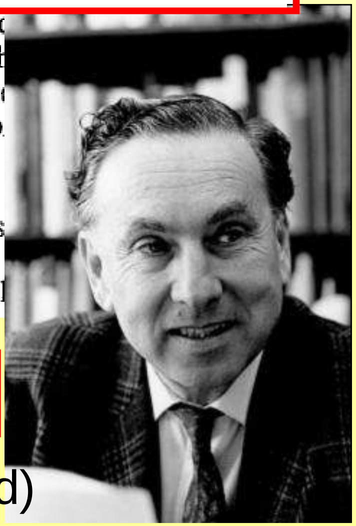
Example:	Percent pulse-height relative to NaI(Tl)
I	37
II	51
III	57
IV	79
V	56
VI	93
VII	88.6

may be nothing more than a portion (not covered by the reflector, should h optical coupling with the mass of th good light transmitting efficiency fro light detector.

Europium when used in amounts parts per million causes an emiss 4300±50 angstroms.

The strontium iodide crystals of t

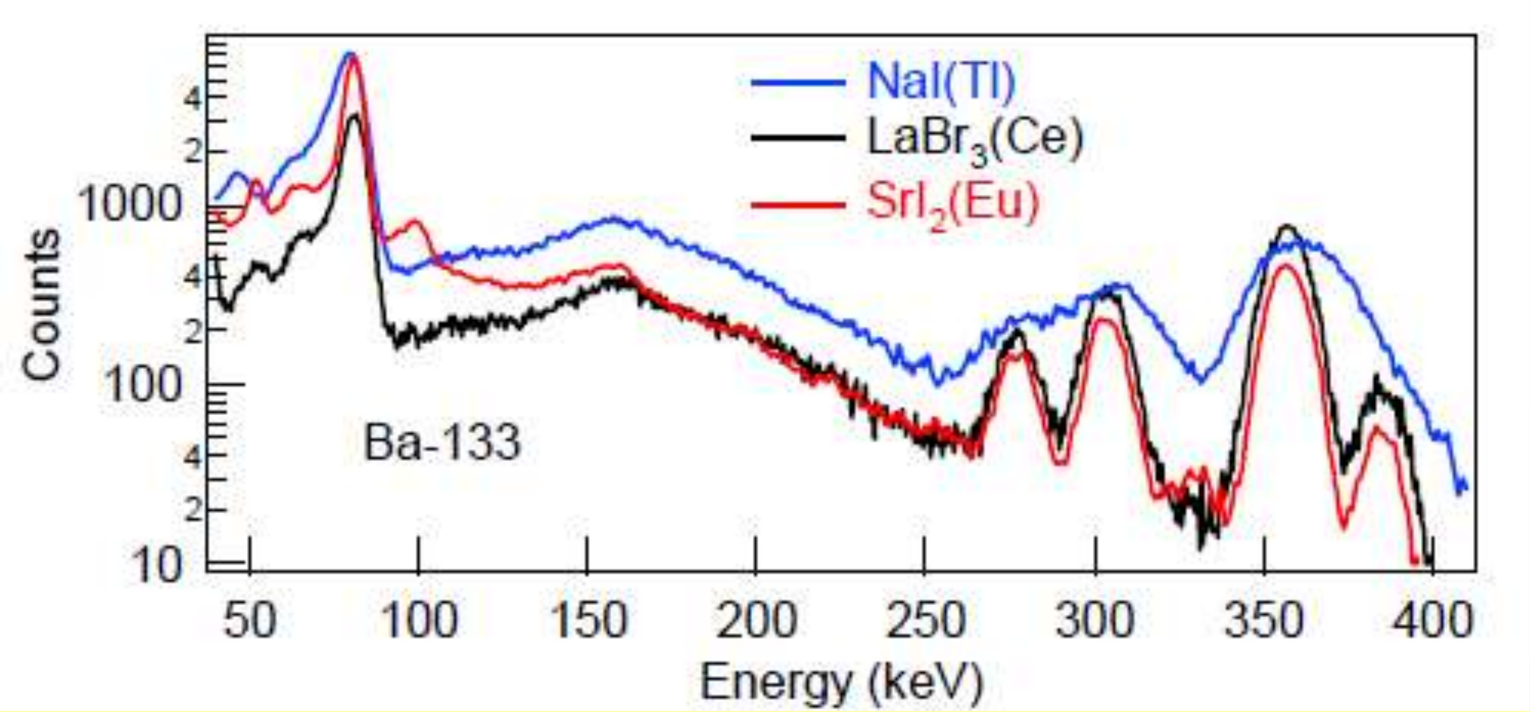
In 1968 scintillation characteristics were worse than for NaI(Tl)



Prof. R.Hofstadter (Stanford)

New sight

Gamma spectra SrI_2:Eu and $LaBr_3$:Ce vs. NaI:Tl *



*** N. Cherepy, at. al., Proc. SPIE, Vol. 7079, 707917, (2008).**

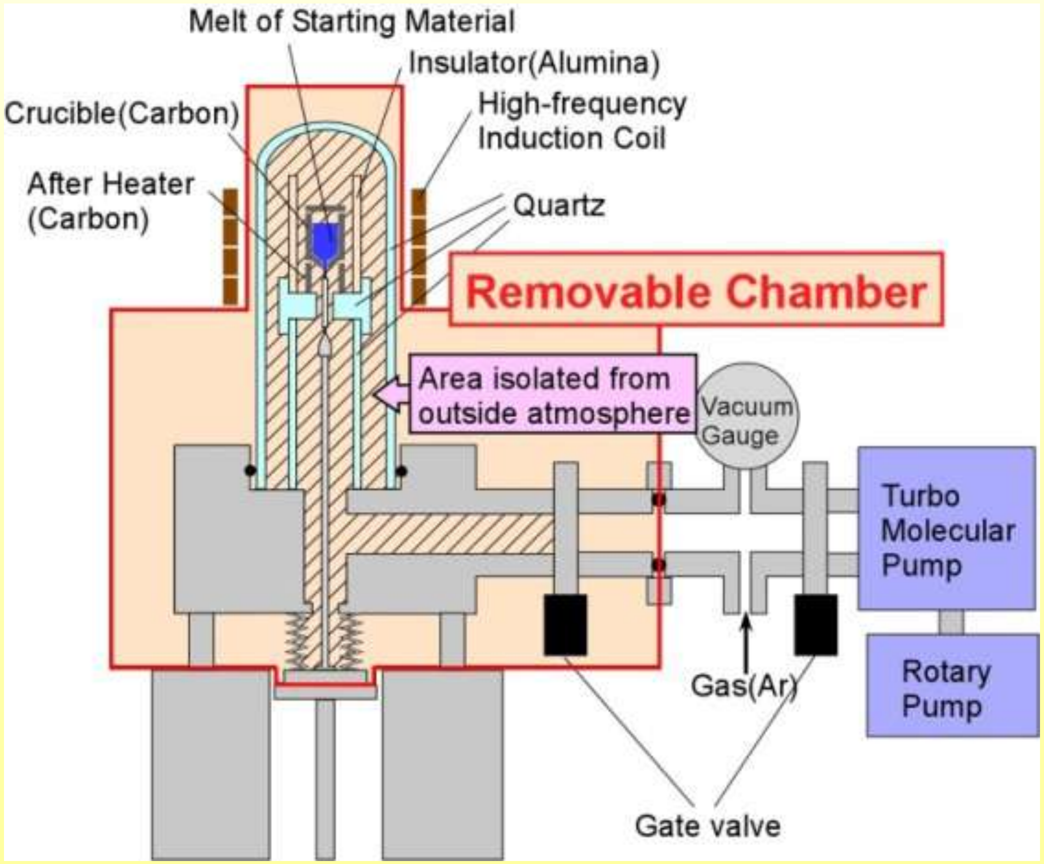
Modern level

	Scintillator	LY, ph/MeV	R (^{137}Cs), %	$/cc
1	$LaBr_3$:Ce	75000	2,6	100 -150
2	SrI_2:Eu	115000	2,6	100 – 150
3	NaI(Tl)	41000	6.5	4

SrI_2:Eu crystals demonstrate superb scintillation characteristics but the price very high!

Is it possible to reduce the price of SrI_2(Eu) to the NaI(Tl) level?

Lab technology



* Yasuhiro Shoji at. al. ICCGE-18, 2016

Ø2''x2'' SrI_2(Eu)

R=3.8±0.1% (662 keV)

Crystal cost structure

	NaI(Tl)	SrI_2(Eu)
Raw material	60%	87%
Crucible	13%	1%
Growth equipment	15%	1%
Power	3%	4%
Labor	4%	4%
Other	5%	3%

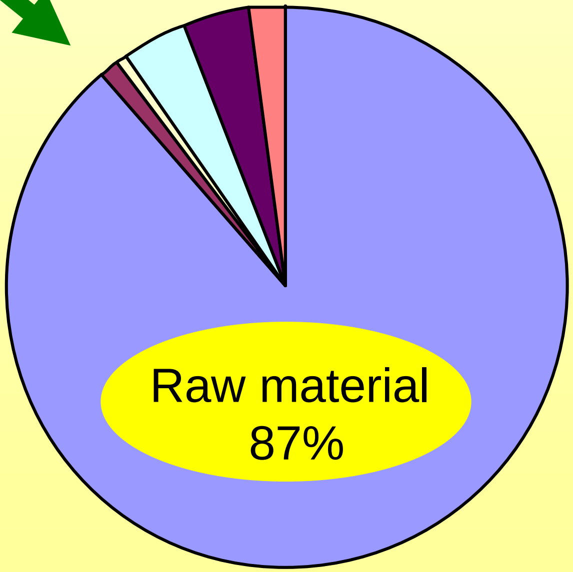
Raw material

NaI – 100$/kg

TlI – 500 $/kg

SrI_2 – 2000$/kg

EuI_2 – 16000 $/kg

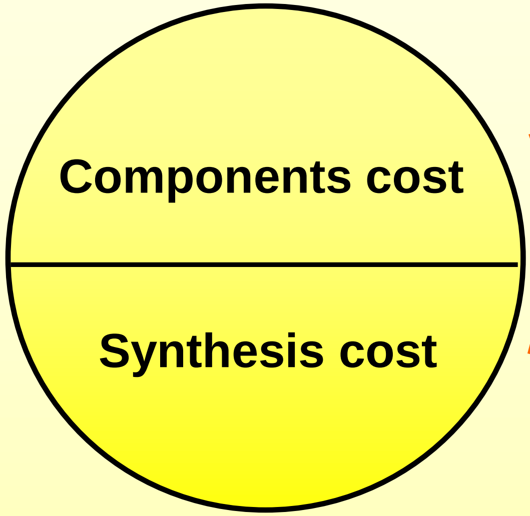


The main cause of high crystal cost:

- High cost of raw material

- Lab level of raw material synthesis and crystal growth technology

Raw material – cost structure



Sr price analog Na

Synthesis technology the same as for alkali halide

Components	*Market price*
$SrCO_3$ – the base of SrI_2	4 $/kg
I_2	30-50 $/kg
Eu_2O_3 – the base of EuI_2	400-1000 $/kg

Target price
SrI_2 → 100 $/kg instead of 2000 $/kg
EuI_2 → 1000 $/kg instead of 16000 $/kg

The way of SrI_2 raw material synthesis

$SrO + 2HI = SrI_2 + H_2O$

$SrCO_3 + 2HI = SrI_2 + H_2O + CO_2\uparrow$

+ Simple technology
- High purity of base components
- High cost of pure HI

$SrCO_3 + I_2 + 5N_2H_4 = SrI_2 + H_2O + CO_2\uparrow + N_2\uparrow$

$SrCO_3 = SrO + CO_2\uparrow$

$SrO + I_2 + 0{,}5N_2H_4 = SrI_2 + H_2O + N_2\uparrow$

$Sr(OH)_2\bullet 8H_2O + I_2 + 0{,}5N_2H_4 = SrI_2 + H2O + N_2\uparrow$ **(•)**

+ It is possible to purification of base components
+ Low cost of components
- Toxicity (N_2H_4)

Own synthesis of SrI_2

$SrCO_3 \rightarrow SrO \rightarrow Sr(OH)_2 \rightarrow SrI_2*6H_2O$

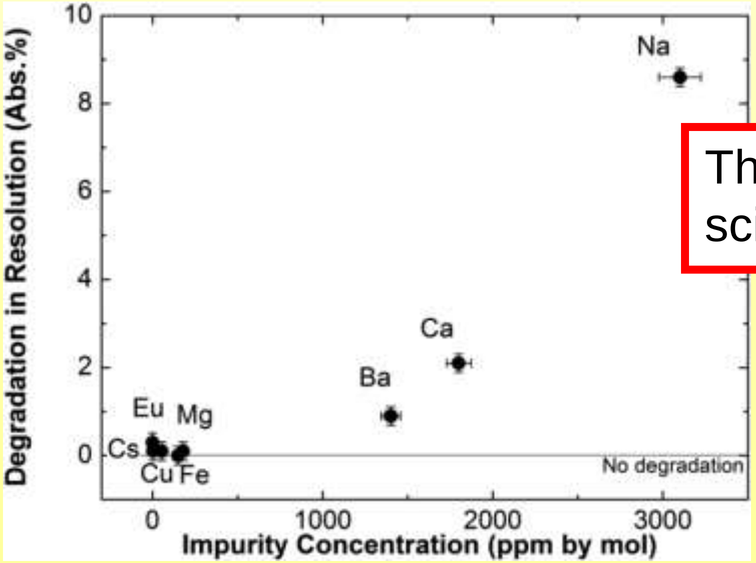
$SrCO_3 = SrO + CO_2$

$SrO + H_2O = Sr(OH)_2$

$2Sr(OH)_2*8H_2O + 2I_2 + N_2H_4*H_2O = 2SrI_2 + N_2 + 21H_2O$

Cationic contamination vs. scintillation performance

$SrI_2(Eu)$ sample co-doped with:	10 mm dia. x 6 mm cylinders: Light yield[a] (ph/MeV)	10 mm dia. x 6 mm cylinders: Energy resolution[b] (%)	10 mm dia. x 6 mm cylinders: Decay time[c] (μs)	7 mm x 6 mm x 2 mm cuboids: Light yield[a] (ph/MeV)	7 mm x 6 mm x 2 mm cuboids: Energy resolution[b] (%)	7 mm x 6 mm x 2 mm cuboids: Decay time[c] (μs)
Eu only	84,900	3.2	1.4	88,600	2.9	1.1
Mg^{2+}	88,200	2.9	1.4	88,600	2.8	1.2
Ba^{2+}	86,800	3.9	1.5	85,900	3.0	1.1
Cs^{+}	86,200	2.9	1.4	93,000	2.8	1.1
Ca^{2+}	85,900	5.1	1.4	84,500	3.0	1.1
Fe^{2+}	85,600	2.9	1.3	89,000	2.9	1.2
Cu^{+}	83,600	2.9	1.5	81,200	2.8	1.5
Na^{+}	75,800	11.8	1.4	84,700	3.2	1.3
Sn^{2+}	48,700	8.1	1.2	49,500	3.7	0.8



The high level of **Ba, Ca, Na** is the cause of scintillation performance degradation

It is important to control concentration of cationic contamination in the raw material!

Stephanie Lam, at. al IEEE TRANSACTIONS ON NUCLEAR SCIENCE, VOL. 62, NO. 6, DECEMBER 2015

Some reaction deteriorated scintillation crystal performance

$SrI_2 \cdot nH_2O = SrI_2 + nH_2O\uparrow$ … dehydration

$SrI_2 + H_2O = SrO + 2HI$ …hydration

$5SrI_2 + 6O_2 = Sr_5(IO_6)_2 + 4I_2$

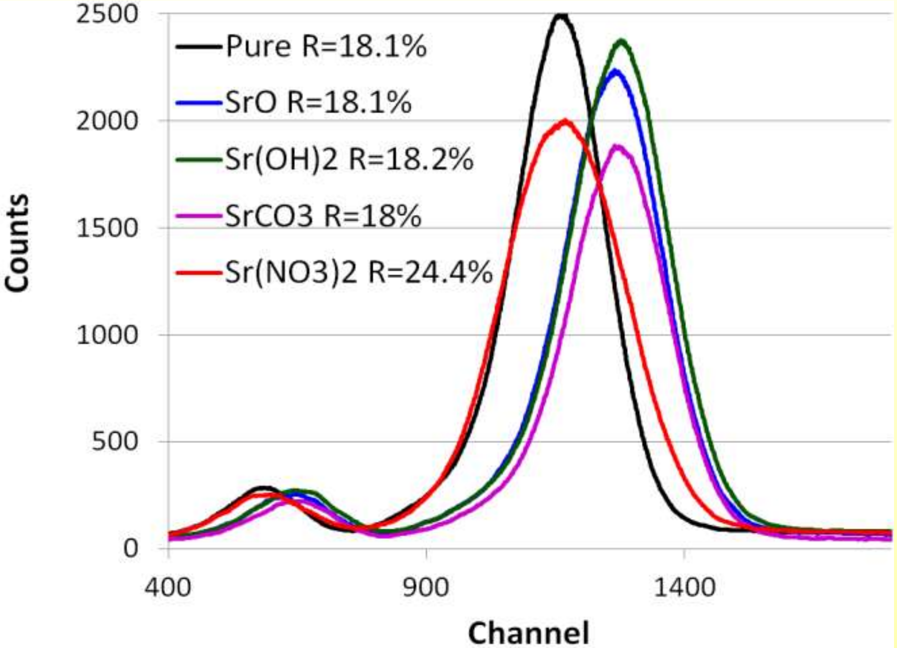
$2SrI_2 + O_2 = 2SrO + 2I_2$

$2SrI_2 + O_2 + 2CO_2 = 2SrCO_3 + 2I_2$

$2SrI_2 + 3O_2 + 2C = 2SrCO_3 + 2I_2$

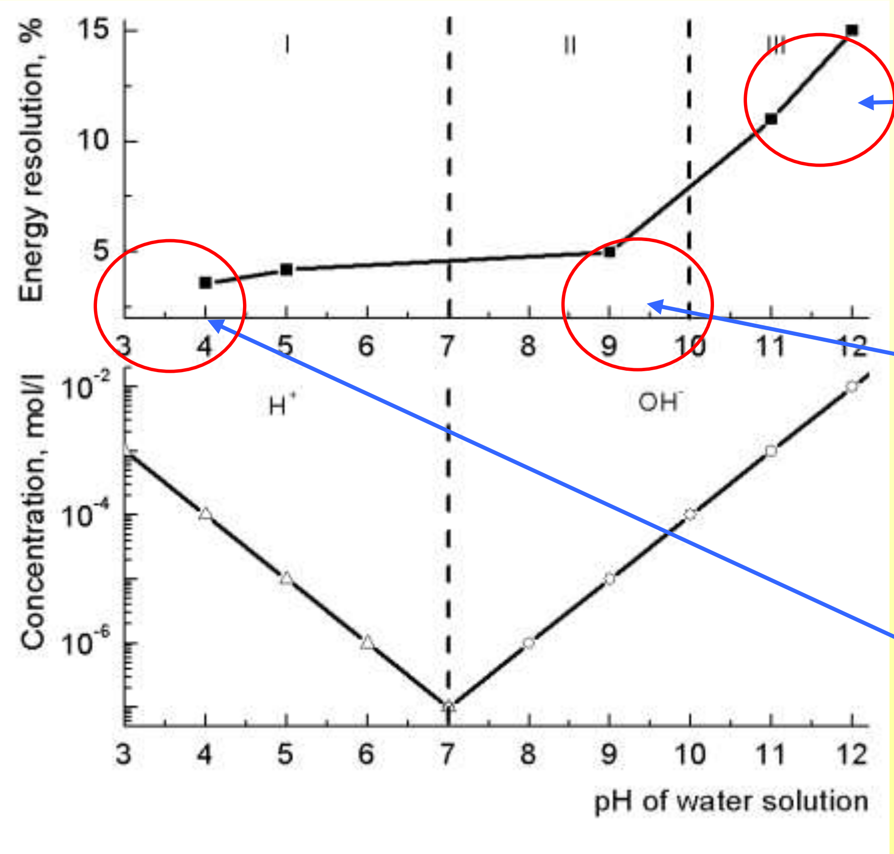
C – as the trace of organics

$SrI_2 \cdot nH_2O = SrO$ or $Sr_5(IO_6)_2 +$ … wrong dehydration technology

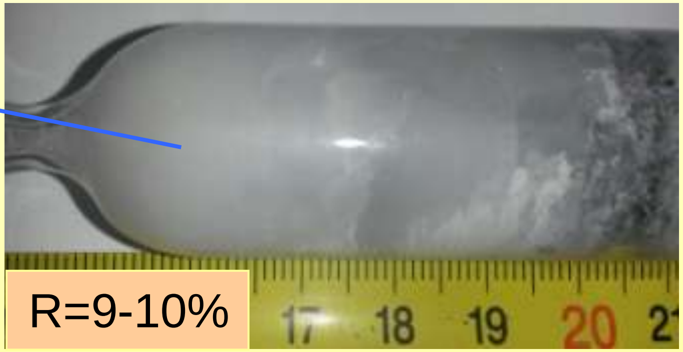


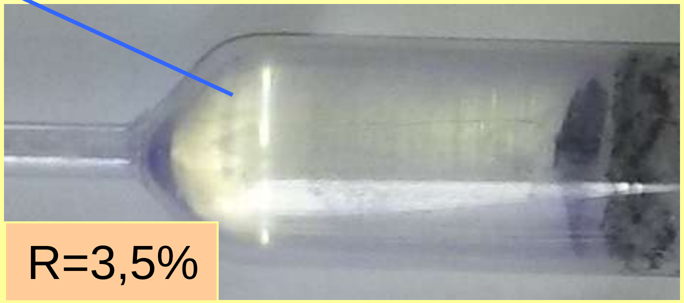
✓ Oxygen impurities can lead to energy storage and degradation of scintillation characteristics.

Raw material pH volume vs. crystal quality

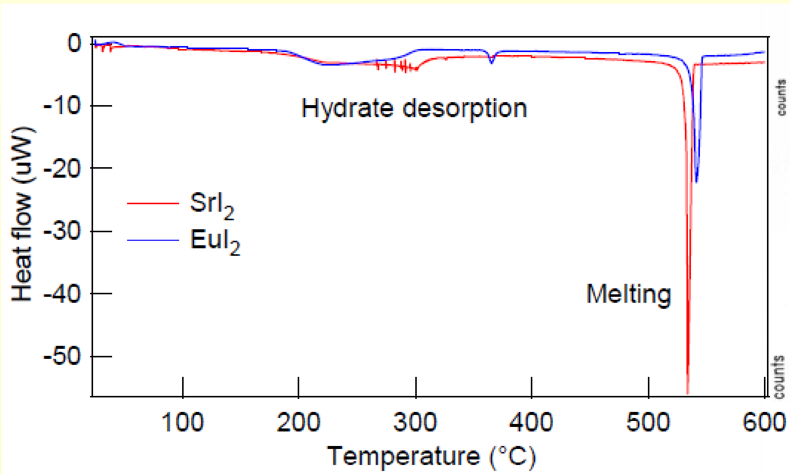


Gektin, Taranyuk at. al., Func. Mat. 23, 3, 2016, 1-5



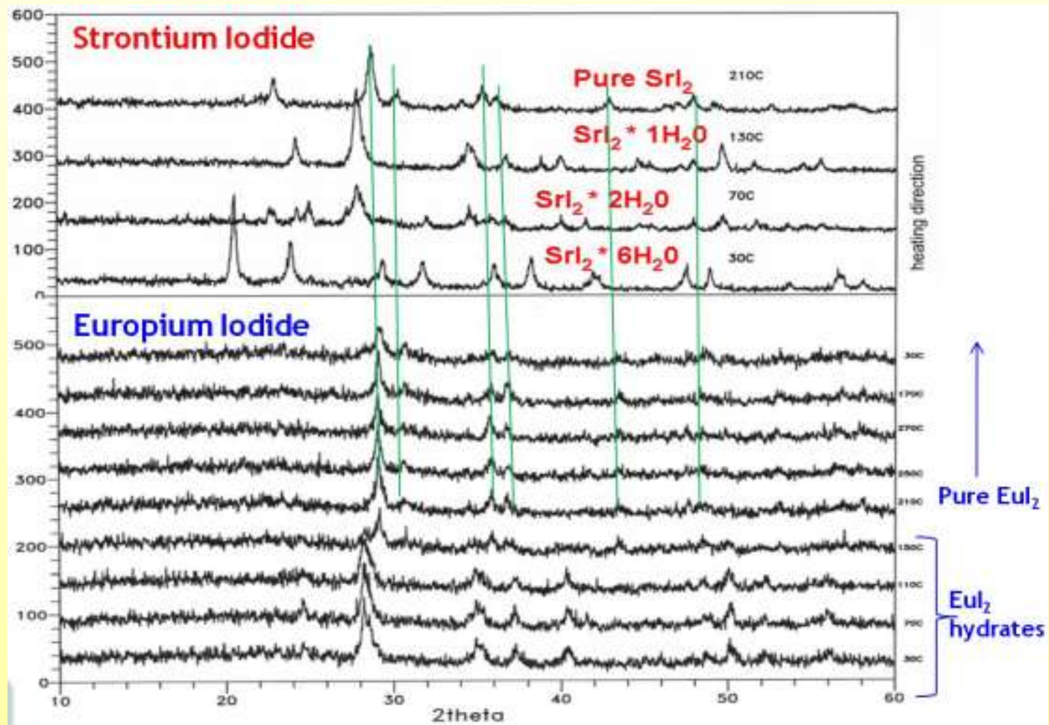


Dehydration of raw material



$SrI_2 \cdot 6H_2O$

$EuI_2 \cdot 7H_2O$



Dehydration of SrI_2, EuI_2 up to 350 °C in vacuum!

N. Cherepy, at. al. LLNL, april 1, 2010

Step-by-step procedure of H_2O and O_2 purification

Dehydration (Heating and evacuation)

+

RAP atmosphere creation ("Liquinert" * process)

$MeO + 2HI \leftrightarrow MeI_2 + H_2O\uparrow$

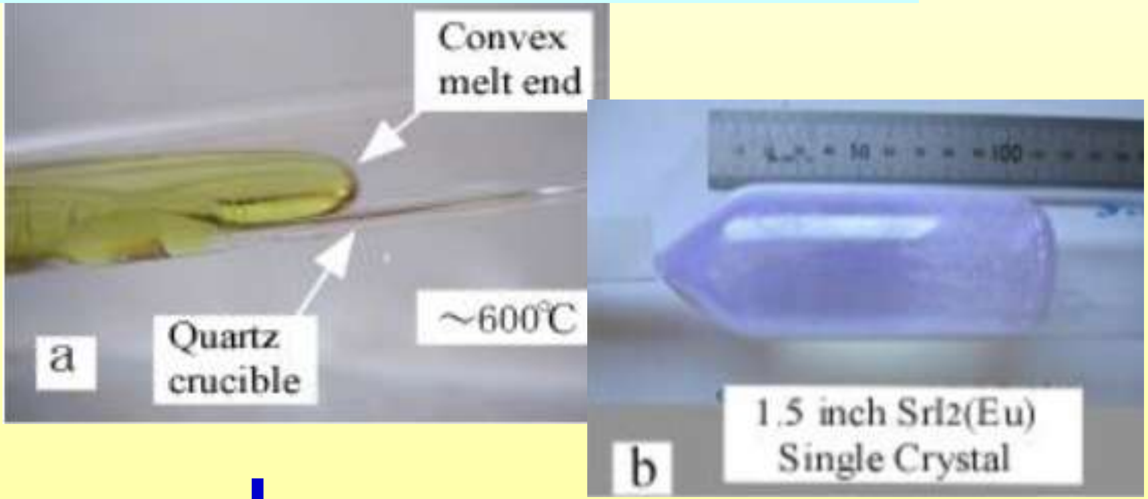
$2MeO + C_2I_4 \leftrightarrow 2MeI_2 + 2CO\uparrow$

$2MeO + CI_4 \leftrightarrow 2MeI_2 + CO_2\uparrow$

$2MeO + 2I_2 \leftrightarrow 2MeI2 + O_2\uparrow$

$MeO + CI_4 \leftrightarrow MeI_2 + CO\uparrow + I_2$

$MeO + I_2 + CO \leftrightarrow MeI_2 + CO_2\uparrow$



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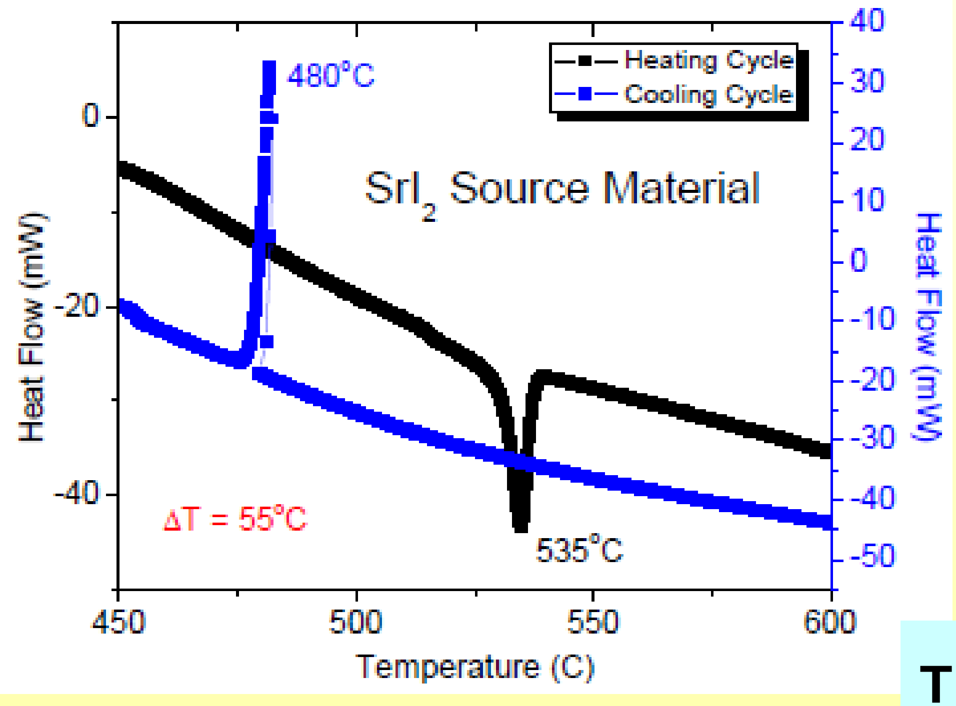
Exclusion of H_2O and O_2 during crystal growth:

- Sealed ampoule/ Inert growth atmosphere

*S.Sakuragi, Proc. of ICCGE-18, Nagoya, Japan 2016.

Specific of SrI_2 crystal growth



E. Rowe, Proc. SORMA 2012

The difference between crystallization point and melting point is <u>55 °C</u> !

The key points of growing process:

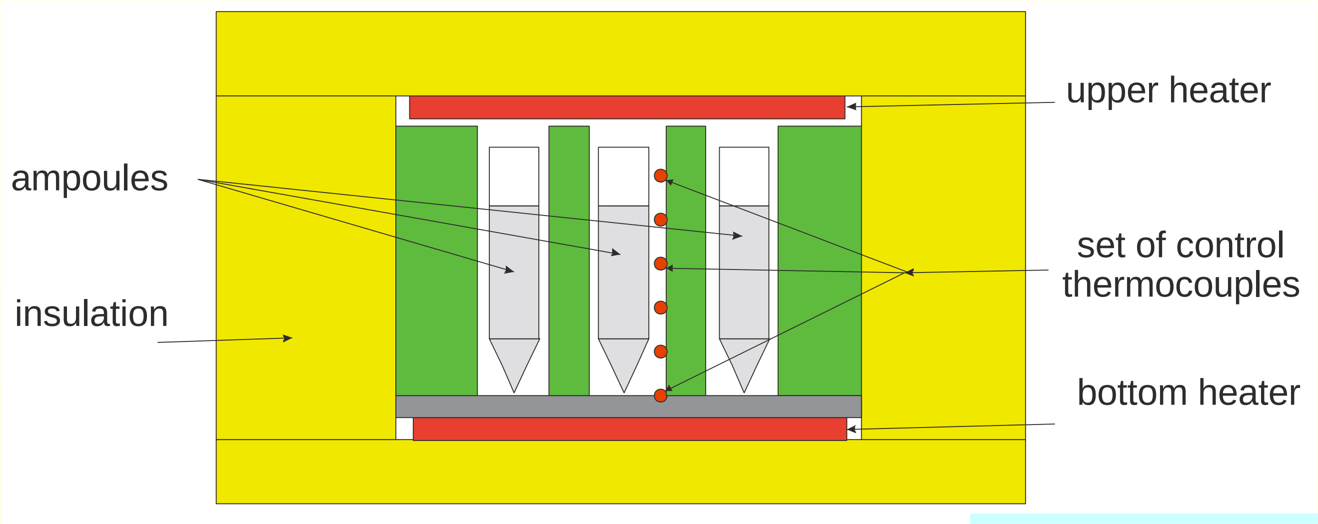
- Shape and material of ampoule

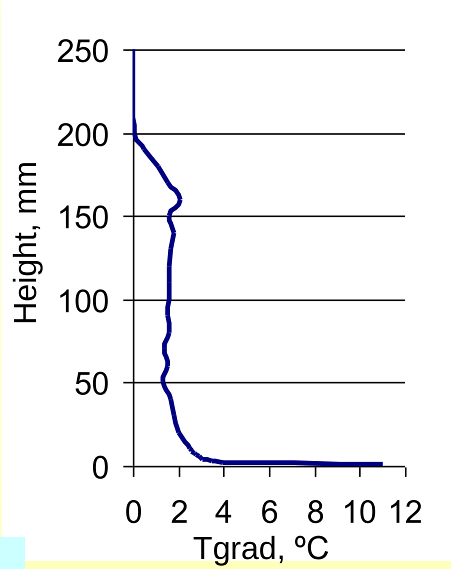
- **Growth rate**

- **Temperature gradient**

- **Growth atmosphere**

Growth equipment





Sealed ampoule

Specification of growth equipment:

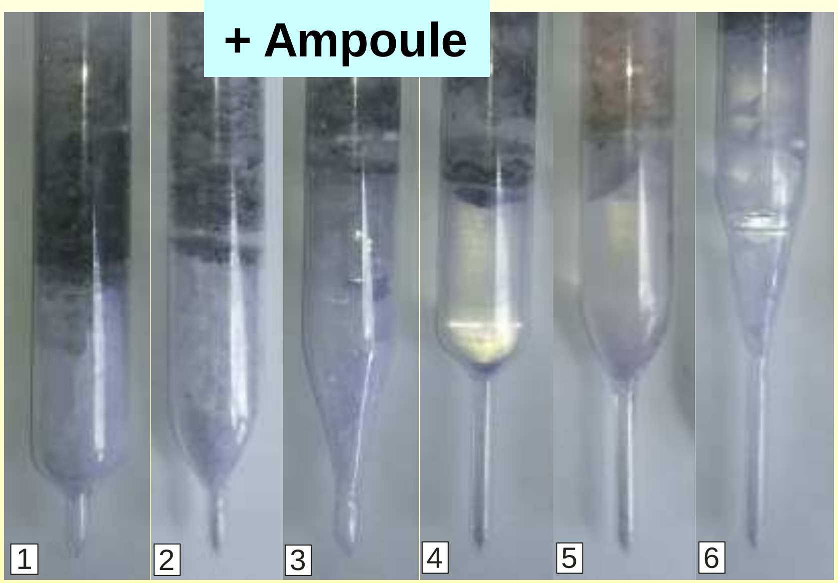
+ 12 crystals Ø 20mm growth at the same time

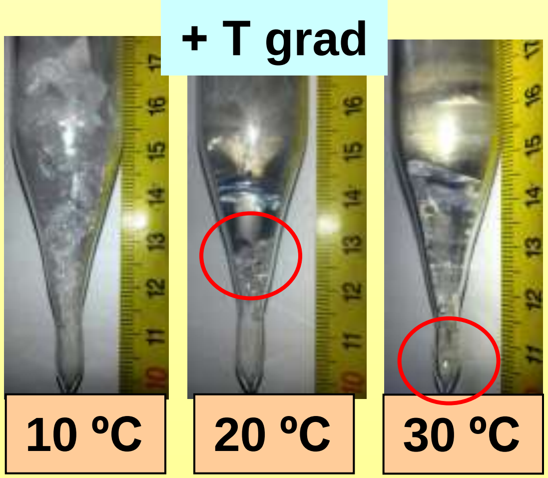
+ ability to chose temperature gradient from 0 to 30 ºC/cm

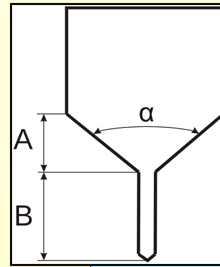
+ growth rate 0,1-10 mm/h.

*Tatanyuk V., Proc. of ICCGE-18, Nagoya, Japan 2016.

Optimization of growth parameters





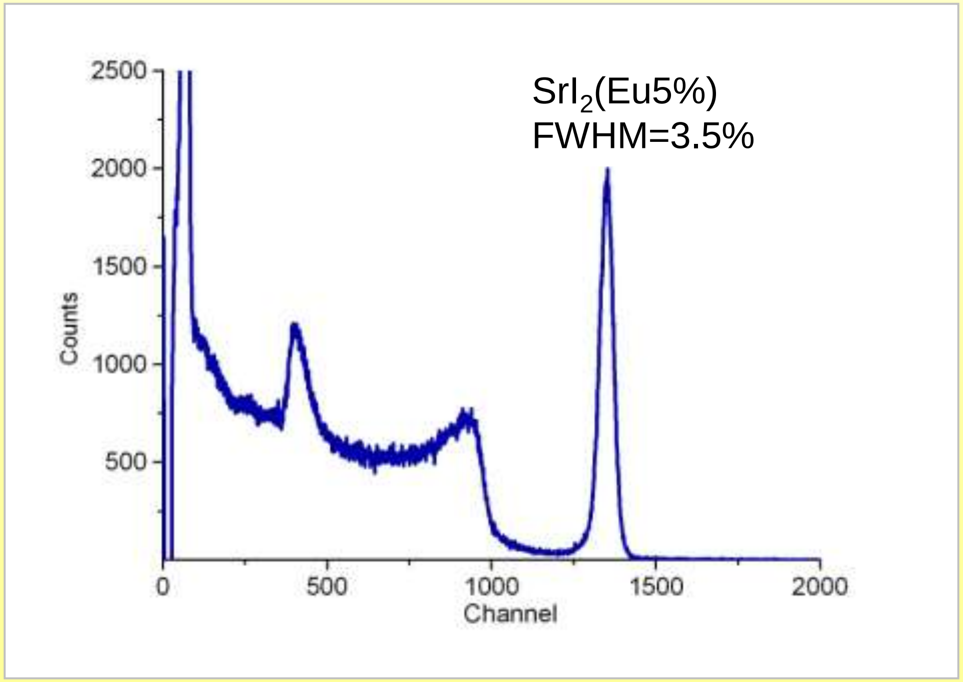


		Height of conical part (A), mm		
Ampoule №		10 (α=90°)	17 (α=60°)	37 (α=30°)
Height of capillary (B), mm	15	1	2	3
	45	4	5	6

Quality of crystal		Temperature gradient, K/cm		
		10	20	30
Ampoule №	1	No crystal	No crystal	Cracked crystal
	2	No crystal	No crystal	Cracked crystal
	3	Cracked crystal	Cracked crystal	Cracked crystal
	4	Crystal	Crystal	Cracked crystal
	5	Crystal	Crystal	Cracked crystal
	6	Cracked crystal	Cracked crystal	Cracked crystal

Scintillation performance

SrI_2(Eu5%) Ø20x40 мм



Conclusion

From our experience we obtain that

• The main cause of high cost of $SrI_2(Eu)$ is Lab level of raw material synthesis and crystal growth technology !!!

And there is no other reason for it !!!

The history to be continued …

Acknowledge

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"New Sensor Materials and Detectors for Ionizing Radiation Detection"

Thank you very much!