Peculiarities of SrI$_2$(Eu) crystal growth

V. Taranyuk, E. Galenin, A. Gektin, O. Sidletskiy, S. Vasukov, N. Nazarenko A. Kolesnikov

Institute for scintillation materials NAS of Ukraine

ISMART-2016, Minsk, Belarus
In 1968 scintillation characteristics were worse than for NaI(Tl).
New sight

Gamma spectra $\text{SrI}_2:\text{Eu}$ and $\text{LaBr}_3:\text{Ce}$ vs. $\text{NaI:Tl}$ *

Modern level

<table>
<thead>
<tr>
<th>Scintillator</th>
<th>LY, ph/MeV</th>
<th>R ($^{137}$Cs), %</th>
<th>$/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 LaBr$_3$:Ce</td>
<td>75000</td>
<td>2.6</td>
<td>100 - 150</td>
</tr>
<tr>
<td>2 SrI$_2$:Eu</td>
<td>115000</td>
<td>2.6</td>
<td>100 – 150</td>
</tr>
<tr>
<td>3 NaI(Tl)</td>
<td>41000</td>
<td>6.5</td>
<td>4</td>
</tr>
</tbody>
</table>

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**

Ø2”x2” SrI$_2$(Eu)

R=3.8±0.1% (662 keV)

* Yasuhiro Shoji at. al. ICCGE-18, 2016*
# Crystal cost structure

<table>
<thead>
<tr>
<th></th>
<th>Nal(Tl)</th>
<th>SrI$_2$(Eu)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Raw material</strong></td>
<td>60%</td>
<td>87%</td>
</tr>
<tr>
<td>Crucible</td>
<td>13%</td>
<td>1%</td>
</tr>
<tr>
<td>Growth equipment</td>
<td>15%</td>
<td>1%</td>
</tr>
<tr>
<td>Power</td>
<td>3%</td>
<td>4%</td>
</tr>
<tr>
<td>Labor</td>
<td>4%</td>
<td>4%</td>
</tr>
<tr>
<td>Other</td>
<td>5%</td>
<td>3%</td>
</tr>
</tbody>
</table>

**Raw material**
- Nal – 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

Components cost

Synthesis cost

Sr price analog Na

Synthesis technology the same as for alkali halide

<table>
<thead>
<tr>
<th>Components</th>
<th>Market price</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCO$_3$ – the base of Srl$_2$</td>
<td>4 $/kg</td>
</tr>
<tr>
<td>I$_2$</td>
<td>30-50 $/kg</td>
</tr>
<tr>
<td>Eu$_2$O$_3$ – the base of Eul$_2$</td>
<td>400-1000 $/kg</td>
</tr>
</tbody>
</table>

Target price
Srl$_2$ → 100 $/kg instead of 2000 $/kg
Eul$_2$ → 1000 $/kg instead of 16000 $/kg
The way of \( \text{SrI}_2 \) raw material synthesis

\[
\begin{align*}
\text{SrO} + 2\text{HI} &= \text{SrI}_2 + \text{H}_2\text{O} \\
\text{SrCO}_3 + 2\text{HI} &= \text{SrI}_2 + \text{H}_2\text{O} + \text{CO}_2 \uparrow
\end{align*}
\]

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

\[
\begin{align*}
\text{SrCO}_3 + \text{I}_2 + 5\text{N}_2\text{H}_4 &= \text{SrI}_2 + \text{H}_2\text{O} + \text{CO}_2 \uparrow + \text{N}_2 \uparrow \\
\text{SrCO}_3 &= \text{SrO} + \text{CO}_2 \uparrow \\
\text{SrO} + \text{I}_2 + 0,5\text{N}_2\text{H}_4 &= \text{SrI}_2 + \text{H}_2\text{O} + \text{N}_2 \uparrow \\
\text{Sr(OH)}_2 \cdot 8\text{H}_2\text{O} + \text{I}_2 + 0,5\text{N}_2\text{H}_4 &= \text{SrI}_2 + \text{H}_2\text{O} + \text{N}_2 \uparrow (\cdot)
\end{align*}
\]

+ It is possible to purification of base components  
+ Low cost of components  
- Toxicity (\( \text{N}_2\text{H}_4 \))
Own synthesis of SrI₂

SrCO₃ → SrO → Sr(OH)₂ → SrI₂·6H₂O

SrCO₃ = SrO + CO₂

SrO + H₂O = Sr(OH)₂

2Sr(OH)₂·8H₂O + 2I₂ + N₂H₄·H₂O = 2SrI₂ + N₂ + 21H₂O
Cationic contamination vs. scintillation performance

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!
Some reaction deteriorated scintillation crystal performance

\[ \text{SrI}_2 \cdot n\text{H}_2\text{O} = \text{SrI}_2 + n\text{H}_2\text{O}\uparrow \ldots \text{dehydration} \]

\[ \text{SrI}_2 + \text{H}_2\text{O} = \text{SrO} + 2\text{HI} \ldots \text{hydration} \]

\[ 5\text{SrI}_2 + 6\text{O}_2 = \text{Sr}_5(\text{IO}_6)_2 + 4\text{I}_2 \]

\[ 2\text{SrI}_2 + \text{O}_2 = 2\text{SrO} + 2\text{I}_2 \]

\[ 2\text{SrI}_2 + \text{O}_2 + 2\text{CO}_2 = 2\text{SrCO}_3 + 2\text{I}_2 \]

\[ 2\text{SrI}_2 + 3\text{O}_2 + 2\text{C} = 2\text{SrCO}_3 + 2\text{I}_2 \]

\[ C \text{ – as the trace of organics} \]

\[ \text{SrI}_2 \cdot n\text{H}_2\text{O} = \text{So} \text{O or Sr}_5(\text{IO}_6)_2 + \ldots \text{wrong} \]

\[ \text{dehydration technology} \]

✔️ 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

R=9-10%

R=3,5%
Dehydration of raw material

SrI$_2$•6H$_2$O
EuI$_2$•7H$_2$O

Dehydration of SrI$_2$, EuI$_2$ up to 350 ℃ in vacuum!

N. Cherepy, at. al. LLNL, april 1, 2010
Step-by-step procedure of H₂O and O₂ purification

Dehydration (Heating and evacuation)

+ 

RAP atmosphere creation (“Liquinert” * process)

MeO + 2HI ↔ Mel₂ + H₂O↑
2MeO + C₂I₄ ↔ 2Mel₂ +2CO↑
2MeO + Cl₄ ↔ 2Mel₂ + CO₂↑
2MeO + 2I₂ ↔ 2Mel2 + O₂↑
MeO + Cl₄ ↔ Mel₂ + CO↑ + I₂
MeO + I₂ +CO ↔ Mel₂ + CO₂↑

+ 

Exclusion of H₂O and O₂ during crystal growth:

- Sealed ampoule/ Inert growth atmosphere

Specific of SrI$_2$ crystal growth

The difference between crystallization point and melting point is $55^\circ$C!

The key points of growing process:
- Shape and material of ampoule
- Growth rate
- Temperature gradient
- Growth atmosphere

E. Rowe, Proc. SORMA 2012
Specification of growth equipment:
+ 12 crystals Ø 20mm growth at the same time
+ ability to chose temperature gradient from 0 to 30 °C/cm
+ growth rate 0,1-10 mm/h.

### Optimization of growth parameters

#### Quality of crystal

<table>
<thead>
<tr>
<th>Ampoule №</th>
<th>10 (α=90°)</th>
<th>17 (α=60°)</th>
<th>37 (α=30°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No crystal</td>
<td>No crystal</td>
<td>Cracked crystal</td>
</tr>
<tr>
<td>2</td>
<td>No crystal</td>
<td>No crystal</td>
<td>Cracked crystal</td>
</tr>
<tr>
<td>3</td>
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#### Temperature gradient, K/cm

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<tr>
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<td>Cracked crystal</td>
<td>Cracked crystal</td>
</tr>
</tbody>
</table>

#### Height of capillary (B), mm

- **15**: 1
- **45**: 4

#### Height of conical part (A), mm

- **10** (α=90°)
- **17** (α=60°)
- **37** (α=30°)

#### Temperature gradient, K/cm

- **10**: 1
- **20**: 2
- **30**: 3
Scintillation performance

SrI$_2$(Eu5%) Ø20x40 mm

FWHM = 3.5%
Conclusion

From our experience we obtain that

• The main cause of high cost of $\text{SrI}_2(\text{Eu})$ 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

NATO multi-year Science for Peace Project NUKR.SFPP 984958 - "New Sensor Materials and Detectors for Ionizing Radiation Detection"
Thank you very much!