Non-proportional response and energy resolution of pure SrI$_2$ and SrI$_2$:5\%Eu scintillators

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Abstract - Non-proportional response of the scintillation yield of un-doped SrI$_2$ and SrI$_2$:5\%Eu$^{2+}$ was studied using highly monochromatic synchrotron irradiation ranging from 10.5 keV to 100 keV. Measurements were performed at 80 K and 295 K for SrI$_2$, and at 80 K, 295 K, 450 K, and 600 K for SrI$_2$:5\%Eu. By making a dense data sampling around the iodine K-edge and using the recently developed K-dip spectroscopy method, the K-shell photoelectron response curves were reconstructed down to 500 eV. Proportionalities of X-ray response and K-shell photoelectron response of both crystals reveal temperature dependence. Energy resolution of the X-ray photopake was analyzed as a function of temperature and deposited energy. Energy resolution improves with better proportionality.

Index Terms - Scintillators, X-ray response, electron response, nonproportionality, strontium iodide.

I. INTRODUCTION

The recently re-discovered scintillator SrI$_2$:Eu$^{2+}$ is a material with a reported very high light yield and excellent energy resolution [1], [2]. Excellent proportionality with a deviation of less than 2\% in the 14 – 1274 keV $\gamma$ and X-ray energy range [1] makes SrI$_2$:Eu$^{2+}$ one of the most proportional scintillators available.

Currently, there are several methods of measuring non-proportional response ($nPR$). First of all, $nPR$ can be studied with a standard set of radioactive sources [3], [4]. However, for energies below, say, 5 keV the X-ray penetration depth is very small and the scintillator surface may affect the photon yield. The second method is to use the Scintillator Light Yield Non-proportionality Characterization Instrument (SLYNCI). It is based on the Compton Coincidence Technique (CCT) [5] and was developed by Choong et al. [6]. This method enables to measure accurate values of $nPR$ beginning from 3 keV electron energy from Compton scattered electrons that are not influenced by surface effects. The Compton scattered electron $nPR$ data of SrI$_2$:Eu$^{2+}$ obtained with SLYNCI shows very good proportionality in comparison to other well known scintillators [2]. The next method, the so-called K-dip spectroscopy method, is based on the photon response to highly monochromatic synchrotron X-ray irradiation in the 9-100 keV energy range. It has been recently developed by Khodyuk et al [7]. This method enables one to get information on electron response starting from energy as low as 100 eV, avoiding the influence of surface effects. A detailed description of this method can be found in section III.C.

In this paper we apply the K-dip spectroscopy method to study $nPR$ and energy resolution of pure SrI$_2$ and SrI$_2$:5\%Eu. The arising questions are whether such a good proportionality is an intrinsic property of SrI$_2$ or due to the doping of Eu, and how $nPR$ is affected by temperature. With studies on LaBr$_3$ scintillators, we for the first time discovered that proportionality can be improved with temperature decrease [10]. Except for [14], no studies on the temperature dependence of $nPR$ of SrI$_2$:Eu have been reported so far, which motivated us to perform this research. We studied the $nPR$ of scintillation yield and energy resolution of SrI$_2$ and SrI$_2$:5\%Eu in the 10.5-100 keV X-ray energy range between 80 K and 600 K. Using the K-dip spectroscopy, we obtained electron response data down to 500 eV. Energy resolution is a crucial parameter required for good scintillation performance. Several contributions that worsen the total energy resolution are treated in this work: 1) the contribution from the PMT and Poisson statistics, 2) from the non-proportional response of the scintillator, 3) from inhomogenieties in the crystal, and 4) from self-absorption of scintillation photons. We applied the experimental results to analyze the energy resolution and its components as a function of temperature, and we found that better proportionality improves the energy resolution.

II. EXPERIMENT

SrI$_2$ and SrI$_2$:5\%Eu crystals were grown from commercially available SrI$_2$ and EuI$_2$ starting material with a conventional crystal growth method from the melt. For this work, we selected two transparent fragments of the original crystals of about 0.05 cm$^3$ each. The experiment was performed at the X-1 beam line at the Hamburger Synchrotronstrahlungslabor (HASYLAB) synchrotron radiation facility in Hamburg. A highly monochromatic pencil X-ray beam in the energy range 10.5 – 100 keV was used as an excitation source. The setup was described in detail in [8]. The sample was fixed at the bottom of a parabolic-like
stainless steel reflector covered with Al foil. The reflector was mounted on a cold finger of a Janis VPF-800 Cryostat operated with a LakeShore 333 Temperature Controller [11]. The reflector faced a Hamamatsu R6231-100 photomultiplier tube (PMT), which was placed outside the cryostat and kept at room temperature during all experiments. The PMT was connected to a Cremat CR-112 pre-amplifier and an Ortec 672 spectroscopic amplifier with 10 µs shaping time.

The number of the photoelectrons produced in the PMT per MeV of absorbed energy was determined from the ratio of the peak position of the $^{137}$Cs 662 keV or $^{241}$Am 59.5 keV photopeak to the position of the mean value of the so-called single photoelectron peak in a pulse-height spectrum [12]. For pure SrI$_2$, the nPR at X-ray energy ($E_x$) was defined as the ratio between the number of photoelectrons per MeV observed at $E_x$ and that observed at 662 keV. For SrI$_2$:5%Eu, we normalized the nPR to 100% at 100 keV. Energy resolution was defined as the Full Width at Half Maximum intensity (FWHM) over the peak position of the photopeak in a pulse-height spectrum.

III. RESULTS

Firstly, we review some results from previous work [13] that are relevant for understanding of the nPR data on SrI$_2$:Eu$^{2+}$. X-ray excited emission spectra of pure SrI$_2$ and SrI$_2$:5%Eu are shown in Fig. 1. Pure SrI$_2$ emission at 80 K consists of three broad emission bands at 360 nm, 430 nm, and 570 nm. The emissions at 360 nm and 430 nm are quenched at 295 K. The relatively narrow SrI$_2$:5%Eu emission at 430 nm is due to 5d-4f emission in Eu$^{2+}$. The photoelectron yield, obtained from $^{137}$Cs 662 keV γ-ray pulse height spectra recorded with a shaping time of 10 µs at room temperature, is 30000 phe/MeV for SrI$_2$:5%Eu and 7000 phe/MeV for undoped SrI$_2$. These values correspond to 85000 photons/MeV and 40000 photons/MeV, respectively. Scintillation decay time varies from 0.5 µs at 295 K to 1.5 µs at 80 K in SrI$_2$, and from 0.5 µs at 80 K to 4.5 µs at 600 K in SrI$_2$:5%Eu. With a shaping time of 10 µs and scintillation decay time of 4.5 µs ballistic deficit does not exceed 10%.

A. Scintillation non-proportionality to X-rays

Figure 2 shows the nPR data as a function of X-ray energy $E_x$ in SrI$_2$ at 80 K and 295 K. The nPR was measured for $E_x$ between 10.5 keV and 100 keV with a step size of 5 keV. A much finer step size of 100 eV was used around the K-shell electron binding energies, the so-called K-edges. The K-edge in Sr is $E_{KSr}=16.105$ keV, and that in I is $E_{KI}=33.169$ keV. As shown in Fig. 2, discontinuities in nPR appear at both energies. The size of the drop in nPR at the K-edge is called the K-dip magnitude. Detailed descriptions of nPR curve shapes and examples obtained with the same method for LuAG, GSO, LSO, LPS, NaI:Tl, LaCl$_3$:Ce, and LaBr$_3$:Ce scintillators can be found in [7] – [9]. Figure 2 shows that the nPR of SrI$_2$ improves significantly with decrease in temperature. Together with the improved nPR, the K-dip magnitude decreases. Some relevant nPR data and characteristics from Fig. 2 are compiled in Table I.
Fig. 3. $nPR$ of Sr$I_2$:5%Eu as a function of X-ray energy. Squares represent the values at 80 K; circles - at 295 K; triangles - at 600 K. The solid lines are drawn to guide the eye. Note that the inset and the main graph have different normalization points.

**B. Energy resolution of X-ray total absorption peaks**

The previous section revealed temperature dependence in the $nPR$ data. The next goal then is to discover whether improvement of the $nPR$ results in improvement of the energy resolution $R$ of the X-ray photopeak.

Data connected by curves 1 and 3 in Figure 4 show the observed energy resolution of pure Sr$I_2$ as a function of X-ray energy on a double-log scale. The resolution at 80 K is on average 1.46 times better than that at 295 K. The insets in Fig. 4 show a step-like increase of the resolution at the Iodine K-edge energy on an enlarged scale.

Figure 5 shows the energy resolution of the X-ray photopeak of Sr$I_2$:5%Eu as a function of X-ray energy. Squares represent the values at 80 K; circles - at 295 K; pointed up triangles - at 450 K; pointed down triangles - at 600 K. The solid lines are drawn to guide the eye.

Figure 6 shows the photoelectron yield and energy resolution of pure Sr$I_2$ and Sr$I_2$:5%Eu as a function of temperature measured in the cryostat under $^{137}$Cs 662 keV γ-ray excitation. In pure Sr$I_2$, the photoelectron yield gradually quenches from 2000 phe/MeV at 80 K with increase in temperature. In Sr$I_2$:5%Eu, the yield increases on heating from 80 K to 100 K, and then gradually decreases with increase in temperature to 600 K. The energy resolution anti-correlates with the photoelectron yield. The energy resolution is optimal at about 150 K, which agrees with the results obtained by Lam et al. [14]. Note that because of the 15-20% scintillation light collection efficiency for a sample mounted in the cryostat in comparison with the almost 100% efficiency for a sample optically coupled to the window of the PMT, the photoelectron yield is rather low and energy resolution is rather poor.
Fig. 6. Top panel, photoelectron yield as a function of temperature. Squares represent the data for SrI$_2$:5%Eu; circles – for pure SrI$_2$. Bottom panel, energy resolution $R$ at 662 keV as a function of temperature: solid squares represent the data for SrI$_2$:5%Eu, solid circles – pure SrI$_2$. Calculated with Eq. (2) statistical contribution $R_{MC}$: open squares – SrI$_2$:5%Eu, open circles – pure SrI$_2$.

C. Scintillation non-proportionality to K-shell photoelectrons

Because of the short attenuation length, most X-rays with energies below 9 keV are absorbed close to the scintillator surface which may affect the light yield. Low energy X-rays also cannot penetrate through the packaging and reflecting covering around the scintillator anymore. This limits the standard method to determine nPR to X-ray energies of about 5 keV. As an alternative to measuring the scintillation response to the low energy X-rays, one may analyze nPR data at energies just above the K-edge. The method is called K-dip spectroscopy. It enables one to reconstruct the nPR curve down to 100 eV.

The method works as follows. The response of a scintillator to an X-ray photon that has interacted with a K-shell photoelectron is equivalent to the response of a scintillator to a sum of two main interaction products: 1) a K-shell photoelectron plus 2) electrons and photons emitted due to the sequence of processes following relaxation of the hole in the K-shell, the so-called K-cascade response. Our strategy is to employ X-ray energies just above $E_{KI}$ [7]. The K-cascade response is assumed independent of the original X-ray energy. This response is found by tuning the X-ray energy very close above $E_{KI}$. By subtracting the K-cascade response from the total X-ray response we are left with the response in photoelectrons from the K-shell photoelectron alone with energy $E_{X} - E_{KI}$. The K-shell photoelectron-nPR curve is then obtained by the $N^\text{PMT}_{\text{phe}}$/MeV at the energy of the K-photoelectron divided by the $N^\text{PMT}_{\text{phe}}$/MeV measured at 662 keV. A more detailed description of the K-dip spectroscopy method can be found in [8].

The K-shell photoelectron nPR obtained with the K-dip spectroscopy method is shown in Figure 7. Going down from 67 keV, the nPR of pure SrI$_2$ at 295 K and at 80 K in Fig. 7 increases by 3-4%, reaching a maximum near 10-25 keV. With further decrease in electron energy the nPR decreases. As for the X-ray response in Fig. 2, the K-shell photoelectron response of SrI$_2$ is most proportional at 80K. Going down from 67 keV, the nPR of SrI$_2$:5%Eu decreases with decrease in electron energy. At 295 K, the K-shell photoelectron response of SrI$_2$:5%Eu is slightly better proportional than that of pure SrI$_2$.

Fig. 7. The K-shell photoelectron response as a function of the electron energy obtained with the K-dip spectroscopy method. Solid squares represent the values for SrI$_2$:5%Eu at 295 K, solid circles - for SrI$_2$ at 80K and solid triangles - for SrI$_2$ at 295 K. Open circles represent the data acquired with SLYNCI [15].

Fig. 8 shows the K-shell photoelectron response of SrI$_2$:5%Eu at 80, 295, 450, and 600 K. The nPR was obtained by the $N^\text{PMT}_{\text{phe}}$/MeV at the energy of the K-shell photoelectron divided by the $N^\text{PMT}_{\text{phe}}$/MeV at 6.8 keV. The normalization point was arbitrarily chosen. The K-shell photoelectron response of SrI$_2$:5%Eu is the most proportional at 80 K at energies between 500 eV and 67 keV.

Fig. 8. The K-shell photoelectron response in SrI$_2$:5%Eu as a function of the electron energy obtained with the K-dip spectroscopy method. Squares represent the values at 80 K, circles - at 295 K, pointed up triangles - at 450 K, and pointed down triangles - at 600 K. Solid lines are drawn to guide the eye.
The Compton scattered electron demonstrates that both for pure and doped SrI$_2$ the contribution from crystal inhomogenieties, and proportional than that of pure SrI$_2$. Second, the nPR of SrI$_2$ and SrI$_2$:5%Eu depend on temperature. In both crystals the K-dip magnitude decreases together with the improved proportionality.

Similar observations are made for the 0.5-66.8 keV K-shell photoelectron nPR data in Figures 7 and 8. Again, at room temperature the response of SrI$_2$:5%Eu is more proportional than that of SrI$_2$. Second, the K-shell photoelectron nPR of both crystals depends on temperature. The Compton scattered electron nPR of SrI$_2$:6%Eu obtained with SLYNCI [15] is added in Fig. 7 and can be compared with the K-shell photoelectron nPR data of SrI$_2$:5%Eu. The SLYNCI Compton scattered electron nPR was normalized in [15] at 446 keV, while our K-shell photoelectron nPR is normalized at 662 keV. Both data sets agree within a few percent with each other. Note that, the SLYNCI nPR tends to decrease somewhat more strongly with decrease of electron energy than the K-shell photoelectron nPR. The true reason is not yet clear. It may be caused by differences in the methods of data analysis and normalization or by properties of the scintillator such as different Eu concentration.

The energy resolution as shown in Fig. 4, 5, and 6 is determined by different contributions that in first approximation can be regarded as independent from each another. One may then write for the observed energy resolution:

$$R^2 = R^2_M + R^2_{nPR} + R^2_{inh} + R^2_{tr}$$

(1)

where $R_M$ is the contribution from the PMT gain and photon detection Poisson statistics, $R_{nPR}$ is the contribution from the non-proportional response of the scintillator, $R_{inh}$ is the contribution from crystal inhomogenieties, and $R_{tr}$ is the contribution from the transfer of the scintillation photons from the crystal to the PMT.

$R_M$ is given by

$$R_M = 2.35 \sqrt{\frac{1 + \text{var}(M)}{N_{phe}^{PMT}}}$$

(2)

where var(M) is the fractional variance in the PMT gain, which is 0.28 for the used Hamamatsu R6231-100 [16] PMT.

Figure 2 shows that in SrI$_2$ the X-ray nPR improves with temperature decrease. Figure 4 shows that the energy resolution of the X-ray photopeak also improves with temperature decrease. However, this does not yet show that the improved nPR results in the improved $R$. Fig. 6 demonstrates that both for pure and doped SrI$_2$ the photoelectron yield versus temperature anti-correlates with the energy resolution, indicating a considerable contribution of $R_M$ to $R$. To verify whether better proportionality improves $R$, we calculated the values of $R_M$, and compared them to $R$. $R_M$ were calculated with Eq. (2) and the number of photoelectrons $N_{phe}^{PMT}$ produced in the PMT. The values of $R_M$ are shown as the data points connected by curves 2 and 4 in Figure 4. The values of $R$ and $R_M$, for example, at 60 keV, are compiled in Table II.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature, K</th>
<th>$N_{phe}^{PMT}$</th>
<th>R, %</th>
<th>$R_M$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrI$_2$</td>
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<td>135</td>
<td>23.3</td>
<td>22.8</td>
</tr>
<tr>
<td></td>
<td>295 K</td>
<td>70</td>
<td>33.5</td>
<td>32.4</td>
</tr>
<tr>
<td>SrI$_2$:5%Eu</td>
<td>295 K</td>
<td>265</td>
<td>16.7</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td>600 K</td>
<td>180</td>
<td>23.9</td>
<td>19.9</td>
</tr>
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</table>

Figure 4 shows that in SrI$_2$ $R$ is 1-2% larger than $R_M$ at 80 K and about 1-5% larger at 295 K. The difference between $R$ and $R_M$ is comparable to the systematic error of $R_M$, which was caused by relatively small number of produced photoelectrons. Calculation of the contribution from $R_{nPR}$, $R_{inh}$ and $R_{tr}$, which is equal to $\sqrt{R^2 - R_M^2}$ according to Eq. (1), is therefore meaningless. However, the average difference between $R$ and $R_M$ at 295 K is larger than that at 80K. Assuming that $R_M$ and $R_{inh}$ are not temperature dependent, this larger difference indicates on the higher contribution of $R_{nPR}$ at 295 K than at 80 K. This is in agreement with the worsening nPR in Fig. 2.

The next observation, showing the influence of nPR on $R$, is the step-like increase of $R$ at $E_{KI}$, depicted in the insets in Fig. 4. At 80K, $R$ increases by $\Delta R=1\%$, whereas $R_M$ increases only by $\Delta R_M=0.2\%$. At 295K $\Delta R=1.5\%$, whereas $\Delta R_M=0.6\%$. Since at both temperatures $R=0$ and $R_M$ at 295 K is larger than that at 80K, $R_M$ is comparable to the systematic error of $R_M$. The result is shown in Fig. 9. Although at both temperatures the contribution of $R_M$ dominates, the difference between $R$ and $R_M$ at 600 K is significantly larger than that at 295 K. This observation agrees with poorer nPR at 600 K in Fig. 3, and it is probably related to higher self-absorption at 600 K [13].

In SrI$_2$:Eu, self-absorption might worsen energy resolution. Eu absorbs and re-emits its own emission with very high probability; a probability that increases with increase of sample size, Eu concentration and temperature [13]. Sturm et al. [17] demonstrated a fluctuation of the light yield depending on the position of the interaction of the γ-ray photon with the SrI$_2$:Eu crystal. When the events, originating from different spots in the same crystal, are accumulated, it will deteriorate the total energy resolution. In SrI$_2$:5%Eu, X-ray attenuation length increases from 50 μm for 15keV X-rays to 1.5 mm for 100keV X-rays. The attenuation length is
comparable to the thickness of the sample we used, and might therefore affect the energy resolution.

![Graph showing energy resolution vs. deposited energy for SrI2:5%Eu](image)

Fig. 9. Energy resolution $R$ of the X-ray photopeak of SrI2:5%Eu as a function of X-ray energy: filled triangles (curve 1) represent the values at 600 K; filled circles (curve 3) – at 295 K. The statistical contribution function of X-ray energy: filled triangles (curve 1) represent the values at 600 K; open circles (curve 4) – at 295 K. The solid lines are drawn to guide the eye.

V. CONCLUSION

The proportionality and energy resolution of pure SrI2 and SrI2:5%Eu were measured using highly monochromatic synchrotron irradiation in the 10.5-100 keV energy range. Both scintillators demonstrate very good proportionality. Using the K-dip spectroscopy method the K-shell photoelectron response curves were obtained down to 500 eV. Both the X-ray $nPR$ and the K-shell photoelectron $nPR$ depend on temperature and Eu doping:

- At room temperature, SrI2:5%Eu is more proportional than SrI2.
- In SrI2, $nPR$ is better at 80 K than at 295 K.
- The X-ray $nPR$ of SrI2:5%Eu improves on heating from 80 K to 295 K, and then worsens with further heating to 600 K. The K-shell photoelectron response demonstrates the best proportionality at 80 K.

Anti-correlation between the photoelectron yield and energy resolution $R$ was observed in both crystals, indicating a considerable contribution of $R_M$ to $R$ for the measurements inside the cryostat. Nevertheless, the analysis of $R$, $R_M$, and $nPR$ as function of temperature showed that improved $nPR$ results in improved $R$.

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