Radioactive contamination of SrI$_2$(Eu) crystal scintillator


A R T I C L E   I N F O

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A B S T R A C T

A strontium iodide crystal doped by europium (SrI$_2$(Eu)) was produced by using the Stockbarger growth technique. The crystal was subjected to a characterization that includes relative photoelectron output and energy resolution for $\gamma$ quanta. The intrinsic radioactivity of the SrI$_2$(Eu) crystal scintillator was tested both by using it as scintillator at sea level and by ultra-low background HPGe spectrometry deep underground. The response of the SrI$_2$(Eu) detector to $\alpha$ particles ($\alpha/\beta$ ratio and pulse shape) was estimated by analyzing the $^{226}$Ra internal trace contamination of the crystal. We have measured: $\alpha/\beta = 0.55$ at $E_{\alpha} = 7.7$ MeV, and no difference in the time decay of the scintillation pulses induced by $\alpha$ particles and $\gamma$ quanta. The application of the obtained results in the search for the double electron capture and electron capture with positron emission in $^{84}$Sr has been investigated at a level of sensitivity: $T_{1/2} \sim 10^{15} - 10^{16}$ yr. The results of these studies demonstrate the potentiality of this material for a variety of scintillation applications, including low-level counting experiments.

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1. Introduction

The strontium iodide was discovered as scintillator by Hofstadter in 1968 [1]. The interest in this material increased in the last few years because of the high light output ($> 100,000$ photons/MeV) and of the good energy resolution ($\approx 3\%$ at 662 keV), recently reported in Refs. [2–4]. The main properties of SrI$_2$(Eu) crystal scintillators are presented in Table 1.

An important advantage of SrI$_2$(Eu) in comparison to other high resolution scintillators, like for instance LaCl$_3$(Ce), LaBr$_3$(Ce), Lu$_2$SiO$_5$(Ce), LuI$_3$(Ce), is the absence of natural long-lived radio-active isotopes (as $^{138}$La in lanthanum and $^{176}$Lu in lutetium). It makes SrI$_2$(Eu) scintillators promising in various applications, in particular for low counting experiments as e.g. those searching for double $\beta$ decay.

The main aim of our study was to test the internal radioactive contamination of a SrI$_2$(Eu) crystal scintillator. We have also estimated the response of the detector to $\alpha$ particles by using the data of low background measurements where events of $^{214}$Po decays (daughter of $^{226}$Ra from the $^{238}$U chain) were recorded. As a by-product of the measurements, we have derived limits on double $\beta$ processes in $^{84}$Sr.

2. Scintillator, measurements, results and discussion

2.1. Development of SrI$_2$(Eu) crystal scintillators

A single crystal of strontium iodide doped by 1.2% of Eu$^3+$ was grown in a quartz ampoule using the vertical Stockbarger method [10]. Anhydrous strontium iodide activated by europium was obtained by the reaction of the strontium carbonate and europium oxide with the hydroiodic acid as described in Ref. [1]. After drying, the obtained hydrate was placed in the quartz ampoule for the crystal growth and slowly heated for five days up to 150 °C.

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with permanent vacuum pumping. As a next step the ampoule was welded and placed in the Stockbarger growing set-up, the temperature was increased up to 538 °C. The crystal was grown with a speed of 20 mm per day as described in Ref. [4]. The crystal boule was cut in a dry box filled by pure nitrogen to obtain a near cylindrical scintillator 13 mm in diameter and 11 mm length (see Fig. 1, left). The crystal was wrapped with PTFE tape and encapsulated using epoxy glue in an oxygen-free high thermal conductivity (OFHC) copper container with a quartz window, all the materials with low level of radioactive contamination. It is shown in Fig. 1, right; as one can see, the crystal scintillator is neither milky nor cracked. However, the scintillator is not of exact cylindrical shape.

2.2. Energy resolution and relative pulse amplitude

In order to investigate its scintillation properties, the SrI₂(Eu) crystal scintillator was coupled to a 3 in. Philips XP2412 photomultiplier (PMT) with a bialkali photocathode using Dow Corning Q2-3067 optical couplant. The detector was irradiated with γ quanta from ⁶⁰Co, ¹³⁷Cs, ²⁰⁷Bi, ²³²Th and ²⁴¹Am γ sources. The measurements were carried out using an ORTEC 572 spectroscopic amplifier with 10 μs shaping time and a peak sensitive analog-to-digital converter. Fig. 2 shows the pulse amplitude spectra measured by the SrI₂(Eu) scintillator with ⁶⁰Co, ¹³⁷Cs, ²⁰⁷Bi and ²⁴¹Am γ sources, respectively. The energy resolution FWHM for the 662 keV line of ¹³⁷Cs is 5.8%; it is worse than the best reported results (FWHM = 2.6–3.7% at 662 keV) [2,4,7,9]. This fact is probably due to not enough high level of the initial purity of the used powder, to not perfect technology of the crystal production (which is under development now), to a lower amount of the Eu dopant and to a possible concentration gradient of the Eu in the crystal. Besides, some degradation of the energy resolution can be due to the irregular shape of the crystal (a clear effect of the shape of the SrI₂(Eu) scintillators on the energy resolution is reported in Ref. [8]). Moreover, we have used a bialkali PMT, while PMTs with a super-bialkali photocathodes have been applied in the works [2,4,7–9].

The energy resolution of the SrI₂(Eu) crystal scintillator measured in the 60–2615 keV energy range is presented in Fig. 3. According to Refs. [11,12] the data were fitted (by the chi-square method; \( \chi^2/n.d.f. = 9.5/5 = 1.9 \), where n.d.f. is number of degrees of freedom) by the function FWHM (%)= \( \sqrt{a+b/E_γ} \) (where \( E_γ \) is the energy of the γ quanta in keV) with parameters \( a=(10 \pm 2) \) and \( b=14200 \pm 1500 \) keV. The relative pulse amplitude of the SrI₂(Eu) detector was found to be 87% of a commercial NaI(Tl) scintillator (Ø 40 mm × 40 mm) (see Fig. 4).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>4.5–4.6</td>
<td>[2,4,5]</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>515</td>
<td>[2]</td>
</tr>
<tr>
<td>Structural type</td>
<td>Orthorhombic</td>
<td>[2]</td>
</tr>
<tr>
<td>Index of refraction</td>
<td>1.85</td>
<td>[6]</td>
</tr>
<tr>
<td>Wavelength of emission maximum (nm)</td>
<td>429–436</td>
<td>[2,4,5]</td>
</tr>
<tr>
<td>Light yield (photons/MeV)</td>
<td>(68–120) × 10³</td>
<td>[2,4,7]</td>
</tr>
<tr>
<td>Energy resolution (FWHM, %) for 662 keV γ of ¹³⁷Cs</td>
<td>2.6–3.7</td>
<td>[2,4,7–9]</td>
</tr>
<tr>
<td>Scintillation decay time (μs) under X-ray/γ ray excitation at 300 K</td>
<td>0.6–2.4</td>
<td>[2,4,7,5]</td>
</tr>
</tbody>
</table>

![Fig. 1](Image)

**Fig. 1.** (Color online) Left: SrI₂(Eu) crystal before encapsulation. Right: Low background SrI₂(Eu) scintillation detector. Arrows show irregularity of the crystal shape.
2.3. Low background measurements in scintillation mode at sea level

The low background set-up installed at sea-level in the Institute for Nuclear Research (INR, Kyiv, Ukraine). In the set-up, a SrI$_2$(Eu) crystal scintillator was optically connected to a 3 in. photomultiplier tube Philips XP2412 through a high purity polystyrene light-guide ($\varnothing$66 x 120 mm). The optical contact between the scintillation crystal, the light-guide and the PMT was provided by Dow Corning Q2-3067 optical couplant. The light-guide was wrapped with aluminised Mylar. The detector was surrounded by a passive shield made of OFHC copper (5–12 cm thick), and lead (5 cm thick). After the first run of measurements over 52 h, an anti-muon veto counter was installed above the set-up. The counter consists of polystyrene based plastic scintillator 50 x 50 x 8 cm viewed by a low background PMT FEU-125 (Ekran Optical Systems, Russia) with a diameter of the photocathode equal to 15 cm. The anti-muon shield suppressed the background caused by cosmic rays by a factor $\approx$ 3 (at the energy $\approx$ 4 MeV).

An event-by-event data acquisition system has recorded the pulse shape of the SrI$_2$(Eu) scintillator over a time window of 100 $\mu$s (by using a 20 MS/s 12 bit transient digitizer [13]), the arrival time of the signals (with an accuracy of 0.3 $\mu$s), and the signals amplitude by a peak sensitive analog-to-digital converter.

The energy scale and the energy resolution of the detector were determined in calibration runs by 60Co, 137Cs and 208Bi $\gamma$ ray sources. The energy resolution becomes slightly worse due to the light-guide used in the low background set-up. It can be fitted by a function: FWHM(%) = $\sqrt{a-b/E_i}$ with parameters $a = (7.4 \pm 4.2)$ and $b = (28100 \pm 8000)$ keV, where $E_i$ is the energy of the $\gamma$ quanta in keV.

A search for internal contamination of the crystal by $\alpha$ particles of 6.3–7.7 MeV is in the range of 0.5–0.6, 2 MeV according to the fast 214Bi–214Po decay sequence. Taking into account the detection efficiency in the time window (15–77) $\mu$s (it contains 21.6% of 210Po decays), the mass of the crystal 6.6 g, the measuring time 101.52 h and the number of selected events (52), one can estimate the activity of 226Ra in the SrI$_2$(Eu) crystal as 100(14) mBq/kg.

By using the result of the double pulses analysis, we have estimated the response of the SrI$_2$(Eu) crystal scintillator to $\alpha$ particles. The quenching of the scintillation light yield can be expressed through the so called $\alpha/\beta$ ratio, which is the ratio of the position of an $\alpha$ peak in the energy scale measured with $\gamma$ quanta to the energy of the $\alpha$ particles. Considering the spectrum presented in Fig. 5(b) as given by $\alpha$ particles of 214Po with energy 7687 keV, we can estimate the $\alpha/\beta$ ratio as 0.55. A similar quenching was observed in Ref. [17] for NaI(Tl) ($\alpha/\beta = 0.66$) and CsI(Tl) ($\alpha/\beta = 0.67$) crystal scintillators with the $\alpha$ particles of a 244Am source with energy 5.48 MeV; in Ref. [18] similar values have been measured in ultra-low background NaI(Tl) for $\alpha$ trace contaminants internal to the crystals. It should be stressed that the energy resolution for the $\alpha$ peak of 214Po (FWHM$_{\alpha} = 12\%$) is worse than that expected at the energy $\approx$ 4.2 MeV according to the calibration with $\gamma$ sources (FWHM$_{\gamma} \approx 3\%$). A similar effect was observed in crystal scintillators with anisotropic crystal structure, as for instance in CdWO$_4$ [14] and ZnWO$_4$ [19].

A search for internal contamination of the crystal by 228Th (daughter of 222Th) was realized with the help of the time-amplitude analysis. To determine the activity of 228Th, the following sequence of $\alpha$ decays was selected: 228Rn ($Q_\alpha = 6405$ keV, $T_{1/2} = 55.6$ s) $\rightarrow$ 218Po ($Q_\alpha = 6907$ keV, $T_{1/2} = 0.145$ s) $\rightarrow$ 218Po. Assuming that the $\alpha/\beta$ ratio for the $\alpha$ particles of 6.3–7.7 MeV is in the range of 0.5–0.6,
the energy interval for both $\alpha$ particles was chosen as 2.8–4.5 MeV. The result of the selection is presented in Fig. 6.

Despite the low statistics (only 12 pairs were found), the positions of the selected events and the distribution of the time intervals between the events do not contradict the expectations for the $\alpha$ particles of the chain. Taking into account the efficiency in the time window 0.01–0.5 s to select $^{216}\text{Po} \rightarrow ^{212}\text{Pb}$ events (86.2%), the activity of $^{228}\text{Th}$ in the crystal can be calculated as $6(2)\text{ mBq/kg.}$

The energy spectrum measured with the SrI$_2$(Eu) scintillator over 101.52 h is presented in Fig. 7. There is a peak in the spectrum at the energy of 665 ± 5 keV, which can be explained by contaminations of the SrI$_2$(Eu) detector or/and of the set-up by $^{137}\text{Cs}$ (probably as a result of pollution after the Chernobyl accident). Taking into account that our set-up is installed at sea level, a significant part of the background above 2.6 MeV (the edge of the $\gamma$ quanta energy from the natural radioactivity) can be attributed to cosmic rays.

Peculiarities in the spectrum in the energy region 2.5–4.5 MeV can be explained by the decays of $\alpha$ active U/Th daughters present in the crystal as trace contamination. To estimate the activity of the $\alpha$ active nuclides from the U/Th families in the crystal, the energy spectrum was fitted in the energy interval 1.8–4.7 MeV by using fourteen Gaussian functions to describe $\alpha$ peaks of $^{232}\text{Th}$, $^{228}\text{Th}$ (and daughters: $^{228}\text{Ra}, ^{220}\text{Rn}, ^{216}\text{Po}, ^{212}\text{Bi}$), $^{238}\text{U}$ (and daughters: $^{234}\text{U}, ^{230}\text{Th}$), $^{226}\text{Ra}$ with daughters ($^{222}\text{Rn}, ^{218}\text{Po}, ^{214}\text{Po}, ^{210}\text{Po}$) plus an exponential function to describe background$^4$. A fit of the spectrum is shown in the Inset of Fig. 7. The main contribution to the $\alpha$ activity in the scintillator gives an activity

$^2$ We assume a broken equilibrium of the U/Th chains in the scintillator.

$^4$ At sea level the energy spectrum of cosmic ray induced background in different nuclear detectors, including scintillating, has a monotonic character, which can be approximated in reasonable narrow energy regions (a few MeV) by an exponential function $\left[22-25\right]$. 

91 ± 8 mBq/kg for the $^{226}\text{Ra}$ and daughters ($^{222}\text{Rn}, ^{218}\text{Po}$ and $^{214}\text{Po}$). This estimate is in agreement with the result of the double pulse analysis ($100 \pm 14$ mBq/kg, see above) and with the
measurements performed deep underground with ultra-low background HPGe γ ray spectrometry (Section 2.5). Because of the low statistics and of the relatively poor energy resolution for α particles, we conservatively give limits on activities of 232Th, 238U and 210Po in the SrI2(Eu) scintillator. The data obtained from the fit are presented in Table 2.

To estimate the contamination of the scintillator by 40K, 60Co, 90Sr−90Y, 137Cs, 138La, 152Eu, 154Eu, 176Lu, 210Pb, 210Bi, their decays in the SrI2(Eu) detector were simulated with the GEANT4 package [26] and the event generator DECAVO [27]. The radioactive contamination of the set-up, in particular, the radioactivity of the PMT can contribute to the background, too. Therefore we have also simulated the contribution from the contamination of the PMT by 232Th, 238U (with their daughters) and 40K. An exponential function was adopted to describe the contribution of the cosmic rays in the sea level installation where these measurements were carried out.

Apart from the peak of 137Cs and the α peaks in the energy region 2.5–4.3 MeV, there are no other peculiarities in the spectrum which could be ascribed to internal trace radioactivity. However, even in the case of 137Cs we cannot surely distinguish the contribution of internal and external contamination. Therefore, only limits on contaminations of the crystal by the possible radionuclides were set on the basis of the experimental data. With this aim the spectrum was fitted in the energy interval 0.2–4.65 MeV by the model composed by the background components 238U (with their daughters) and α particles irradiation.

Despite the sea level location and the modest shield of the scintillation set-up, the measurements allowed the detection of the internal contamination of the scintillator by 228Ra and 228Th; besides, we have estimated limits on activities of 238U, 232Th, 210Pb, 210Po, 90Sr. It should be stressed that these radionuclides are rather hard to detect due to the absence of noticeable γ rays. Moreover, the measurements allowed us to estimate the α/β ratio and to measure the pulse shape for α particles (see the next section) by recording the pulse profiles of 214Po α events inside the scintillator.

### 2.4. Pulse shape of scintillation for γ quanta (β particles) and α particles from the sea level measurements

The pulse profiles of 41 α events of 214Po were selected with the help of the double pulse analysis from the data of the low background measurements (see Section 2.3 and Fig. 5). The sum of the pulses is presented in Fig. 8 where also the sum of approximately two thousands of background γ (β) events with energies ≈ 1.5 MeV is drawn.

The distributions were fitted in the time interval 0–10 μs by the following function:

\[ f(t) = A(t) = e^{-(t/t_\gamma)} - e^{-(t/t_\alpha)}, \quad t > 0, \]

where \( A \) is the intensity (in arbitrary units), and \( t \) is the decay constant of the light emission; \( t_{\alpha} \) is the integration constant of the electronics (≈ 0.08 μs). The fit gives the scintillation decay times in the SrI2(Eu) crystal scintillator: \( t_\alpha = (1.75 \pm 0.01) \mu s \) and \( t_\gamma = (1.73 \pm 0.02) \mu s \) for γ quanta (β particles) and α particles, respectively. Therefore we have not observed any clear indication on differences in the kinetics of the scintillation decay in the SrI2(Eu) crystal scintillator under γ quanta (β particles) and α particles irradiation.

### 2.5. Measurements with ultra-low background HPGe γ ray spectrometry deep underground

The SrI2(Eu) crystal scintillator was measured for 706 h with the ultra-low background HPGe γ ray spectrometer GeCris. The detector has a volume of 468 cm³ and a 120% efficiency relatively to a 3 in. × 3 in. NaI(Tl). This detector has a rather thin Cu window of 1 mm thickness. The passive shield of the detector consists of 15 cm of OFHC copper and 20 cm of low radioactive lead. The whole set-up is sealed in an air-tight plexiglass box continuously flushed with high purity nitrogen gas to avoid the presence of residual environmental radon. The facility is located deep underground in the Gran Sasso National Laboratories of the I.N.F.N. (average overburden of 3600 m water equivalent) [28,29]. The background data were accumulated over 1046 h (see Fig. 9).

In order to determine the radioactive contamination of the sample, the detection efficiencies were calculated using a Monte Carlo simulation based on the GEANT4 software package [26]. The peaks in the measured spectra are due to the naturally occurring radionuclides of the uranium and thorium chains, 40K and 137Cs. We have detected contaminations by 137Cs and 226Ra (the γ lines of 137Cs, 214Bi and 214Pb were observed) in the crystal scintillator.

### Table 2

<table>
<thead>
<tr>
<th>Chain (sub-chain)</th>
<th>Activity (mBq/kg)</th>
<th>Measured in scintillation mode</th>
<th>Measured by HPGe</th>
</tr>
</thead>
<tbody>
<tr>
<td>40K</td>
<td>≤ 200</td>
<td>≤ 255</td>
<td></td>
</tr>
<tr>
<td>60Co</td>
<td>≤ 540</td>
<td>≤ 16</td>
<td></td>
</tr>
<tr>
<td>90Sr−90Y</td>
<td>≤ 90</td>
<td>≤ 53 ± 11</td>
<td></td>
</tr>
<tr>
<td>137Cs</td>
<td>≤ 1100</td>
<td>≤ 20</td>
<td></td>
</tr>
<tr>
<td>138La</td>
<td>≤ 840</td>
<td>≤ 108</td>
<td></td>
</tr>
<tr>
<td>152Eu</td>
<td>≤ 910</td>
<td>≤ 67</td>
<td></td>
</tr>
<tr>
<td>154Eu</td>
<td>≤ 970</td>
<td>≤ 143</td>
<td></td>
</tr>
<tr>
<td>176Lu</td>
<td>≤ 3</td>
<td>≤ 68</td>
<td></td>
</tr>
<tr>
<td>210Pb, 210Bi</td>
<td>6 ± 2</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>232Th</td>
<td>≤ 40</td>
<td>≤ 120 ± 50</td>
<td></td>
</tr>
<tr>
<td>238U</td>
<td>100 ± 14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>210Po</td>
<td>≤ 180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>210Pb−210Bi</td>
<td>≤ 60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
at the level of 53(11) mBq/kg and 120(50) mBq/kg, respectively, while limits were obtained for other potential contaminations. The measured activities and the limits are presented in Table 2.

In addition, we have observed the 1157 keV peak of the SrI$_2$(Eu) scintillator which could indicate double $\beta$ activity of $^{84}$Sr. Therefore, only lower half-life limits (lim $T_{1/2}$) can be set according to the formula: $\lim T_{1/2} = N \times \frac{t}{\eta \cdot T}$, where $N$ is the number of $^{84}$Sr nuclei in the sample, $\eta$ is the detection efficiency, $t$ is the measuring time, and $S$ is the number of events of the effect searched for which can be excluded at given confidence level (C.L.; all the limits obtained in the present study are given at 90% C.L.). The efficiencies of the detector for the double $\beta$ processes in $^{84}$Sr were calculated with the GEANT4 code [26] and DECAV0 event generator [27].

One positron can be emitted in the $e\beta^+$ decay of $^{84}$Sr with energy up to (765 ± 4) keV. The annihilation of the positron will give rise to two 511 keV $\gamma$ quanta leading to an extra rate in the annihilation peak. The part of the spectrum in the energy interval 450–550 keV is shown in Fig. 11.

There are peculiarities in both the spectra accumulated with the SrI$_2$(Eu) sample [(111 ± 14) counts at 510.9 ± 0.2 keV] and in the background [(12 ± 5) counts at 510.8 ± 0.3 keV], which can be ascribed to annihilation peaks. The main contribution to the 511 keV peak [(108 ± 22) counts] is coming from decays of $^{44}$Sc (daughter of $^{44}$Ti) present in the HPGe detector as contamination (see Section 3.4), (8 ± 3) counts corresponds to the background of the detector before the contamination. The difference in the areas of the annihilation peak: (−5 ± 26) counts, which can be

### Table 3

Radioactive contaminations of SrI$_2$(Eu) crystal scintillator. Data for NaI(Tl), CsI(Tl), LaCl$_3$(Ce), LaBr$_3$(Ce), Lu$_2$SiO$_5$(Ce), LuI$_2$(Ce) are given for comparison. Activities of LaBr$_3$(Ce), Lu$_2$SiO$_5$(Ce) and LuI$_2$(Ce) are calculated values based on the $^{134}$La and $^{176}$Lu half-lives [16], on the abundances of the isotopes [31] and on the chemical formula of the compounds.

<table>
<thead>
<tr>
<th>Scintillator</th>
<th>Activity (mBq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{40}$K</td>
<td>$^{134}$La</td>
</tr>
<tr>
<td>SrI$_2$(Eu)$^a$</td>
<td>≤ 255</td>
</tr>
<tr>
<td>NaI(Tl) [18]</td>
<td>&lt; 0.6</td>
</tr>
<tr>
<td>CsI(Tl) [30]</td>
<td></td>
</tr>
<tr>
<td>LaCl$_3$(Ce)</td>
<td></td>
</tr>
<tr>
<td>LaBr$_3$(Ce)</td>
<td></td>
</tr>
<tr>
<td>Lu$_2$SiO$_5$(Ce)</td>
<td></td>
</tr>
<tr>
<td>LuI$_2$(Ce)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ This work.

We do not observe any peaks in the spectrum accumulated with the SrI$_2$(Eu) scintillator which could indicate double $\beta$ activity of $^{84}$Sr. Therefore, only lower half-life limits (lim $T_{1/2}$) can be set according to the formula: $\lim T_{1/2} = N \times \frac{t}{\eta \cdot T}$, where $N$ is the number of $^{84}$Sr nuclei in the sample, $\eta$ is the detection efficiency, $t$ is the measuring time, and $S$ is the number of events of the effect searched for which can be excluded at given confidence level (C.L.; all the limits obtained in the present study are given at 90% C.L.). The efficiencies of the detector for the double $\beta$ processes in $^{84}$Sr were calculated with the GEANT4 code [26] and DECAV0 event generator [27].

One positron can be emitted in the $e\beta^+$ decay of $^{84}$Sr with energy up to (765 ± 4) keV. The annihilation of the positron will give rise to two 511 keV $\gamma$ quanta leading to an extra rate in the annihilation peak. The part of the spectrum in the energy interval 450–550 keV is shown in Fig. 11.

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**Fig. 9.** Energy spectra accumulated with the SrI$_2$(Eu) sample over 706 h, and without sample over 1046 h (BG) by ultra-low background HPGe $\gamma$ spectrometer deep underground. The energies of the $\gamma$ lines are in keV. The background was accumulated before the contamination of the HPGe set-up by $^{44}$Ti.

**Fig. 10.** Expected decay scheme of $^{84}$Sr [16]. The energies of the excited levels and of the emitted $\gamma$ quanta are in keV.

**Fig. 11.** Energy spectra accumulated with the SrI$_2$(Eu) sample over 706 h, and without sample over 1046 h (BG) by ultra-low background HPGe $\gamma$ spectrometer deep underground. The spectra are normalized on the time of the measurements with the SrI$_2$(Eu) sample.
attributed to electron capture with positron emission in $^{84}$Sr, gives no indication on the effect. In accordance with the Feldman–Cousins procedure [34] (here and hereafter we use this approach to estimate the values of $\lim S$ for all the processes searched for) we should take $\lim S = 38$ counts which can be excluded at 90% C.L. Taking into account the number of $^{84}$Sr nuclei in the sample ($6.5 \times 10^{19}$) and the detection efficiency ($\eta = 7.2\%$), we have calculated the following limit on the half-life of $^{84}$Sr relatively to $\beta^+$ decay:

$$T_{\beta^+} = \left(6.9 \times 10^{15}\right) \text{ yr.}$$

We cannot study the 0$\nu$2K capture in $^{84}$Sr to the ground state of $^{84}$Kr because the energies of the expected X-rays after the decay are too low in energy (the binding energy of electrons at K shell of krypton atom is only 14.3 keV [16]) while the energy threshold of the HPGe detector is $\approx 20$ keV.

In the neutrinoless double electron capture to the ground state of the daughter nucleus, in addition to the X-rays, some other particle(s) must be emitted to take away the rest of the energy. Usually one bremsstrahlung $\gamma$ quantum is assumed. The energy of the $\gamma$ quantum is expected to be equal to $E_\gamma = Q_{2\beta} - E_{b1} - E_{b2}$, where $E_{b1}$ and $E_{b2}$ are the binding energies of the first and of the second captured electrons on the atomic shell. The binding energies on the K, L1, L2 and L3 shells in Kr are equal to $E_K = 14.3$ keV, $E_{L1} = 1.9$ keV, $E_{L2} = 1.7$ keV, respectively [16]. Therefore, the expected energies of the $\gamma$ quanta for the 0$\nu$2K capture in $^{84}$Sr to the ground state of $^{84}$Kr are in the intervals:

(i) $E_\gamma = (1754–1762)$ keV for the 0$\nu$2K; (ii) $E_\gamma = (1767–1775)$ keV for the 0KL; (iii) $E_\gamma = (1779–1788)$ keV for the 0$\nu$2L process.

No events are detected (see Fig. 12a) in the energy intervals 1754–1762 and 1779–1788 keV, where the g.s. → g.s. 0$\nu$2K and 0$\nu$2L decay of $^{84}$Sr is expected.

According to Ref. [34] we should take 2.4 events as $\lim S$. Therefore, taking into account the detection efficiencies of the effects (4.0% and 3.9%, respectively), we can set the following limits on the processes:

$$T_{1/2}^{0\nu2K} (\text{g.s. } \rightarrow \text{ g.s.}) \geq 6.0 \times 10^{16} \text{ yr},$$

$$T_{1/2}^{0\nu2L} (\text{g.s. } \rightarrow \text{ g.s.}) \geq 5.9 \times 10^{16} \text{ yr}.$$

There are three events at energy $\approx 1770$ keV (due to $^{207}$Bi in the background) where the 0KL decay of $^{84}$Sr is expected. Taking in this case $\lim S = 7.4$ counts, while the detection efficiency is 3.9%, one can obtain the following half-life limit on the 0KL process in $^{84}$Sr:

$$T_{1/2}^{0\nuKL} (\text{g.s. } \rightarrow \text{ g.s.}) \geq 1.9 \times 10^{16} \text{ yr}.$$

To search for the double electron capture of $^{84}$Sr to the excited level $2^+$ of $^{84}$Kr, the experimental data were fitted in the energy interval 868–896 keV by a Gaussian function (to describe the gamma peak with the energy of 881.6 keV) and a polynomial function of second degree (to approximate the background, see Fig. 12b). The fit gives an area of $S = (-1.2 \pm 4.9)$ counts for the double $\beta$ process searched for, giving no evidence for the effect ($\lim S = 6.9$ counts). Taking into account the detection efficiency for the $\gamma$ quanta with energy 882 keV (5.8%), we set the following limit on the process:

$$T_{1/2}^{2\nu}(\text{g.s. } \rightarrow 881.6 \text{ keV}) \geq 3.1 \times 10^{16} \text{ yr}.$$

In the neutrinoless 2$\nu$ capture to the $2^+$ level, two $\gamma$ quanta should be emitted. The interaction of the additional $0.9$ MeV $\gamma$ quantum with the HPGe detector slightly decreases the efficiency for the 882 keV peak (5.0%) leading to the limit:

$$T_{1/2}^{0\nu2\beta}(\text{g.s. } \rightarrow 881.6 \text{ keV}) \geq 2.6 \times 10^{16} \text{ yr}.$$

All the half-life limits on 2$\beta$ decay processes in $^{84}$Sr, obtained in the present experiment, are summarized in Table 4. Previously, only one limit on 0$\nu$2$\beta^-$ mode was known; it was derived in Ref. [35] on the basis of the data of an old experiment with photoemulsions [36], and is two orders of magnitude lower than the one obtained in this work. It should be also noted that an experiment to search for 2$\beta$ decays in $^{84}$Sr with SrCl$_2$ crystal

<table>
<thead>
<tr>
<th>Process of decay</th>
<th>Decay mode</th>
<th>Level of daughter nucleus (keV)</th>
<th>$E_\gamma$ (keV)</th>
<th>$\eta$ (%)</th>
<th>$T_{1/2}$ (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0\beta^-$</td>
<td>0</td>
<td>g.s.</td>
<td>511</td>
<td>7.2</td>
<td>$&gt; 6.9 \times 10^{15}$</td>
</tr>
<tr>
<td>$0\beta^-$</td>
<td>2</td>
<td>g.s.</td>
<td>511</td>
<td>7.2</td>
<td>$&gt; 6.9 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>2K</td>
<td>g.s.</td>
<td>1754–1762</td>
<td>4.0</td>
<td>$&gt; 6.0 \times 10^{16}$</td>
</tr>
<tr>
<td></td>
<td>KL</td>
<td>g.s.</td>
<td>1767–1775</td>
<td>3.9</td>
<td>$&gt; 1.9 \times 10^{16}$</td>
</tr>
<tr>
<td></td>
<td>2L</td>
<td>g.s.</td>
<td>1779–1788</td>
<td>3.9</td>
<td>$&gt; 1.9 \times 10^{16}$</td>
</tr>
<tr>
<td>$2\nu$</td>
<td>0</td>
<td>$2^+$ 881.6</td>
<td>881.6</td>
<td>5.0</td>
<td>$&gt; 2.6 \times 10^{16}$</td>
</tr>
<tr>
<td>$2\nu$</td>
<td>2</td>
<td>$2^+$ 881.6</td>
<td>881.6</td>
<td>5.8</td>
<td>$&gt; 3.1 \times 10^{16}$</td>
</tr>
</tbody>
</table>
scintillator (Ø 2 × 1.5 cm) with 4× CsI(Tl) active shielding is in progress in the Yang–Yang underground laboratory [37] which has a potential to improve the limits presented here.

4. Conclusions

The radioactive contamination of the SrI₂(Eu) crystal scintillator obtained using a Stockbarger growth technique was estimated with the help of two approaches: by low background measurements in scintillation mode at sea level, and with the help of ultra-low background HPGe γ ray spectrometry deep underground. We have found a contamination of the scintillator by 137Cs, 226Ra and 228Th on the level of 0.05 Bq/kg, 0.1 Bq/kg and 0.01 Bq/kg, respectively. Only limits were set on the contamination of the detector by 138La at level of ≤ 0.02 Bq/kg, while the activities of 40K, 90Sr, 152Eu, 154Eu, 176Lu are below the detection limits of 0.1–0.3 Bq/kg. The intrinsic radiopurity of the SrI₂(Eu) scintillator is still far from NaI(Tl) and CsI(Tl) scintillators developed for low counting experiments, while it is three orders of magnitude better than that of the scintillation materials containing La, and five orders of magnitude better than that of the scintillators containing Lu.

The response of the SrI₂(Eu) crystal scintillator to α particles was estimated by using the trace contamination of the crystal by 226Ra. The α/β ratio was measured as 0.55 for 7.7 MeV α particles of 214Po. No difference in pulse shapes of scintillation for γ quanta and α particles was observed (the decay time was estimated to be: ≈ 1.7 μs).

Applicability of SrI₂(Eu) crystal scintillators to the search for the double beta decay of 84Sr was demonstrated for the first time. New improved half-life limits were set on double electron capture and electron capture with positron emission in 84Sr at level of $T_{1/2} \sim 10^{15} – 10^{16}$ yr.

The results of these studies demonstrate the possible perspective of the SrI₂(Eu) highly efficient scintillation material in a variety of applications, including low counting measurements.

An R&D of SrI₂(Eu) crystal scintillators is in progress. We are going to study radioactive contaminations of larger volume SrI₂(Eu) crystal scintillators both by ultra-low background HPGe γ spectrometry and low background scintillation counting at the Gran Sasso National Laboratory.

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References