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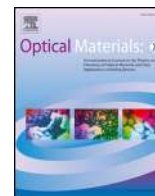
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Invited Article

The quest for high resolution γ -ray scintillators

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A B S T R A C T

There are many properties of scintillators that are of importance for application. One property is the energy resolution for the detection of γ -rays, and during past 20 years we witnessed enormous progress. The state of the art resolution for the detection of 662 keV γ photons was 5–6% at the end of the 20th century, and today scintillators with 2.2% resolution are commercially available. This work will provide a review on the development of high resolution chloride, bromide, and iodide based scintillators that occurred since the discovery of the $\text{LaCl}_3:\text{Ce}^{3+}$ scintillator in 2000. Bandgap engineering and co-doping to eliminate afterglow or to improve proportionality have become new tools in optimizing scintillator performance. At the end of the review the prospects for the development of scintillators with resolution <2% are addressed together with new research strategies that might be required to accomplish that.

1. Introduction

The energy resolution is a key parameter of a scintillation detector, and in this work it will be defined as the full width at half maximum intensity of the total absorption peak of a γ -ray photon in a so-called pulse height spectrum. Fig. 1 shows the best ever recorded pulse height spectrum for the detection of γ -ray photons from a ^{137}Cs -source with a scintillation detector. It was obtained with a small Sr^{2+} co-doped $\text{LaBr}_3:5\%\text{Ce}^{3+}$ scintillator coupled to a Hamamatsu super-bialkali photomultiplier tube [1,2]. The total absorption peak at 662 keV shows an unprecedented energy resolution of 2.04%. Beside energy resolution, there are many other aspects of scintillators like scintillation speed, stopping power, production cost, timing resolution, type of application, type of activator (Ce^{3+} , Eu^{2+} , Tl^+ , Pr^{3+} etc.), type of compound (oxides, halides, sulfides), crystal dimensions, afterglow, detection modalities (continuous mode or X-ray, γ -ray, thermal neutrons event mode) [3]. The aspects are clearly too many to cover in a single review. This work will limit to the quest for high resolution scintillators with a focus on what type of compounds and activators were studied together with the ideas and research strategies behind it.

Back in 2002, Marvin Weber presented a review on the inorganic scintillators of "today and tomorrow" [4], and as a tribute to his accomplishments in the field of luminescence and scintillation this work will start where he ended and will borrow now and then terminology and ideas from his review. Fig. 2 shows for example the history of scintillator discovery up to today. A similar figure was presented by Weber, and he distinguished three phases. Phase I is the early phase following Röntgen's discovery of X-rays and the discovery of α -particles beginning 1900. Scintillation light and pulses were detected with the human eye. The invention of the photomultiplier tube (PMT) around

the 1940'ties triggered phase II. The most famous scintillator $\text{NaI}:\text{Tl}^+$ was discovered by Hofstadter [5,6] in 1948. After 1960 industry was able to purify the rare earths to a degree that the lanthanides became available as luminescence center. Phase III from 1970 to 2000 covers the period where lanthanide activated scintillators were developed and crystal growth technology was able to synthesize high melting point oxide single crystals. During phase III the important scintillator $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) was discovered by Weber and Monchamp [7] in 1973, $\text{Gd}_2\text{SiO}_5:\text{Ce}^{3+}$ (GSO) by Takagi and Fukazawa [8] in 1983, $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ (LSO) by Melcher and Schweitzer [9] in 1992, and $\text{LaCl}_3:\text{Ce}^{3+}$ by van Loef et al. [10] in 2000.

In this work the materials and research strategies in what will be called phase IV in scintillator research and development will be reviewed. Phase III then ended with the discovery of $\text{LaCl}_3:\text{Ce}^{3+}$. During phase IV mostly lanthanide (Ce^{3+} and Eu^{2+}) activated halide (chloride, bromide, iodide) compounds were developed and discovered. Also new research strategies like bandgap engineering and co-doping were used to improve the scintillator properties. The fundamental new insight that has been gained during phase IV will be addressed. In discussing strategies, this work will again follow Weber who distinguished three sorts of strategies in scintillation research; 1) the accidental discovery (*serendipity*), 2) the Edisonian approach of trial and error (*cook and look*), and 3) the rational design (*enlightment*). At the end of this review, some recent developments are addressed that may develop into new lines of research in the tomorrow phase V.

Other reviews have appeared on scintillators during phase IV. Melcher in 2005 [11] addressed the drivers and strategies of future scintillator development that still apply to large extend today. Krämer et al. in 2006 reviewed the development of the Ce^{3+} doped halide scintillators. Nikl and Yoshikawa [13] addressed the research trends

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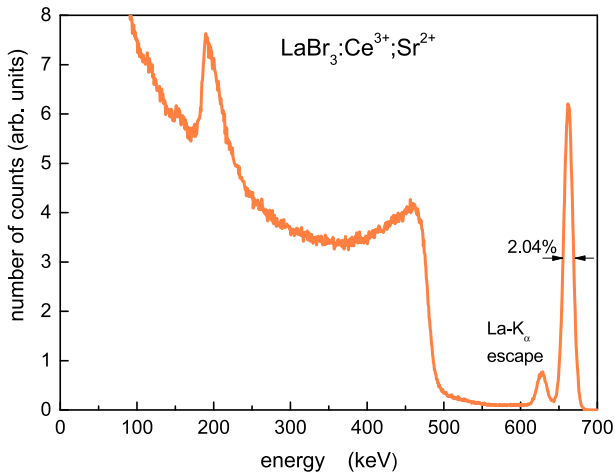


Fig. 1. The ^{137}Cs pulse height spectrum recorded with a Sr^{2+} co-doped $\text{LaBr}_3:\text{Ce}^{3+}$ scintillator by Alekhin et al. in Refs. [1,2].

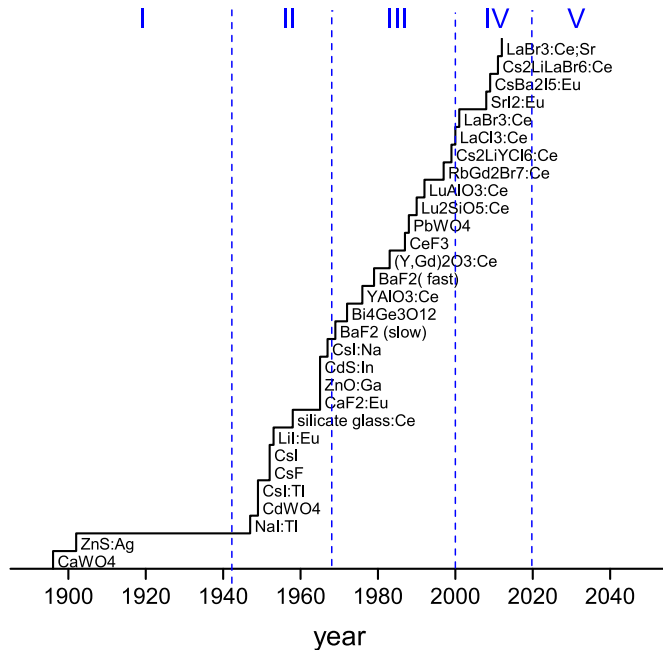


Fig. 2. History of scintillator discovery that distinguishes phases I to IV and phase V for future discoveries.

covering the period 2005–2015, i.e., large part of phase IV. It covers the development of the Ce^{3+} and Eu^{2+} doped halides, the garnet compounds, aluminum perovskite compounds, and the ortho- and pyro-silicates. Most recently in 2019, Maddalena et al. [14] presented an extensive review addressing traditional scintillators, lanthanide activated scintillators, scintillation mechanism and applications, and recent developments with the halide perovskite and nano-structured scintillators. Rather than updating these reviews, the focus will be in this work entirely on the energy resolution and research strategies to develop high resolution scintillators. Energy resolution appears to be highest for chloride, bromide, and iodide compounds and most research activity during phase IV went into that direction. This review will therefore limit to the halide family of compounds. Besides halides, many other scintillators were studied. To obtain a good overview, one may consult the crystal data base developed and maintained by Steven Derenzo et al. at the Lawrence Berkeley National Laboratory [15] where basic properties like density, light yield (photons/MeV), decay time, emission peak and energy resolution at 662 keV γ -detection together with

references can be found. Within the halide family of compounds this review will, apart from few special cases, only address those compounds and reports that show energy resolution better than 10% at 662 keV.

2. The energy resolution of scintillators

One may distinguish three main contributions to the energy resolution R for γ -ray detection [16–18].

$$R^2 = R_{stat}^2 + R_{np}^2 + R_{in}^2 \quad (1)$$

where R_{stat} is mainly determined by the standard deviation in the number (N_{dp}) of detected photons and R_{np} is due to the non-proportional response of the scintillator. All the rest is contained in R_{in} and includes a non-uniform response at different locations in the scintillator, non-uniformities in the light collection efficiency and light conversion efficiency in the photon detector. This contribution can be minimized by perfect crystal synthesis, perfect packaging technology and excellent photon detector properties. R_{stat} is a fundamental characteristic of the scintillator with photon detector, and determined by Poisson statistics

$$R_{stat} = 2.36 \sqrt{\frac{1 + v(M)}{N_{dp}}} \quad (2)$$

where $v(M)$ is a contribution from the variance in the electron multiplication in e.g. the PMT or avalanche photodiode (APD). Clearly we need a high light output scintillator emitting at wavelengths where the quantum efficiency (QE) of the photon detector is maximal. The fundamental limit in N_{dp} at 662 keV can be expressed as

$$N_{dp} = QE \times \frac{662000}{\approx 2.5 E_{VC}} \quad (3)$$

where E_{VC} the energy difference between the valence band (VB) top of conduction band (CB) bottom. The value of ≈ 2.5 arises from momentum conservation in the electron-electron interactions [19].

The best energy resolution of 2% measured for Sr^{2+} co-doped $\text{LaBr}_3:5\% \text{Ce}^{3+}$ in Fig. 1 was obtained with a superbialkali photomultiplier tube detecting $N_{dp} = 24300$ photons at 662 keV. With $v(M) \approx 0.27$ [2], Eq. (2) then predicts a fundamental statistical limit of 1.7%.

Even when $R_{in} = 0$, the statistical limit is never reached because of the so-called non-proportional response which means that the light yield of the scintillator is not proportional to the energy of the electrons that creates (parts of) the ionization track [17,18]. This is shown for several scintillators in Fig. 3 as determined by monochromatic X-ray excitation [1,20–22]. Here the scintillator response in ph/MeV as function of X-ray energy is shown relative to that at 662 keV. Only for the ideal response, R_{np} will not contribute. NaI:Tl shows a strong positive deviation in the 10–100 keV region and LSO a strong negative deviation. The relatively poor resolution of 6–8% displayed by traditional scintillators like NaI:Tl $^{+}$, CsI:Tl $^{+}$, BGO, $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ from phase II and III is all caused by such poor proportionality [17,23]. The $\text{LaBr}_3:\text{Ce}^{3+}$ scintillator discovered in 2001 by van Loef et al. [24] displays at least two times better resolution of 2.8%, and Fig. 3 shows a response that is much closer to the ideal one. A small addition of 50 ppm Sr^{2+} dramatically improves the proportionality towards the ideal response with as consequence the unprecedented energy resolution of 2.04% in Fig. 1.

Since R_{np} appears a limiting factor, many research activities started around 2007 to gain better insight in the theory and processes responsible for non-proportionality, see e.g. Refs. [25–31]. Also many experimental studies were conducted to quantify the non-proportionality as function of electron energy [20–22,32], temperature [33–36], time [37,38], and co-dopant concentration [39,40]. The results of all this work is the realization (*enlightment*) that non-proportionality is

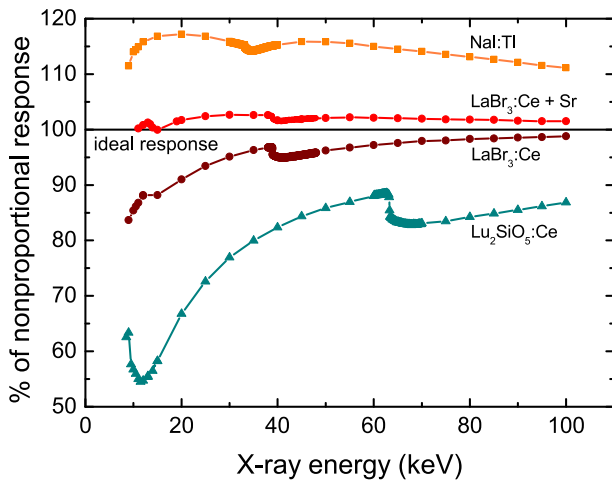


Fig. 3. The non-proportionality curves for various scintillators as function of X-ray energy.

determined by many different mechanisms of radiation less recombination of free electrons with holes (quenching) that take place inside the ionization track on a ps time and nm length scale. Those quenching processes depend not only on ionization density and temperature, but also on defect concentration.

3. Phase IV in scintillation research

Phase 4 witnessed several discoveries that initiated 3 main lines of research as illustrated in Fig. 4. 1) The research on Ce^{3+} activated halides (curve a) increasing from 2000 and diminishing around 2014 with a reviving line of research (curve d) on Ce^{3+} activated Tl-based halides that started in 2015; 2) the research on Eu^{2+} activated halides (curve b) starting from 2008; and 3) the research on co-doped scintillators (curve c) containing an activator for the luminescence and a co-dopant to either improve properties or to add functionality increasing from 2012.

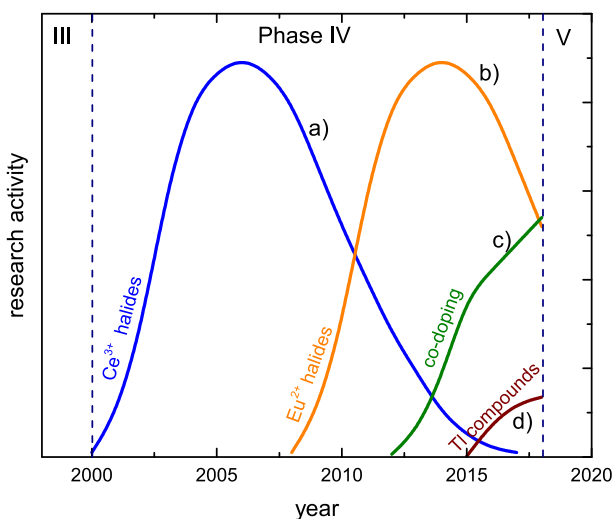


Fig. 4. Main lines of research during phase IV of scintillator discovery. a) The research on Ce^{3+} activated halide compounds inspired by the discovery of $LaBr_3:Ce^{3+}$, b) the research on Eu^{2+} doped halide compounds initiated by the re-discovery of $SrI_2:Eu^{2+}$, c) the increased research on co-doped scintillators stimulated by discovery of Sr^{2+} co-doped $LaBr_3:Ce^{3+}$, d) the research on Ce^{3+} activated Tl-based compounds initiated by $Tl_2LiGdCl_6$.

Table 1

Yield (ph/MeV) and resolution R (%) for Ce^{3+} doped halide compounds. Reference to the first report and the reports with best resolution (<10%) or light yield (photons/MeV) are given.

compound	year	R	yield	Ref.
K_2LaCl_5	1995	5.1	29000	[41,42,115]
$RbGd_2Br_7$	1997	3.8	54000	[116]
Cs_2LiYCl_6	1999	4.5	22000	[46,47,50]
$LuBr_3$	1999	6	32000	[43,117]
$LuCl_3$	1999	11.4	5400	[43,117]
$LaCl_3$	1999	3.1	46000	[10,43]
$LaBr_3$	2001	2.8	61000	[24]
$GdBr_3$	2001	>10	44000	[118]
Cs_2LiYBr_6	2002	7	23600	[47,119]
LuI_3	2004	3.3	98000	[45,120,121]
K_2LaI_5	2005	4.5	55000	[115]
K_2LaBr_5	2005	5	40000	[115]
$Cs_2LiLuCl_6$	2005	–	7000	[122]
$Cs_2NaLaBr_6$	2006	3.9	46000	[123,124]
$PrBr_3$	2006	6.9	21000	[125]
$Cs_2NaLuBr_6$	2006	5.8	10500	[123]
Cs_2NaYBr_6	2006	6.3	9500	[123]
Cs_3LaBr_6	2007	4.9	32500	[124,126,127]
$Cs_3Lu_2I_9$	2007	9	22800	[126]
Rb_2LiYBr_6	2007	4.7	23000	[128]
YI_3	2008	9.3	99000	[129]
$Rb_2LiLaBr_6$	2008	4.8	33000	[48]
GdI_3	2008	4.7	44000	[129,130]
$SrI_2:Ce; Na$	2008	6.4	16000	[60]
Rb_2LiYBr_6	2008	4.7	23000	[48]
$BaBr_2:Ce; K$	2008	9.8	10300	[58]
$NaGdCl_4$	2009	n.r.	39400	[131]
$LiGdCl_4$	2009	n.r.	64600	[131]
$Cs_2LiGdCl_6$	2009	5	20000	[132]
$Cs_2LiLaCl_6$	2009	3.4	35000	[49,50]
$Cs_2LiGdCl_6$	2010	5	20000	[133]
$Cs_2LiLaBr_6$	2011	2.9	60000	[50]
$CsGd_2Cl_7$	2011	n.r.	38000	[134]
KGd_2Cl_7	2011	10	30000	[135]
$Rb_2LiGdCl_6$	2013	6.8	18500	[136]
$Cs_2NaGdBr_6$	2013	3.3	48000	[137,138]
$Cs_2NaLaCl_6$	2014	4.4	26400	[124]
$Cs_2NaLaBr_3I_3$	2014	2.9	58000	[139]
$Cs_2NaGdCl_6$	2014	4	27000	[138,140]
$Cs_2NaYBr_3I_3$	2014	3.3	43000	[139]
Cs_3LaCl_6	2014	8.6	16000	[124,127]
Cs_3GdCl_6	2014	4.5	24500	[138]
Cs_3GdBr_6	2014	4	47000	[138]
$Cs_2LiGdBr_6$	2014	7.1	30500	[142]

3.1. The Ce^{3+} activated halides

In Table 1 the energy resolution at 662 keV γ detection and the photon yield at that energy in photons per MeV absorbed γ photon energy (ph/MeV) for Ce^{3+} activated scintillators are listed in order of the year of first report. In the year 2000 and 2001, Technical University Delft together with Bern University discovered the scintillation properties of Ce^{3+} activated $LaCl_3$ and $LaBr_3$ [10,24]. The outstanding energy resolution of 2.8% for the detection of 662 keV gamma quanta together with 35 ns decay time for $LaBr_3:Ce^{3+}$ in the initial report was a leap forward in scintillator resolution performance. Also the release of research funds after the 2001, 9–11 terrorist attack on the Twin Towers in New York triggered much scintillation research activity in the Ce^{3+} doped halide family of compounds (chlorides, bromides, iodides), and many Ce^{3+} activated halide scintillators were studied since [15].

Considering the importance of the $LaBr_3:Ce^{3+}$ scintillator some personal words will be spent on how that invention came to be. In 1992, H.U. Güdel and K. W. Krämer from Bern University (Switzerland) kindly provided C.W.E. van Eijk and P. Dorenbos from Delft University (The Netherlands) with Tb^{3+} doped Cs_2LiYCl_6 and Ce^{3+} doped K_2LaCl_5 from their collection. $K_2LaCl_5:Ce^{3+}$ appeared to be a very good scintillator and this started a long standing and still active collaboration in

scintillator research and development between Delft and Bern University. Serendipity led to the discovery of $\text{K}_2\text{LaCl}_5:\text{Ce}^{3+}$ published in 1995 [41,42] with 5.1% energy resolution at 662 keV and 29000 ph/MeV. This raised our interest in Ce^{3+} doped halides, and the scintillation properties of Ce-doped LuCl_3 , LuBr_3 , and LaCl_3 compositions (*cook and look*) were first reported by us in 1999 [43]. With 0.56% Ce^{3+} , the properties of LaCl_3 were not yet that extraordinary. Inspired by the similarity in scintillation mechanism (*enlightment*) between $\text{LaCl}_3:0.56\% \text{Ce}^{3+}$ and $\text{K}_2\text{LaCl}_5:\text{Ce}^{3+}$ [42] it was decided to synthesize LaCl_3 with higher Ce^{3+} concentration. One year later in 2000 van Loef et al. reported the 3.1% energy resolution and 46000 ph/MeV for $\text{LaCl}_3:10\% \text{Ce}^{3+}$ [10]. A resolution almost twice better than commercial scintillators at that time. All Ce^{3+} doped REX_3 (RE = La, Ce, Gd, Y, Lu and X = Cl, Br, I) were studied in the years to follow (*cook and look*). Already our first study on $\text{LaBr}_3:0.5\% \text{Ce}$ demonstrated the excellent scintillation performance with 2.8% resolution and 61000 ph/MeV [24]. First studies on iodides were presented by the Delft-Bern team in 2005 for $\text{LaI}_3:\text{Ce}^{3+}$ [44] and $\text{LuI}_3:\text{Ce}^{3+}$ [45].

Serendipity also led to the discovery of the thermal neutron scintillation properties of Ce^{3+} doped $\text{Cs}_2\text{LiYCl}_6$ (CLYC) from the elpasolite family by the Delft-Bern team in 1999 [46]. By replacing Cs by Rb, replacing Y by La, Gd, or Lu, and replacing Cl by Br or I other compositions can be made and many of them were tried (*cook and look*). $\text{Cs}_2\text{LiYBr}_6$ was first reported by Bessiere et al. [47] in 2004, $\text{Rb}_2\text{LiYBr}_6$ and five other elpasolites by Birowosuto et al. [48] in 2008. Other laboratories also entered the field and $\text{Cs}_2\text{LiLaCl}_6$ in 2009 and $\text{Cs}_2\text{LiLaBr}_6$ in 2011 were reported by Glodo et al. [49,50]. Within the elpasolite family, Ce^{3+} doped $\text{Cs}_2\text{LiYCl}_6$ (CLYC) and $\text{Cs}_2\text{LiLaBr}_6$ (CLLB) were developed and commercialized as thermal neutron scintillator. A review on thermal neutron scintillators was made by van Eijk in 2012 [51].

Eighteen years after its discovery, $\text{LaBr}_3:\text{Ce}^{3+}$ still appears the best scintillator in terms of energy resolution. Only $\text{Cs}_2\text{NaLaBr}_3\text{I}_3$ and $\text{Cs}_2\text{LiLaBr}_6$ with 2.9% approach LaBr_3 . It seems that with $\text{LaBr}_3:\text{Ce}^{3+}$ the best halide was found, and research activities in this field are declining. Yet there appears a small revival with Ce^{3+} doped Tl-based compounds, see Table 2. Kim and co-workers were the first to explore Ce^{3+} scintillation in the Tl-based compound $\text{Tl}_2\text{LiGdCl}_6$ [52,53] in 2015 and found quite good properties. Tl⁺ is about 10% smaller than Cs⁺, and the Cs-based compounds of Table 1 can also be synthesized as Tl-based compounds. Many Tl-based compounds were studied soon after 2015 (*cook and look*). The best one $\text{Tl}_2\text{LaCl}_5:\text{Ce}^{3+}$ shows 3.4% resolution and 76000 ph/MeV [54].

3.2. The Eu^{2+} activated halides

The first Eu^{2+} doped halide scintillator was LiI for thermal neutron

Table 2

Yield (ph/MeV) and resolution R (%) for Tl-based compounds. Reference to the first report and the reports with best resolution (<10%) or light yield (photons/MeV) are given.

compound	year	R	yield	Ref.
$\text{Tl}_2\text{LiGdCl}_6:\text{Ce}$	2015	4.6	58000	[52]
$\text{Tl}_2\text{LiYCl}_6:\text{Ce}$	2016	4	25000	[143–145]
$\text{Tl}_2\text{LiGdBr}_6:\text{Ce}$	2016	17	17400	[145]
$\text{Tl}_2\text{LaBr}_5:\text{Ce}$	2017	5	43000	[146]
$\text{Tl}_2\text{LaCl}_5:\text{Ce}$	2017	3.4	70000	[54,147]
$\text{Tl}_2\text{LiLuCl}_6:\text{Ce}$	2017	5.6	27000	[151]
$\text{TlMgCl}_3:\text{undoped}$	2017	3.7	30600	[148]
$\text{TlCaCl}_3:\text{undoped}$	2017	5	30600	[149]
$\text{Tl}_2\text{Sr}_2\text{Br}_5:\text{undoped}$	2017	4.6	37600	[150]
$\text{TlCaI}_3:\text{undoped}$	2017	6.2	42200	[148]
$\text{Tl}_2\text{GdCl}_5:\text{Ce}$	2018	5	53000	[152]
$\text{TlSr}_2\text{I}_5:\text{Eu}$	2018	4.2	70000	[153]
$\text{Tl}_2\text{ZrCl}_6:\text{undoped}$	2018	4.3	47000	[74,75]

Table 3

Yield (ph/MeV) and resolution R (%) for Eu^{2+} doped halide compounds. Reference to the first report and the reports with best resolution (<10%) or light yield (photons/MeV) are given.

compound	year	R	yield	Ref.
LiI	1953	7.5	15000	[55,63]
CaI_2	1964	5.2	90000	[154]
SrI_2	1968	2.6	90000	[57,59,60,65]
BaCl_2	2008	3.5	52000	[58,155]
BaBr_2	2008	6	49750	[58,156]
BaI_2	2008	5.6	38000	[59,156]
CsBa_2I_5	2009	2.3	97000	[61,62,157]
BaBrI	2010	3.4	91000	[157,158]
CaBa_2Br_5	2011	n.r.	92000	[159]
CsSrI_3	2011	3.9	73000	[160,161]
CsCaI_3	2012	8	38500	[161]
CsCaCl_3	2012	8.9	18000	[161]
BaClBr	2012	3.55	52000	[162]
BaFI	2012	8.5	55000	[162]
BaClI	2012	9	54000	[162]
CaBr_2	2013	8.9	36000	[163]
CsCaBr_3	2013	9.3	28000	[164]
KCaI_3	2015	3	72000	[165,166]
KSr_2I_5	2015	2.4	94000	[167]
KSr_2Br_5	2015	3.5	75000	[168]
KBa_2I_5	2016	2.4	90000	[169]
K_2BaI_4	2016	2.9	63000	[169]
CsSrBr_3	2016	4.9	40200	[170]
$\text{KCa}_{0.8}\text{Sr}_{0.2}\text{I}_3$	2016	2.8	73000	[171,172]
LiCa_2I_5	2016	5.6	90000	[173]
LiSr_2I_5	2016	3.5	60000	[173]
LiSr_2Br_5	2016	6.1	32000	[173]
$\text{CsCa}_{10.2}\text{Br}_{0.2}:\text{Eu}^{2+}$	2017	5.2	40000	[174]
RbSr_2Br_5	2017	4	64700	[175]
RbSr_2I_5	2017	3	90400	[175]
LiSrI_3	2017	5.2	35000	[176]
Cs_3KCaI_6	2018	3.9	62000	[177]
Cs_4CaI_6	2018	3.6	51800	[177,178]
$\text{Cs}_3\text{RbCaI}_6$	2018	4.5	38000	[177]
Cs_4SrI_6	2018	3.3	62300	[177,178]
$\text{Cs}_3\text{RbSrI}_6$	2018	5.1	31000	[177]
Cs_3KSrI_6	2018	5	29000	[177]
$\text{Cs}_{3.5}\text{Rb}_{0.5}\text{SrI}_6$	2018	3.3	75000	[177]
CsSrBrI_2	2019	3.4	65300	[179]
CsSrClBr_2	2019	3.6	35100	[179]
CsCaBaI_2	2019	3.9	51800	[179]
CsSrBr_3	2014	9	31300	[180]

detection discovered by Schenck in 1953 [55] followed later by CaI_2 reported by Hofstadter et al. [56] in 1964 and SrI_2 patented by Hofstadter in 1968 [57]. Thereafter, the research on Eu^{2+} doped scintillators more or less stopped. It started again in 2008 with Eu^{2+} doped BaCl_2 and BaBr_2 reported by Selling et al. [58] and SrI_2 and BaI_2 reported by Cherepy and co-workers [59,60]. The rediscovery of $\text{SrI}_2:\text{Eu}^{2+}$ with 2.8% energy resolution and about 100000 photons/MeV triggered, just like $\text{LaBr}_3:\text{Ce}^{3+}$ before, a wide research activity but now into Eu^{2+} activated halide compounds. Table 3 compiles the main results obtained since.

Eu^{2+} has different valence than Ce^{3+} and almost all studies deal with compounds where Eu^{2+} is on a divalent lattice site. For Eu^{2+} on a trivalent site the 5d-level is usually located inside the conduction band preventing any 5d-4f emission, and for Eu^{2+} on a monovalent site a charge compensator is needed. Experience teaches that this introduces charge carrier traps and loss of scintillation performance. For the same reasons, most studied compounds for Ce^{3+} in Table 1 pertain to Ce on trivalent lattice sites.

Inspecting the Eu^{2+} doped compounds in Table 3 they generally display higher light yields than the Ce^{3+} doped ones and several of them, like KSr_2I_5 , CsBa_2I_5 , and $\text{KCa}_{0.8}\text{Sr}_{0.2}\text{I}_3:\text{Eu}^{2+}$ even surpass $\text{LaBr}_3:\text{Ce}^{3+}$ in terms of energy resolution. All of these are iodide compounds, and the best so far is CsBa_2I_5 discovered by Bourret-Courchesne

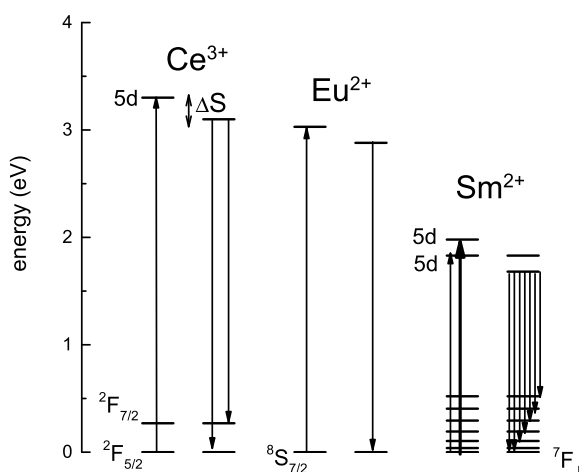


Fig. 5. The Ce^{3+} , Eu^{2+} , and Sm^{2+} level energies typical for in an iodide compound. In each case optical absorption starts from the 4f ground state and emission starts from the lowest 5d-state. Typical values of 0.3 eV, 0.2 eV, and 0.2 eV for the Stokes shift of Ce^{3+} , Eu^{2+} , and Sm^{2+} were used. There are one, two, and seven final states in emission for Eu, Ce, and Sm, respectively.

et al. [61] with 2.3% energy resolution and 93000 photons/MeV reported for a small sample by Alekhin et al. [62]. Unfortunately, the properties of Eu^{2+} doped compounds worsen quite significantly when large crystals are synthesized. This was already noted for $\text{LiI}:\text{Eu}^{2+}$ by Syntfeld et al. in 2005 [63], and Glodo et al. [64] in 2010 found for SrI_2 a lengthening of the scintillation decay time with Eu^{2+} concentration and the volume of the scintillator. Large 6 cm sized crystals of $\text{SrI}_2:\text{Eu}$ can be grown as shown by Boatner et al. [65] but at the expense of energy resolution; a 26 cm^3 sized crystal displayed 3.8% resolution. The resolution degradation and decay time lengthening was attributed to radiation trapping or self-absorption. The emission of Eu^{2+} is re-absorbed by another Eu^{2+} , re-emitted again etc., and in the process it may get lost by radiation less decay, or at defects, or at the crystal-reflector interface [66,67]. By crystal growth technology defect concentrations can be reduced, and today 1" diameter and 1" tall scintillators are commercially available with resolution down to 2.9%. Although not as good as $\text{LaBr}_3:\text{Ce}$, SrI_2 has the advantage that it is free from intrinsic radioactivity.

Fig. 5 shows typical 4f and 5d level energies for Eu^{2+} and Ce^{3+} . After optical absorption to the 5d level, the 5d level lowers in energy with respect to the ground state due to lattice relaxation. The energy difference is the Stokes shift ΔS . In the case of Eu^{2+} , the 5d-4f emission is always from the lowest 5d excited state to the $^8\text{S}_{7/2}$ 4f ground state, and the 5d-4f emission appears as a single band with width (FWHM) of the same order as the size of the Stokes shift. This means that the short wavelength side of the Eu^{2+} emission can be re-absorbed by another Eu^{2+} . In the case of Ce^{3+} , the 5d-4f emission appears as a doublet band due to transitions to the $^2\text{F}_{5/2}$ ground state and the $^2\text{F}_{7/2}$ state at 2200 cm^{-1} (0.27 eV) higher energy. Only the emission to the ground state has significant probability to be reabsorbed by another Ce^{3+} . After absorption, Ce^{3+} again gives doublet emission. Effectively this means that the $^2\text{F}_{5/2}$ emission is partly converted into $^2\text{F}_{7/2}$ emission. After several re-emission cycles, only 5d- $^2\text{F}_{7/2}$ emission is left and self-absorption stops. Furthermore, Ce^{3+} emission tends to have 50% larger Stokes shift than Eu^{2+} emission [68] which further helps in reducing self-absorption. LaCl_3 and LaBr_3 are very special because the Stokes shift of Ce^{3+} emission is almost 1 eV and self-absorption is not an issue even for 3" large crystals with 100% Ce^{3+} concentration as in CeBr_3 .

The search for Eu^{2+} doped halide scintillators still continues, but one may wonder whether much improvements can still be expected. The self-absorption in Eu^{2+} will remain a fundamental issue. Although for small samples, compounds with better energy resolution than that of SrI_2 were found, it remains to be seen whether it will still apply for large

Table 4

Yield (ph/MeV) and resolution R (%) for other activators than Ce and Eu. Reference to the first report and the reports with best resolution (<10%) or light yield (photons/MeV) are given.

Compound	year	R	yield	Ref.
$\text{LaBr}_3:\text{Pr}^{3+}$	2005	3.2	60000	[69]
CeBr_3	2005	3.6	60000	[72,181]
$\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}^{3+}$	2006	4.6	19000	[70,71]
BaBr_2	2007	5.4	19300	[182]
K_2CeCl_5	2007	5.8	30000	[183]
K_2CeBr_5	2008	6.3	50000	[184]
CsCe_2Cl_7	2008	5.5	28000	[185]
$\text{Cs}_2\text{NaCeCl}_6$	2009	8.3	20000	[186]
Rb_2CeBr_5	2009	6.9	34000	[187]
$\text{Cs}_2\text{LiCeCl}_6$	2010	5.5	22000	[188]
$\text{Cs}_2\text{NaCeBr}_6$	2010	6.7	25000	[189]
$\text{Rb}_2\text{LiCeBr}_6$	2010	6.3	33000	[190]
Cs_3CeCl_6	2011	8.4	19000	[191]
$(\text{Lu}_{0.75}\text{Y}_{0.25})_3\text{Al}_5\text{O}_{12}:\text{Pr}^{3+}$	2012	4.4	33000	[192,193]
$\text{Rb}_2\text{LiCeCl}_6$	2012	7.9	23000	[194]
$\text{SrI}_2:\text{Yb}^{2+}$	2013	4.35	56000	[195]
$\text{CsBa}_2\text{I}_5:\text{Yb}^{2+}$	2013	5.7	54000	[195]
Cs_2HfCl_6	2015	3.3	54000	[73,196]
CsCe_2Br_7	2015	7	35500	[197]
Tl_2ZrCl_6	2018	4.3	47000	[74,75]
Cs_2HfI_6	2018	4.2	64000	[76,77]

crystals, and in that respects $\text{LaBr}_3:\text{Ce}^{3+}$ is still the best. In order to pass the 2% energy resolution target, other research strategies may be needed.

3.3. Other dopants and intrinsic scintillators

Phase IV also witnessed research activities with other dopants than Ce^{3+} or Eu^{2+} . The 5d-4f scintillation of Yb^{2+} was studied in SrI_2 and CsBa_2I_5 and resolution down to 4.3% was demonstrated, see Table 4. Pr^{3+} was introduced as activator in LaBr_3 by Glodo et al. [69] showing several 4f-4f line emissions between 490 nm and 750 nm. It is one of the first red emitting scintillators that show good resolution of 3.2% but the scintillation decay of about 10 μs is rather slow. Although not a halide, Pr^{3+} activated $\text{Lu}_3\text{Al}_5\text{O}_{12}$ reported in 2006 by Ogino et al. [70] is also listed in Table 4. Here, the fast 20 ns 5d-4f emission of Pr^{3+} provides the main scintillation decay component. A resolution of 4.6% with 19000 ph/MeV was reported by Drozdowski et al. in 2008 [71]. By making solid solutions with yttrium, the properties were further improved to 4.4% resolution and 33000 ph/MeV.

Table 4 and also Table 2 lists various undoped compounds. The Ce-based halides might as well be considered as the isostructural La-based halides with 100% Ce^{3+} doping, and properties appear so far always less than that of the Ce^{3+} doped analogues in Table 1. CeBr_3 can for example be considered as $\text{LaBr}_3:100\% \text{Ce}^{3+}$ and was first studied by Shah et al. [72] in 2005. In 2015 the γ -ray scintillation properties of undoped Cs_2HfCl_6 were first reported by Burger et al. [73]. It shows excellent energy resolution of 3.3%. The related compounds Tl_2ZrCl_6 [74,75] and Cs_2HfI_6 also demonstrates good scintillation properties [76,77].

3.4. Co-doped scintillators

The main dopant in impurity activated scintillators is always the carrier recombination or luminescence center. With co-dopants we generally mean additional dopants that are not active as luminescence center but have otherwise a positive effect on the scintillator properties. One may distinguish several functions; 1) co-doping to improve crystal growth yield and crystal properties, 2) co-doping to reduce afterglow, 3) co-doping as a charge compensator, 4) co-doping to affect the scintillation mechanism, 5) co-doping to affect the scintillation decay (to introduce e.g. particle discrimination modalities). Various references to

where and how co-dopants have been used in scintillators can be found in Refs. [78,79]. Here we will concentrate on co-dopants that affect energy resolution and light yield studied during phase IV.

Harrison et al. [80,81] applied aliovalent co-doping to strengthen CeBr_3 and to improve ingot yields. Slight changes in emission and increase in fracture toughness were observed. Industry used similar method for $\text{LaBr}_3:\text{Ce}^{3+}$, and Yang et al. [82] reported in 2012 that the scintillation properties of 6 cm diameter $\text{LaBr}_3:\text{Ce}$ crystals can be improved by Sr^{2+} or Ba^{2+} co-doping. The resolution improved from 3.7% to 3.0% and the scintillator showed particularly below 100 keV a better proportionality. This finding went parallel to the realization in 2011–2012 that non-proportionality is a property of a compound that can be altered by dopants. The 2% energy resolution of small sized $\text{LaBr}_3:\text{Ce}^{3+};\text{Sr}^{2+}$ shown in Fig. 3 was a result of such *enlightment*. That only 50 ppm of optically inactive Sr^{2+} or Ca^{2+} co-doping can have such significant improvement on the proportionality curve as shown in Fig. 3 was one of the main triggers to increase research initiatives on co-doped scintillators following 2012. Soon it was found that the same co-dopants improve the resolution of the 70 years old scintillator $\text{NaI}:\text{Tl}^+$ to 5.3% [83].

There were other triggers for co-doping studies. Ca^{2+} as a co-doping in $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ was first introduced as a means to suppress the afterglow [78,84] but has also a positive effect on the scintillation speed and light yield. Blahuta et al. [85] performed more detailed studies into this phenomenon and showed in 2013 that Ca^{2+} co-doping increases the Ce^{4+} concentration in the materials. Instead of first capture of a hole by Ce^{3+} followed by electron capture and 5d-4f emission, a more rapid recombination route of scintillation is introduced. In the presence of Ce^{4+} just the capture of a free electron already causes the scintillation. The hole can be captured at a later stage by another Ce^{3+} to convert that one into Ce^{4+} . The original $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio is then restored. Note that here two different Ce atoms are involved in the scintillation. Although, similar phenomenon was observed already in 1992 for the cathode luminescence of Ca^{2+} co-doped $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ [86], the phenomenon for the scintillator $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ created *enlightment* and a new research tool to optimize other Ce-doped scintillators. It was applied to garnet scintillators like $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ and $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Ce}^{3+}$ where Mg^{2+} co-doping gives significant improvement in the light yield [87,88] or response time [89] due to Ce^{4+} formation.

The development of the Ce^{3+} and Pr^{3+} activated $\text{Lu}_3\text{Al}_5\text{O}_{12}$ derived scintillators illustrates nicely how performance can be improved by band gap engineering and co-doping strategies. Nikl et al. [90] in their review paper of 2013 describe the discovery and development of bandgap engineering for multicomponent $(\text{Gd},\text{Lu})_3(\text{Ga},\text{Al})_5\text{O}_{12}:\text{Ce}^{3+}$ scintillators. The admixture of Ga^{3+} and Gd^{3+} leads to conduction band engineering, and otherwise present afterglow can be replaced for prompt scintillation. Table 4 shows that the light yield of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}^{3+}$ is increased from 19000 to 33000 with resolution improvement from 4.6% to 4.4% by forming a solid solution with $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Pr}^{3+}$. Foster et al. [91] showed in 2018 that resolution even further improves to 4.1% with Li^+ co-doping. The precise role of Li^+ is not clear yet. It appears not to affect the proportionality, and resolution improvement must be caused by the other terms of Eq. (1).

Co-doping can also benefit Eu^{2+} activated scintillators as demonstrated for $\text{KCaI}_3:\text{Eu}^{2+}$ [92] and $\text{SrI}_2:\text{Eu}^{2+}$ [93] where Zr^{4+} co-doping improves resolution. Ca^{2+} improves the energy resolution of $\text{NaI}:\text{Tl}^+;\text{Eu}^{2+}$ as demonstrated by Khodyuk et al. [94]. Note, that in this compound the emission is from Eu^{2+} . Tl^+ is not acting as luminescence center but it seems to act as the electron-hole capture center with subsequent energy transfer to Eu^{2+} .

Above results and Table 5 demonstrate that scintillator resolution can often be improved by means of suitable co-dopants, and expectedly this line of research will remain active for each scintillator that has not reached its fundamental limit of resolution dictated by R_{stat} in Eq. (1).

Table 5

Yield (ph/MeV) and resolution R (%) for scintillators with co-doping. Reference to the first report and the reports with best resolution (<10%) or light yield (photons/MeV) are given.

Compound	year	R	yield	Ref.
$\text{NaI}:\text{Tl}^+;\text{Eu}^{2+};\text{Ca}^{2+}$	2010	4.9	52000	[94,198]
$\text{LaBr}_3:\text{Ce}^{3+};\text{Sr}^{2+}$	2012	2	78000	[1,82]
$\text{Lu}_{1.8}\text{Y}_{0.2}\text{SiO}_5:\text{Ce}^{3+};\text{Ca}^{2+}/\text{Mg}^{2+}$	2013	8.4	34000	[85]
$\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+};\text{Mg}^{2+}$	2014	n.r.	21900	[87,88]
$\text{CeBr}_3:\text{Sr}^{2+}$	2014	3	55000	[199,200]
$\text{NaI}:\text{Tl}^+;\text{Ca}^{2+}/\text{Sr}^{2+}$	2015	5.3	30000	[83]
$\text{KCaI}_3:\text{Eu}^{2+};\text{Zr}^{4+}$	2018	2.7	72000	[92]
$(\text{Lu}_{0.75}\text{Y}_{0.25})_3\text{Al}_5\text{O}_{12}:\text{Pr}^{3+};\text{Li}^+$	2018	4.1	25000	[91]
$\text{SrI}_2:\text{Eu}^{2+};\text{Zr}^{4+}$	2019	2.5	95000	[93]

4. Below 2% energy resolution; phase V in scintillator research

In the 2018 prospect paper of Dujardin et al. [3] on the needs, trends, and advances in inorganic scintillators several challenges were formulated: 1) Energy resolution of 2–3% for energy discrimination in nuclear security and spectroscopy, 2) sub 100 ps timing resolution for next generation PET scanners in medical imaging and particle physics experiments, 3) high γ detection efficiency which means high density and high effective atomic number, and this all together with 4) low cost production techniques.

Since this review focusses on the first challenge one may ask what is the ultimate resolution achievable and what research strategies may lead to such scintillator? In the 2006 review paper of Krämer et al. [12] it was already predicted that the ultimate energy resolution for Ce^{3+} doped compounds will be below 2%. It seems that seven years later with $\text{LaBr}_3:\text{Ce}^{3+};\text{Sr}^{2+}$ we have more or less reached that fundamental limit. The high light output, the total absence of self-absorption, and the engineered very good proportionality has led to 2% energy resolution for small sized scintillators. Industry managed to synthesize large $\text{LaBr}_3:\text{Ce}^{3+};\text{Sr}^{2+}$ scintillators maintaining excellent energy resolution of 2.2%.

A first requirement to go below 2% is to have scintillators with ideal proportionality. Phase IV taught us that the nonproportionality can to some or even large extent be engineered by co-doping. It also taught us that iodides generally show very good proportionality. A second requirement is to have scintillators with a high photon yield, and then a small band gap, as expressed by Eq. (3), is crucial. Small band gap iodides that combine excellent proportionality with high light output have then highest potential. Indeed Tables 1 and 3 demonstrate that the highest light yield and best resolution scintillators are almost all iodide compounds. Particularly $\text{CsBa}_2\text{I}_5:\text{Eu}^{2+}$ with 2.3% and 97000 ph/MeV seems very promising. With such light yield and using the best PMT with $v(M) = 0.2$ and $\text{QE} = 40\%$, Eq. (3) and Eq. (2) predict an ultimate resolution of $R = R_{\text{stat}} = 1.6\%$. Apparently there is still room to go below 2%, and possibly with suitable co-dopants further progress can be made. However, the aspect of self-absorption of Eu^{2+} emission will remain an issue the moment large crystals are synthesized.

The energy resolutions listed in the various tables are all obtained with a photomultiplier tube which is not the most sensitive photon detector. The number of detected photons can be increased and therefore R_{stat} decreased with Si-based photodetectors. Avalanche photodiodes (APDs) can reach 80–100% quantum efficiency. In theory with twice higher QE, R_{stat} will be reduced by a factor of 1.4 which would imply an ultimate resolution near 1.2% for CsBa_2I_5 . Of course this can only be reached when the noise contribution from the photon detector is negligible, when proportionality is ideal, and when crystal quality and light collection efficiency is perfect. To approach such limit we need to avoid the Eu^{2+} self-absorption problem and to use an activator that emits in the red to infra-red in order to exploit the high QE of Si-based photon detectors. In other words we need other research

strategies in phase V.

4.1. Small bandgap near infra-red emitting scintillators

NaI:Tl^+ is like CsI:Tl^+ so popular because it can be produced at low cost, but light yield, resolution, and proportionality for both compounds are far from optimal. Many efforts were put in improving NaI:Tl scintillators by co-doping. By adding Li^+ , the materials becomes thermal neutron sensitive which has led to a new industrial product for dual γ neutron spectroscopy. Khodyuk et al. [94] used a combinatorial search and found that $\text{NaI:Tl}^+;\text{Eu}^{2+};\text{Ca}^{2+}$ has improved properties. A resolution of 4.9% with 52000 photons/MeV scintillation yield was obtained. The addition of Eu^{2+} replaces the broad band Tl^+ emission near 415 nm by the more narrow band Eu^{2+} emission near 460 nm. It seems that the role of Tl^+ is the capture of the charge carriers from the ionization track and to transfer the excitation energy to Eu^{2+} . Eu^{2+} is then the luminescence center. This is a first example that one activator is used to capture the carriers and another for the scintillation. However with Eu^{2+} one still has to deal with self-absorption issues.

The Delft-Bern team recently followed an approach to convert blue Eu^{2+} scintillating halides into an infrared emitting scintillator. For that purpose Sm^{2+} is used, and the typical Sm^{2+} level scheme is shown in Fig. 5. The $5d-4f$ emission of Sm^{2+} is always at 1.20 eV lower energy than the Eu^{2+} emission [95]. The idea is that Eu^{2+} still acts as a center to efficiently capture the free charge carriers from the ionization track, but that it will transfer its excitation energy to the co-dopant Sm^{2+} which will then emit in the infrared. This idea was first tested for Sm^{2+} co-doped $\text{SrI}_2;\text{Eu}^{2+}$ [96]. With proper doping concentration, the Eu^{2+} emission is fully converted into infrared 750 nm Sm^{2+} emission. The emission from Sm^{2+} is much less self-absorbed than that of Eu^{2+} because 1) its concentration can be kept small, 2) the absorption strength to the lowest $4f^55d$ level is relatively weak, 3) the emission can be from transitions to several ${}^7F_{J=0,1,2,3,4,5,6}$ final states as illustrated in Fig. 5. Like with Ce^{3+} , the re-emission effectively causes a red shift and self-absorption will automatically stop. Although the principle works, the energy resolution was disappointing. Another attempt with Sm^{2+} co-doped $\text{CsBa}_2\text{I}_5;\text{Eu}^{2+}$ was much more successful [97]. With APD and Si-PM readout, energy resolutions of 3.2% and 5.4% were obtained as shown in Fig. 6. This first result is very encouraging and it may initiate a new strategy in scintillation research.

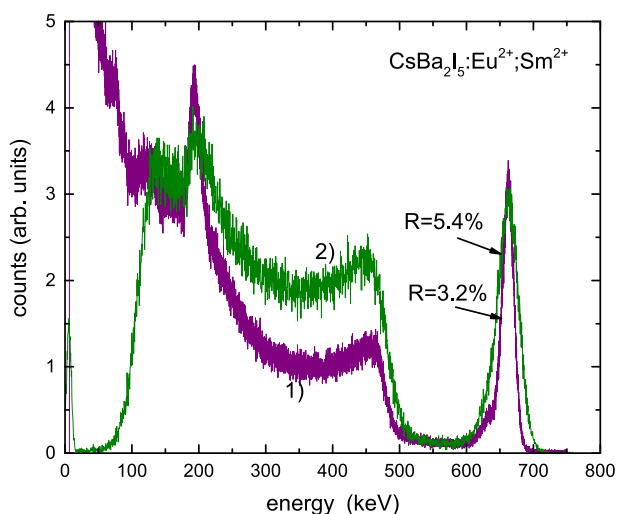


Fig. 6. Pulse height spectrum of the first high resolution near infrared scintillator $\text{CsBa}_2\text{I}_5;\text{Eu}^{2+};\text{Sm}^{2+}$ as reported by Wolszczak et al. in Ref. [97] read out by 1) an APD and 2) a Si-PM.

4.2. Perovskite scintillators

Scintillation properties of organic-inorganic methylammonium (MA) lead halide perovskites under proton irradiation were first reported by Shibuya et al. in 2002 [98] and the first γ -ray pulse height spectrum, although still with poor energy resolution, was reported on $(\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3)_2\text{PbBr}_4$ by van Eijk et al. in 2008 [99]. Four years later the same family of materials becomes a hot topic for solar cell applications. In the family of Pb-perovskite halides, the life time of free charge carriers (electrons and holes) is very long enabling solar energy harvesting with 15% efficiency as demonstrated in 2012 by Lee et al. [100]. The same long carrier lifetime can also be utilized for solid state semi-conductor scintillation detection. By applying an electric field, the charge carriers are separated efficiently, and Wei et al. first demonstrated the detecting capability of continuous wave X-rays [101]. One year later the first 662 keV γ -ray pulse height spectrum with 6.5% resolution was presented [102] for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ diluted with 6% Cl^- . Crystals can be produced with wet chemistry from solution at room temperatures and at low cost. Because of the small band gap of 2.5–3 eV (verify) about 150000 electron hole pairs are created per MeV, and when this can be converted into photons in theory scintillators with $R_{\text{stat}} < 1\%$ are possible.

Birwosuto *et al.* [103] studied the scintillation properties of 3-D and 2-D layered perovskites under X-ray excitation. MAPbBr_3 emits at 550 nm and MAPBI_3 at 750 nm which is attributed to exciton emission near the band gap of the compounds. In this first generation of Pb-halide perovskites the emission is strongly quenched at room temperature and less than 1000 ph/MeV survive. At 10 K however intense emission is observed and [103] write about yields up to 200000 ph/MeV. The quenching is attributed to the small e-h binding energy in the exciton that decreases for Cl to Br to I [104]. Interestingly one may replace the organic MA group with Cs^+ to obtain full inorganic CsPbX_3 halide perovskites. Depending on the Cl, Br, I content the triplet X-ray excited exciton emission can be tuned from 430 nm to 700 nm [105,106]. One may also dilute Cs with Rb to obtain similar tuning [107]. Above very recent developments demonstrate that the organic-inorganic and all inorganic Pb-halide perovskites have various interesting properties that may lead to an important phase V scintillator research initiative. The small band gap and expectedly good proportionality of especially the iodides with emission in the infrared then already meet many of the requirements for <2% resolution scintillators. The challenge is then to find suitable activators or dopants to capture and stabilize the triplet excitons. Additional advantage for this class of materials is the low cost of the wet chemistry production technique and the presence of Pb^{2+} which provides it with good γ -ray stopping power.

4.3. New research strategies

With the studies on the Ce^{3+} and Eu^{2+} doped halides in phase IV of scintillator discovery, the compositional space of research was still limited. We deal with only one single dopant, and the amount of potential compounds was still manageable. A research strategy based on *serendipity* and on *cook and look* still sufficed. However, with the *enlightenment* that scintillator performance can be much improved by 1) band gap engineering, 2) co-doping, and 3) energy transfer to other activators, the compositional space has become enormously large. This will require research strategies like a combinatorial approach to screen large number of compositions and/or rational design (*enlightenment*) to select the most potential areas within the compositional space.

During phase IV much progress was made to understand and predict the location of impurity levels within the band gap of compounds which to large or some extend enables rational design. Fig. 7 shows for example the type of diagrams that can be made more or less routinely now. It is a stacked vacuum referred binding energy (VRBE) diagram where the Eu^{2+} and Ce^{3+} levels together with the top of the valence and bottom of the conduction bands are shown relative to the vacuum

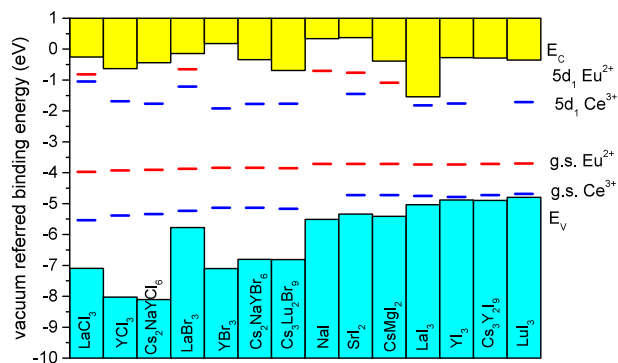


Fig. 7. The vacuum referred binding energy of an electron in the Ce^{3+} and Eu^{2+} 4f ground and lowest 5d excited state within the band gap of halide compounds. Large part of the diagram can also be found in Ref. [108].

level.

The ground state energy of Eu^{2+} is always near -4 eV and changes few 0.1 eV in a predictable fashion with compound properties [109]. That of Ce^{3+} is at lower energy but also changes in a predictable fashion. The same applies for all other lanthanides. The VRBE in the excited 5d-level shows more variation, and Fig. 8 illustrates this for 150 different compounds against the so-called U-parameter of the host compound. This U-parameter is a key parameter in the construction of VRBE diagrams [109]. It is large 7.4-7.6 eV in fluoride crystals and decreases towards chlorides, bromides, and iodides. On average, the lowest Ce^{3+} 5d-level is at -1.8 eV and the ± 0.5 eV variations are caused by the 5d-crystal field splitting. The VRBE in the lowest level of Eu^{2+} is always at higher energy and on average near -0.99 eV.

In design strategies for an Eu^{2+} or Ce^{3+} activated scintillator, the emitting 5d-level should be well below the conduction band bottom E_C , otherwise emission is quenched at low temperature or even entirely absent. The Ce^{3+} emission in LaI_3 quenches for example already at 120K because of too close proximity of the CB-bottom as illustrated in Fig. 7.

Recently Awater et al. conducted a search on the spectroscopy of Tl^+ , Pb^{2+} , and Bi^{3+} activated compounds to establish the VRBEs. Tl^+ , Pb^{2+} , and Bi^{3+} share the same $6s^2$ ground state electron configuration, and the only difference between these activators is then a different nuclear charge. Fig. 9 from Awater et al. [110] shows the VRBE for an electron in the Bi^{3+} ground and excited state in different compounds as function of U. It illustrates that the binding decreases (VRBE less negative) with smaller U-value. That of the ground state decreases more rapidly than that of the excited state. Similar type of figures with about

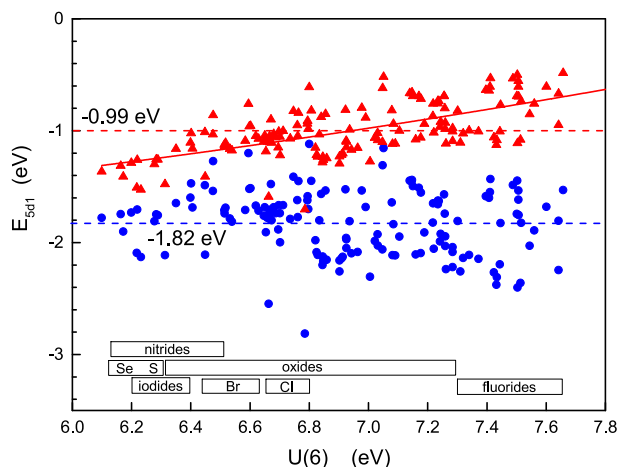


Fig. 8. The VRBE in the lowest Ce^{3+} and lowest Eu^{2+} 5d level in 150 different compounds. The ranges of U-values for different compound types are indicated.

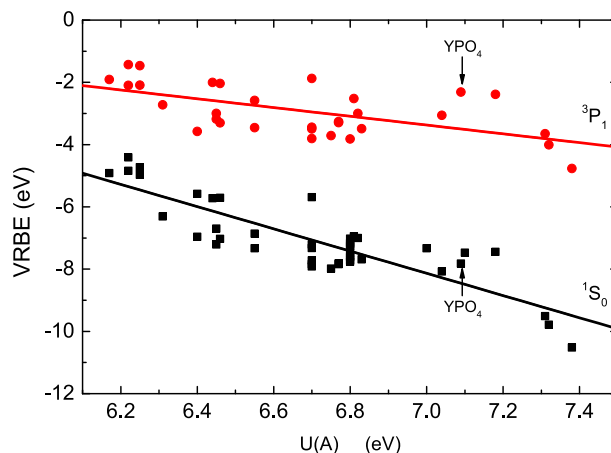


Fig. 9. The VRBE in the Bi^{3+} ground and excited state in compounds.

the same VRBE energies apply for Pb^{2+} and Tl^+ although there is a slight tendency of decreasing binding energy with smaller charge in going from Bi to Pb to Tl.

It was also found that the VRBE in the Bi^{2+} ground state is always somewhat (≈ 0.5 eV) below the VRBE in the Bi^{3+} excited state, and similar applies for Pb- and Tl-based compounds [111]. Since the CB-bottom in Bi-based compounds is derived from the Bi^{2+} ground state orbitals, this means that E_C will be at lower energy than the 3P_1 Bi^{3+} excited state level. Combining the results of Fig. 9 with that of Fig. 8, one may conclude that the VRBE in the lowest Ce^{3+} 5d-level will always be close or above the CB-bottom of Bi^{3+} based compounds. Indeed Ce^{3+} emission has never been reported in Bi-based and also not in Pb-based compounds. The best changes to observe Ce^{3+} emission in $6s^2$ -based compounds is in Tl-compounds with small U-values. The compounds of Table 2 are precisely that family.

Fig. 9 and similar for Pb^{2+} and Tl^+ combined with diagrams like in Fig. 7 are not yet conclusive enough to arrive at a full rational design, however, they do provide a guide in what areas of the compositional space to search. Even more importantly it provides a guide in what areas not to search. We know for example that the chances to find lanthanide 5d-4f emission in the Pb-halide perovskite family of compounds are very small because the emitting 5d-level is-predicted always in the conduction band.

From the field of luminescence and scintillation, a wealth of spectroscopic data is available in the archival literature on lanthanides, $6s^2$ elements, transition metal elements etc. Part of that information was collected and analyzed during a time span of 20 years which led to various empirical models on lanthanide luminescence and to the theory and methods behind the stacked VRBE diagrams as in Fig. 7. However, still only a fraction of information is collected, and one may expect more and better predicting models when a much larger effort is undertaken. A possible new strategy is then to exploit machine learning algorithms for retrieving predictive trends or materials design criteria from collected data [112]. First steps into that directions for band gap prediction were made by Zhuo et al. [113] and for scintillator discovery by Pilania et al. [114].

5. Summary, conclusions and outlook

The quest for high resolution scintillators during Phase IV of scintillator research during past 20 years has been reviewed in this work. Resolution at 662 keV γ -detection has improved impressively with almost a factor of three from 5 to 6% down to 2%. We learned a lot about the non-proportional response, where it comes from and how it affects energy resolution. We also learned that scintillation properties can be improved a lot by band gap engineering with solid solutions and by the use of optically inactive co-dopants. When we look at the prospects of

developing scintillators with below 2% energy resolution, theoretically 1.5% is feasible. To accomplish that we need high light output (>100000 ph/MeV) scintillators combined with 90–100% effective quantum efficiency Si-based detectors, and almost ideal proportionality. This dictates smaller than 4 eV band gap materials and new research strategies. How this will progress, we have to experience what phase V will eventually lead to.

References

- [1] M.S. Alekhin, J.T.M. de Haas, I.V. Khodyuk, K.W. Krämer, P.R. Menge, V. Ouspenski, P. Dorenbos, *Appl. Phys. Lett.* 102 (2013) 161915.
- [2] M.S. Alekhin, D.A. Biner, K.W. Krämer, P. Dorenbos, *J. Appl. Phys.* 113 (2013) 224904.
- [3] C. Dujardin, E. Auffray, E. Bourret-Courchesne, P. Dorenbos, P. Lecoq, M. Nikl, A.N. Vasilev, A. Yoshikawa, R.-Y. Zhu, *IEEE Trans. Nucl. Sci.* 65 (2018) 1977.
- [4] M.J. Weber, *J. Lumin.* 100 (2002) 35.
- [5] R. Hofstadter, *Phys. Rev.* 75 (1949) 796.
- [6] R. Hofstadter, *IEEE Trans. Nucl. Sci.* 22 (1975) 13.
- [7] M.J. Weber, R.R. Monchamp, *J. Appl. Phys.* 44 (1973) 5495.
- [8] K. Takagi, T. Fukazawa, *Appl. Phys. Lett.* 42 (1983) 43.
- [9] C.L. Melcher, J.S. Schweitzer, *Nucl. Instr. Meth.* A314 (1992) 212.
- [10] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K. Krämer, H.U. Güdel, *Appl. Phys. Lett.* 77 (10) (2000) 1467.
- [11] C.L. Melcher, *Nucl. Instr. Meth.* A537 (2004) 6.
- [12] K.W. Krämer, P. Dorenbos, H.U. Güdel, C.W.E. van Eijk, *J. Mater. Chem.* 16 (2006) 2773.
- [13] M. Nikl, A. Yoshikawa, *Adv. Opt. Mater.* 3 (2015) 463.
- [14] Francesco Maddalena, Liliana Tjahjana, Aozhen Xie, Arramel, Shuwen Zeng, Hong Wang, Philippe Coquet, Winicjusz Drozdowski, Christophe Dujardin, Cuong Dang, Muhammad Danang Birowosuto, *Crystals* 9 (2019) 88.
- [15] <http://scintillator.lbl.gov/> created by Stephen Derenzo, Martin Boswell, Marvin Weber, and Kathleen Brennan at the Lawrence Berkeley National laboratory with support from the Department of Homeland security (DHS).
- [16] P. Dorenbos, *IEEE Trans. Nucl. Sci.* 57 (2010) 1162.
- [17] P. Dorenbos, J.T.M. de Haas, C.W.E. van Eijk, *IEEE Trans. Nucl. Sci.* 42 (1995) 2190.
- [18] M. Moszynski, *Nucl. Instr. Meth.* A505 (2003) 101.
- [19] P.A. Rodnyi, P. Dorenbos, C.W.E. van Eijk, *Phys. stat. sol.(b)* 187 (1995) 15.
- [20] I.V. Khodyuk, J.T.M. de Haas, P. Dorenbos, *IEEE Trans. Nucl. Sci.* 57 (2010) 1175.
- [21] I.V. Khodyuk, P.A. Rodnyi, P. Dorenbos, *J. Appl. Phys.* 107 (2010) 113513.
- [22] I.V. Khodyuk, P. Dorenbos, *J. Phys. Cond. Mat.* 22 (2010) 485402.
- [23] M. Moszynski, *Rad. Meas.* 45 (2010) 372.
- [24] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K. Krämer, H.U. Güdel, *Appl. Phys. Lett.* 79 (2001) 1573.
- [25] G. Bizarri, N.J. Cherepy, W.S. Choong, G. Hull, W.W. Moses, S.A. Payne, J. Singh, J.D. Valentine, A.N. Vasilev, R.T. Williams, *IEEE Trans. Nucl. Sci.* 56 (2009) 2313.
- [26] J.Q. Grim, K.B. Ucer, A. Burger, P. Bhattacharya, E. Tupitsyn, E. Rowe, V.M. Buliga, L. Trefilova, A. Gektin, G.A. Bizarri, W.W. Moses, R.T. Williams, *Phys. Rev. B87* (2013) 125117.
- [27] S. Kerisit, K.M. Rosso, B.D. Cannon, Fei Gao, Yulong Xie, *J. Appl. Phys.* 105 (2009) 114915.
- [28] Li Qi, J.Q. Grim, R.T. Williams, G.A. Bizarri, W.W. Moses, *Nucl. Instr. Meth.* A652 (2011) 288.
- [29] X. Lu, S. Gridin, R.T. Williams, M.R. Mayhugh, A. Gektin, A. Syntfeld-Kazuch, L. Swiderski, M. Moszynski, *Phys. Rev. Appl.* 7 (2017) 014007.
- [30] J. Singh, *J. Appl. Phys.* 110 (2011) 024503.
- [31] R.T. Williams, J.Q. Grim, Q. Li, K.B. Ucer, W.W. Moses, *Phys. Stat. Sol.(b)* 248 (2011) 426.
- [32] Woon-Seng Choong, K.M. Vetter, W.W. Moses, G. Hull, S.A. Payne, N.J. Cherepy, J.D. Valentine, *IEEE Trans. Nucl. Sci.* 55 (2008) 1073.
- [33] K.D. Ianakiev, M.E. Abhold, B.S. Alexandrov, M.C. Browne, R.M. Williams, P.B. Leillewood, *Nucl. Instr. Meth.* A579 (2007) 34.
- [34] I.V. Khodyuk, M.S. Alekhin, J.T.M. de Haas, P. Dorenbos, *Nucl. Instr. Meth.* A642 (2011) 75.
- [35] M. Grodzicka, M. Moszynski, T. Szczesniak, Czarnacki, M. Szawowski, L. Swiderski, L. Kazmierczak, K. Grodzicki, *Nucl. Instr. Meth.* A707 (2013) 73.
- [36] Xinfu Lu, Li Qi, G.A. Bizarri, Kan Yang, M.R. Mayhugh, P.R. Menge, R.T. Williams, *Phys. Rev. B92* (2015) 115207.
- [37] M. Moszynski, A. Nassalski, A. Syntfeld-Kazuch, L. Swiderski, T. Szczesniak, *IEEE Trans. Nucl. Sci.* 55 (2008) 1062.
- [38] W.S. Choong, G. Bizarri, N.J. Cherepy, G. Hull, W.W. Moses, S.A. Payne, *Nucl. Instr. Meth.* A646 (2011) 95.
- [39] I.V. Khodyuk, F.G.A. Quarati, M.S. Alekhin, P. Dorenbos, *J. Appl. Phys.* 114 (2013) 123510.
- [40] S.B. Donald, R. Williams, C.L. Melcher, F. Meng, M. Koschan, S. Friedrich, J.A. Johnson, J.P. Hayward, *IEEE Trans. Nucl. Sci.* 65 (2018) 1218.
- [41] J.C. van't Spijker, P. Dorenbos, J.T.M. de Haas, C.W.E. van Eijk, K. Krämer, H.U. Güdel, *Rad. Meas.* 24 (1995) 379.
- [42] J.C. van't Spijker, P. Dorenbos, C.W.E. van Eijk, K. Krämer, H.U. Güdel, *J. Lumin.* 85 (1999) 1.
- [43] O. Guillot-Noël, J.T.M. de Haas, P. Dorenbos, C.W.E. van Eijk, K. Krämer, H.U. Güdel, *J. Lumin.* 85 (1999) 21.
- [44] A. Bessiere, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *Nucl. Instr. Meth.* A537 (2005) 22.
- [45] M.D. Birowosuto, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *IEEE Trans. Nucl. Sci.* 52 (4) (2005) 1114.
- [46] C.M. Combes, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *J. Lumin.* 82 (1999) 299.
- [47] A. Bessiere, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *IEEE Trans. Nucl. Sci.* 51 (2004) 2970.
- [48] M.D. Birowosuto, P. Dorenbos, G. Bizarri, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *IEEE Trans. Nucl. Sci.* 55 (2008) 1152.
- [49] Jarek Glodo, Rastgo Hawrami, Edgar van Loef, William Higgins, Urmila Shirwadkar, Kanai S. Shah, *Proc. SPIE Vol. 7449* 74490E.
- [50] J. Glodo, E.V.D. van Loef, R. Hawrami, W.M. Higgins, A. Churilov, U. Shirwadkar, K.S. Shah, *IEEE Trans. Nucl. Sci.* 58 (2011) 333.
- [51] C.W.E. van Eijk, *IEEE Trans. Nucl. Sci.* 59 (2012) 2242.
- [52] H.J. Kim, Rooh Gul, H. Park, Sunghwan Kim, *J. Lumin.* 164 (2015) 86.
- [53] H.J. Kim, Rooh Gul, H. Park, Sunghwan Kim, *Rad. Meas.* 90 (2016) 279.
- [54] R. Hawrami, E. Ariesanti, H. Wei, J. Finkelstein, J. Glodo, K.S. Shah, *Nucl. Instr. Meth.* A869 (2017) 107.
- [55] J. Schenck, *Nature* 171 (1953) 518.
- [56] R. Hofstadter, E.W. O'Dell, C.T. Schmidt, *IEEE Trans. Nucl. Sci.* 11 (1964) 12.
- [57] R. Hofstadter, *U.S. Patent No. 3,373,279*, 2 March 1968.
- [58] Selling Julia, Stefan Schweizer, D. Birowosuto Muhammad, Pieter Dorenbos, *IEEE Trans. Nucl. Sci.* 55 (3) (2008) 1183.
- [59] N.J. Cherepy, G. Hull, A.D. Drobshoff, S.A. Payne, E. van Loef, C.M. Wilson, K.S. Shah, U.N. Roy, A. Burger, L.A. Boatner, W.-S. Choong, W.W. Moses, *Appl. Phys. Lett.* 92 (2008) 083508.
- [60] C.M. Wilson, E.V. van Loef, J. Glodo, N. Cherepy, B. Hull, S. Payne, W.-S. Choong, W. Moses, K.S. Shah, *Proc. SPIE* 7079 (2008) 707917.
- [61] E.D. Bourret-Courchesne, G. Bizarri, R. Borade, Z. Yan, S.M. Hanrahan, G. Gundiah, A. Chaudhry, A. Canning, S.E. Derenzo, *Nucl. Instr. Meth.* A612 (2009) 138.
- [62] M.S. Alekhin, D.A. Biner, K.W. Krämer, P. Dorenbos, *J. Lumin.* 145 (2014) 723.
- [63] A. Synthfeld, M. Moszynski, R. Arit, M. Balcerzyk, M. Kapusta, M. Majorov, R. Marcinkowski, P. Schotanus, M. Swoboda, D. Wolski, *IEEE Trans. Nucl. Sci.* 51 (2005) 3151.
- [64] J. Glodo, E.V. van Loef, N.J. Cherepy, S.A. Payne, K.S. Shah, *IEEE Trans. Nucl. Sci.* 57 (2010) 1228.
- [65] L.A. Boatner, J.O. Ramey, J.A. Kolopus, R. Hawrami, W.M. Higgins, E. vanLoef, J. Glodo, K.S. Shah, Emmanuel Rowe, Pijush Bhattacharya, Michael Groza EugeneTupitsyn, Arnold Burger, N.J. Cherepy d, S.A. Payne, *J. Cryst. Growth* 379 (2013) 63.
- [66] M.S. Alekhin, J.T.M. de Haas, K.W. Krämer, P. Dorenbos, *IEEE Trans. Nucl. Sci.* 58 (2011) 2519.
- [67] M.S. Alekhin, K.W. Krämer, P. Dorenbos, *Nucl. Instr. Meth.* A714 (2013) 13.
- [68] P. Dorenbos, *J. Phys. Cond. Matter.* 15 (2003) 4797.
- [69] J. Glodo, R. Farrell, E.V.D. van Loef, W.M. Higgins, K.S. Shah, *Conf. Record. IEEE NSS and MIC conference, 2005*, p. 98 Puerto Rico, October.
- [70] H. Ogino, A. Yoshikawa, M. Nikl, A. Krasnikov, K. Kamada, T. Fukuda, *J. Cryst. Growth* 287 (2006) 335.
- [71] W. Drozdowski, P. Dorenbos, J.T.M. de Haas, R. Drozdowska, A. Owens, K. Kamada, K. Tsutsumi, Y. Usuki, T. Yanagida, A. Yoshikawa, *IEEE Trans. Nucl. Sci.* 55 (2008) 2420.
- [72] K.S. Shah, J. Glodo, W. Higgins, E.V.D. van Loef, W.M. Moses, S.E. Derenzo, M.J. Weber, *IEEE Trans. Nucl. Sci.* 52 (2005) 3157.
- [73] A. Burger, E. Rowe, M. Groza, K. Morales Figueroa, N.J. Cherepy, P.R. Beck, S. Hunter, S.A. Payne, *Appl. Phys. Lett.* 107 (2015) 143505.
- [74] Q.V. Phan, H.J. Kim, G. Rooh, S.H. Kim, *J. Alloy. Comp.* 766 (2018) 326.
- [75] Yutaka Fujimoto, Keiichiro Saeki, Daisuke Nakauchi, Takayuki Yanagida, Masanori Koshimizu, Keisuke Asai, *Sensor. Mater.* 30 (7) (2018) 1577.
- [76] Shohei Kodama, Shunsuke Kurosawa, Akihiro Yamaji, Pejchal Jan, Robert Kral, Yuji Ohashi, Kei Kamada, Yuui Yokota, Nikl Martin, Akira Yoshikawa, *J. Cryst. Growth* 492 (2018) 1.
- [77] Shohei Kodama, Shunsuke Kurosawa, Maki Ohno, Akihiro Yamaji, Masao Yoshino, Pejchal Jan, Robert Kral, Yuji Ohashi, Kei Kamada, Yuui Yokota, Nikl Martin, Akira Yoshikawa, *Rad. Meas.* 124 (2019) 54.
- [78] M.A. Spurrier, P. Szupryczunski, K. Yang, A.A. Carey, C.L. Melcher, *IEEE Trans. Nucl. Sci.* 55 (2008) 1178.
- [79] M. Nikl, V. Babin, J. Pejchal, V.V. Laguta, M. Buryi, J.A. Mares, K. Kamada, S. Kurosawa, A. Yoshikawa, D. Panek, T. Parkman, P. Bruza, K. Mann, M. Müller, *IEEE Trans. Nucl. Sci.* 63 (2) (2016) 433 Part I.
- [80] M.J. Harrison, C. Linnick, B. Montag, S. Brinton, M. McCreary, F.P. Doty, D.S. McGregor, *IEEE Nucl. Sci. Symp. Conf. Record N40-7* (2009), 2008, p. 2850.
- [81] M.J. Harrison, P. Ugorowski, C. Linnick, S. Brinton, D.S. McGregor, F.P. Doty, S. Kirpatrick, D.F. Bahr, *Proc. SPIE* 7806 (2010) 78060M-1.
- [82] K. Yang, P.R. Menge, J.J. Buzniak, V. Ouspenski, *IEEE Nucl. Sci. Symposium and Medical Imaging Conference Record (NSS/MIC) N1-135* (2012), (2012), p. 308.
- [83] K. Yang, P.R. Menge, *J. Appl. Phys.* 118 (2015) 213106.
- [84] P. Dorenbos, B. Ferrand, B. Viana, L. Pícol, *US patent 2010/0065778 A1*.
- [85] S. Blahuta, A. Bessiere, B. Viana, P. Dorenbos, V. Ouspenski, *IEEE Trans. Nucl. Sci.* 60 (2013) 3134.
- [86] S.R. Rotman, H.L. Tuller, C. Warde, *J. Appl. Phys.* 71 (1992) 1209.
- [87] Shuping Liu, Xiqi Feng, Zhiwei Zhou, Nikl Martin, Yun Shi, Yubai Pan, *Phys. Stat. Sol. RRL* 8 (2014) 105.
- [88] Nikl Martin, Kei Kamada, Vladimir Babin, Pejchal Jan, Katerina Pilarova, Eva Mihokova, Alena Beitelrova, Karol Bartosiewicz, Shunsuke Kurosawa,

- Akira Yoshikawa, *Cryst. Growth Des.* 14 (2014) 4827.
- [89] Etienne Auffray, Ramunas Augulis, Andrei Fedorov, Georgy Dosovitskiy, Larisa Grigorjeva, Vidmantas Gulbinas, Merry Koschan, Marco Lucchini, Charles Melcher, Saulius Nargelas, Gintautas Tamulaitis, Augustas Vaitkevicius, Aleksejs Zolotarjovs, Mikhail Korzhik, *Phys. Stat. Sol.(a)* 215 (2018) 1700798.
- [90] M. Nikl, A. Yoshikawa, K. Kamada, K. Nejezchleb, C.R. Stanek, J.A. Mares, K. Blazek, *Prog. Cryst. Growth Char. Mater.* 59 (2013) 47.
- [91] C. Foster, Yuntao Wu, Merry Koschan, Charles L. Melcher, *Phys. Stat. Sol. RRL* 12 (2018) 1800280.
- [92] Yuntao Wu, Li Qi, Daniel J. Rutstrom, Mariya Zhuravleva, Matthew Loyd, Luis Stand, Merry Koschan, Charles L. Melcher, *Phys. Stat. Sol. RRL* 12 (2018) 1700403.
- [93] Yuntao Wu, Qi Li, D.J. Rutstrom, I. Greeley, L. Stand, M. Loyd, M. Koschan, C.L. Melcher, *Nucl. Instr. Meth.* (2019), <https://doi.org/10.1016/j.nima.2018.09.077> A in press.
- [94] I.V. Khodyuk, S.A. Messina, T.J. Hayden, E.D. Bourret, G.A. Bizarri, *J. Appl. Phys.* 118 (2015) 084901.
- [95] P. Dorenbos, *J. Phys. Condens. Matter* 15 (2003) 575.
- [96] R.H.P. Awater, M.S. Alekhin, D.A. Biner, K.W. Krämer, P. Dorenbos, *J. Lumin.* 212 (2019) 1.
- [97] W.W. Wolszczak, K.W. Krämer, P. Dorenbos, *Phys. Stat. Sol. RRL* (2019) 1900158.
- [98] K. Shibuya, M. Koshimizu, Y. Takeoka, K. Asai, *Nucl. Instr. Meth. B194* (2003) 207.
- [99] Carel W.E. van Eijk, Johan T.M. de Haas, Piotr A. Rodnyi, Ivan V. Khodyuk, Kengo Shibuya, Fumihiko Nishikido, Masanori Koshimizu, *IEEE Nucl. Sci. Symposium Conference Record N69-3* (2008), 2008, p. 3525.
- [100] Michael M. Lee, Joël Teuscher, Tsutomu Miyasaka, Takuro N. Murakami, Henry J. Snaith, *Science* 338 (2012) 643.
- [101] Haotong Wei, Yanjun Fang, Padhraic Mulligan, William Chuirazzi, Hong-Hua Fang, Congcong Wang, Benjamin R. Ecker, Yongli Gao, Maria Antonietta Loi, Lei Cao, Jinsong Huang, *Nat. Photon.* 10 (2016) 338.
- [102] Haotong Wei, Dylan De Santis, Wei Wei, Yehao Deng, Dengyang Guo, Tom J. Savenije, Lei Cao, Jinsong Huang, *Nat. Mater.* 16 (2017) 826.
- [103] M.D. Birowosuto, D. Cortecchia, W. Drozdowski, K. Brylew, W. Lachmanski, A. Bruno, *C. Soci. Sci. Rep.* 6 (2016) 37254.
- [104] Aozhen Xie, Tien Hoa Nguyen, Chaturanga Hettiarachchi, Marcin E. Witkowski, Winicjusz Drozdowski, Muhammad Danang Birowosuto, Hong Wang, *J. Phys. Chem. C* 122 (2018) 16265.
- [105] Sergii Yakunin, Loredana Protesescu, Franziska Krieg, Maryna I. Bodnarchuk, Georgian Nedelcu, Markus Humer, Gabriele De Luca, Manfred Fiebig, Wolfgang Heiss, Maksym V. Kovalenko, *Nat. Commun.* 6 (2015) 8056.
- [106] Qishui Chen, Jing Wu, Xiangyu Ou, Jawaher Almutlaq, AyanA. Zhumekenov, Xinwei Guan, Sanyang Han, Liangliang Liang, Zhigao Yi, Juan Li, Xiaoji Xie, Yu Wang, Ying Li, Dianyuan Fan, Daniel B.L. Teh, Angelo H. All, Omar F. Mohammed, Osman M. Bakr, Tom Wu, Marco Bettinelli, Huanghao Yang, Wei Huang, Xiaogang Liu, *Nature* 561 (2018) 88.
- [107] Hao Wu, Yong Yang, Dacheng Zhou, Kuangran Li, Jie Yu, Jin Han, Zhencai Li, Zhangwen Long, Jiao Ma, Jianbei Qiu, *Nanoscale* 10 (2018) 3429.
- [108] Pieter Dorenbos, Aday Josef, T. Johan, M. de Haas, Karl W. Krämer, *J. Lumin.* 208 (2019) 463.
- [109] P. Dorenbos, *Phys. Rev. B* 85 (2012) 165107.
- [110] R. Awater, P. Dorenbos, *J. Lumin.* 184 (2017) 221.
- [111] Roy.H.P. Awater, Pieter Dorenbos, *J. Lumin.* 188 (2017) 487.
- [112] Rampi Ramprasad, Rohit Batra, Ghanshyam P. P. Arun Mannodi-Kanakithodi, Chiho Kim, *npj Comput. Mater.* 3 (2017) 54.
- [113] Ya Zhuo, Aria Mansouri Tehrani, Anton O. Oliynyk, Anna C. Duke, Jakoah Brgoch, *Nat. Commun.* 9 (2018) 4377.
- [114] G. Pilania, K.J. McClellan, C.R. Stanek, B.P. Uberuaga, *J. Chem. Phys.* 148 (2018) 241729.
- [115] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *Nucl. Instr. Meth. A537* (2005) 232.
- [116] P. Dorenbos, J.C. van't Spijker, O.W.V. Frijs, C.W.E. van Eijk, K. Krämer, H.U. Güdel, A. Ellens, *Nucl. Instr. Meth. B132* (1997) 728.
- [117] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *Nucl. Instr. Meth. A496* (2003) 138.
- [118] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K. Krämer, H.U. Güdel, *Optics Comm.* 189 (2001) 297.
- [119] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *J. Phys. Cond. Matter* 14 (2002) 8481.
- [120] K.S. Shah, J. Glodo, M. Klugerman, W. Higgins, T. Gupta, P. Wong, W.W. Moses, S.E. Derenzo, M.J. Weber, P. Dorenbos, *IEEE Trans. Nucl. Sci.* 51 (2004) 2302.
- [121] M.D. Birowosuto, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *J. Appl. Phys.* 99 (2006) 123520.
- [122] A. Bessiere, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, A. Galtayries, *J. Lumin.* 117 (2006) 187.
- [123] M.D. Birowosuto, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *J. Phys. Cond. Matter* 18 (2006) 6133.
- [124] G. Gundiah, K. Brennan, Z. Yan, E.C. Samulon, G. Wu, G.A. Bizarri, S.E. Derenzo, E.D. Bourret-Courchesne, *J. Lumin.* 149 (2014) 374.
- [125] M.D. Birowosuto, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *IEEE Trans. Nucl. Sci.* 53 (2006) 3028.
- [126] M.D. Birowosuto, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *Phys. Stat. Sol.(a)* 204 (2007) 850.
- [127] Hua Wei, M. Zhuravleva, M. Tyagi, C.L. Melcher, *IEEE Trans. Nucl. Sci.* 61 (2014) 390.
- [128] M.D. Birowosuto, P. Dorenbos, J.T.M. de Haas, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *J. Appl. Phys.* 101 (2007) 066107.
- [129] E.V. van Loef, W.M. Higgins, J. Glodo, A.V. Churilov, K.S. Shah, *J. Cryst. Growth* 310 (2008) 2090.
- [130] M.D. Birowosuto, P. Dorenbos, G. Bizarri, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, *IEEE Trans. Nucl. Sci.* 55 (2008) 1164.
- [131] Y.D. Porter-Chapman, E. Bourret-Courchesne, G.A. Bizari, M.J. Weber, S.E. Derenzo, *IEEE Trans. Nucl. Sci.* 56 (2009) 881.
- [132] G. Rooh, H.J. Kim, S. Kim, *Rad. Meas.* 45 (2010) 412.
- [133] G. Rooh, H.J. Kim, H. Park, S. Kim, *J. Cryst. Growth* 15 (2010) 2243.
- [134] Kan Yang, Mariya Zhuravleva, Matthew Ürferr, Laurence F. Miller, Charles L. Melcher, *Nucl. Instr. Meth. A656* (2011) 92.
- [135] M. Zhuravleva, K. Yang, A. Green, C.L. Melcher, *J. Cryst. Growth* 318 (2011) 796.
- [136] G. Rooh, H.J. Kim, H. Park, Sunghwan Kim, *J. Cryst. Growth* 377 (2013) 28.
- [137] Rooh Gul, H.J. Kim, H. Park, Sunghwan Kim, *J. Lumin.* 132 (2012) 713.
- [138] E.C. Samulon, G. Gundiah, M. Gascon, I.V. Khodyuk, S.E. Derenzo, G.A. Bizarri, E.D. Bourret-Courchesne, *J. Lumin.* 153 (2014) 64.
- [139] Hua Wei, Luis Stand, Mariya Zhuravleva, Fang Meng, Victoria Martin, Charles L. Melcher, *Opt. Mater.* 38 (2014) 154.
- [140] G. Rooh, H.J. Kim, H. Park, S. Kim, H. Liang, *IEEE Trans. Nucl. Sci.* 61 (2014) 397.
- [142] G. Rooh, H.J. Kim, H. Park, Sunghwan Kim, *J. Lumin.* 146 (2014) 404.
- [143] R. Hawrami, E. Ariesanti, L. Soundara-Pandian, J. Glodo, K.S. Shah, *IEEE Trans. Nucl. Sci.* 63 (2016) 2838.
- [144] R. Hawrami, E. Ariesanti, H. Wei, J. Finkelstein, J. Glodo, K. Shah, *Cryst. Growth Des.* 17 (2017) 3960.
- [145] H.J. Kim, Rooh Gul, H. Park, Sunghwan Kim, *Rad. Meas.* 90 (2016) 279.
- [146] H.J. Kim, Rooh Gul, Arshad Khan, Sunghwan Kim, *Nucl. Instr. Meth. A* 849 (2017) 72.
- [147] H.J. Kim, Rooh Gil, Sunghwan Kim, *J. Lumin.* 186 (2017) 219.
- [148] R. Hawrami, E. Ariesanti, H. Wei, J. Finkelstein, J. Glodo, K.S. Shah, *J. Cryst. Growth* 475 (2017) 216.
- [149] Arshad Khan, Rooh Gul, H.J. Kim, H. Park, Sunghwan Kim, *Rad. Meas.* 107 (2017) 115.
- [150] Rooh Gul, Arshad Khan, H.J. Kim, H. Park, Sunghwan Kim, *Opt. Mater.* 73 (2017) 523.
- [151] Rooh Gul, H.J. Kim, Jonghun Jang, Sunghwan Kim, *J. Lumin.* 187 (2017) 347.
- [152] Arshad Khan, Rooh Gul, H.J. Kim, Sunghwan Kim, *J. All. Comp.* 741 (2018) 878.
- [153] H.J. Kima, Rooh Gul, Arshad Khan, H. Park, Sunghwan Kim, *Opt. Mater.* 82 (2018) 7.
- [154] R. Hofstadter, E.W. O'Dell, C.T. Schmidt, *Rev. Sci. Instrum.* 35 (1964) 246.
- [155] Zewu Yan, Gregory Bizarri, Edith Bourret-Courchesne, *Nucl. Instr. Meth. A698* (2013) 7.
- [156] Zewu Yan, Gautam Gundiah, G. Bizarri, E.C. Samulon, S.E. Derenzo, E.D. Bourret-Courchesne, *Nucl. Instr. Meth. A735* (2014) 83.
- [157] G. Bizarri, E.D. Bourret-Courchesne, Z. Yan, S.E. Derenzo, *IEEE Trans. Nucl. Sci.* 58 (2011) 3403.
- [158] E.D. Bourret-Courchesne, G. Bizarri, S.M. Hanrahan, G. Gundiah, Z. Yan, S.E. Derenzo, *Nucl. Instr. Meth. A613* (2010) 95.
- [159] R. Borade, E. Bourret-Courchesne, S. Derenzo, *Nucl. Instr. Meth. A652* (2011) 260.
- [160] Kan Yang, Mariya Zhuravlev, Charles L. Melcher, *Phys. Stat. Sol. RRL* 1 (2011) 43.
- [161] M. Zhuravleva, B. Blalock, K. Yang, M. Koschan, C.L. Melcher, *J. Cryst. Growth* 352 (2012) 115.
- [162] E.D. Bourret-Courchesne, G. Bizarri, R. Borade, G. Gundiah, E.C. Samulon, Z. Yan, S.E. Derenzo, *J. Cryst. Growth* 352 (2012) 78.
- [163] A.Yu Grippa, N.V. Rebrova, T.E. Gorbacheva, V.Yu Pedash, N.N. Kosinov, V.L. Cherginets, V.A. Tarasov, O.A. Tarasenko, *Nucl. Instr. Meth. A729* (2013) 356.
- [164] A.Yu Grippa, N.V. Rebrova, T.E. Gorbacheva, V.Yu Pedash, N.N. Kosinov, V.L. Cherginets, V.A. Tarasov, O.A. Tarasenko, A.V. Lopin, *J. Cryst. Growth* 371 (2013) 112.
- [165] Adam C. Lindsey, Mariya Zhuravleva, Luis Stand, Yuntao Wu, Charles L. Melcher, *Opt. Mater.* 48 (2015) 1.
- [166] Matthew Loyd, Lindsey Adam, Yuntao Wu, Luis Stand, Micah Folsom, Daniel Rutstrom, Merry Koschan, Charles L. Melcher, Mariya Zhuravleva, *Nucl. Instr. Meth. A914* (2019) 8.
- [167] L. Stand, M. Zhuravleva, A. Lindsey, C.L. Melcher, *Nucl. Instr. Meth. A780* (2015) 40.
- [168] L. Stand, M. Zhuravleva, H. Wei, C.L. Melcher, *Opt. Mater.* 46 (2015) 59.
- [169] L. Stand, M. Zhuravleva, B. Chakoumakos, J. Johnson, A. Lindsey, C.L. Melcher, *J. Lumin.* 169 (2016) 301.
- [170] Sasmit S. Gokhale, Luis Stand, Adam Lindsey, Merry Koschan, Mariya Zhuravleva, Charles L. Melcher, *J. Cryst. Growth* 445 (2016) 1.
- [171] Yuntao Wu, Mariya Zhuravleva, Adam C. Lindsey, Merry Koschan, Charles L. Melcher, *Nucl. Instr. Meth. A820* (2016) 132.
- [172] Yuntao Wu, Li Qi, Bryan C. Chakoumakos, Mariya Zhuravleva, Adam C. Lindsey, Jesse Ashby Johnson II, Luis Stand, Merry Koschan, Charles L. Melcher, *Adv. Opt. Mater.* 4 (2016) 1518.
- [173] L. Soundara-Pandian, R. Hawram, J. Glodo, E. Ariesanti, E.V. van Loef, K. Shah, *IEEE Trans. Nucl. Sci.* 63 (2016) 490.
- [174] M. Loyd, A. Lindsey, L. Stand, M. Zhuravleva, C.L. Melcher, M. Koschan, *Opt. Mater.* 68 (2017) 47.
- [175] L. Stand, M. Zhuravleva, J. Johnson, M. Koschan, E. Lukosi, C.L. Melcher, *Opt. Mater.* 73 (2017) 408.
- [176] Kei Kamada, Hiroyuki Chiba, Masao Yoshino, Akihiro Yamaji, Yasuhiro Shojic, Shunsuke Kurosawa, Yuui Yokota, Yuji Ohashi, Akira Yoshikawa, *Opt. Mater.* 68 (2017) 70.
- [177] J.A. Johnson, M. Zhuravleva, L. Stand, B.C. Chakoumakos, Y. Wu, I. Greely,

- D. Rutstrom, M. Koschan, C.L. Melcher, *Cryst. Growth Des.* 18 (2018) 5220.
- [178] L. Stand, M. Zhuravleva, Chakoumakos, J. Johnson, M. Loyd, Y. Wu, M. Koschan, C.L. Melcher, *J. Cryst. Growth* 486 (2018) 162.
- [179] L. Stand, M. Zhuravleva Chakoumakos, H. Wei, J. Johnson, V. Martin, M. Loyd, D. Rutstrom, W. McAlexander, Y. Wu, M. Koschan, C.L. Melcher, *J. Lumin.* 207 (2019) 70.
- [180] V.L. Cherginets, N.V. Rebrova, A.Yu Grippa, YuN. Datsko, T.V. Ponomarenko, V.Yu Pedash, N.N. Kosinov, V.A. Tarasov, O.V. Zelenskaya, I.M. Zenya, A.V. Lopin, *Mater. Chem. Phys.* 143 (2014) 1296.
- [181] W. Drozdowski, P. Dorenbos, A.J.J. Bos, G. Bizarri, A. Owens, F.G.A. Quarati, *IEEE Trans. Nucl. Sci.* 55 (2008) 1391.
- [182] J. Selling, M.D. Birowosuto, P. Dorenbos, S. Schweizer, *J. Appl. Phys.* 101 (2007) 034901.
- [183] U.N. Roy, M. Groza, Y. Cui, A. Burger, N. Cherepy, S. Friedrich, S.A. Payne, *Nucl. Instr. Meth. A* 579 (2007) 46.
- [184] R. Hawrami, A.K. Batra, M.D. Aggarwal, U.N. Roy, M. Groza, Y. Cui, A. Burger, N. Cherepy, T. Niedermayr, S.A. Payne, *J. Cryst. Growth* 310 (2008) 2099.
- [185] Rooh Gul, Heedong Kang, H.J. Kim, H. Park, SihHong Doh, Sungwhan Kim, *J. Cryst. Growth* 311 (2008) 128.
- [186] Rooh Gul, Heedong Kang, H.J. Kim, H. Park, Sungwhan Kim, *J. Cryst. Growth* 311 (2009) 2470.
- [187] Sunghwan Kim, Joon Il Lee, Sih-Hong Doh, Hong Joo Kim, Hwanbae Park, Heedong Kang, Dosung Kim, U. Hong, *IEEE Trans. Nucl. Sci.* 56 (2009) 982.
- [188] G. Rooh, H.J. Kim, S. Kim, *IEEE Trans. Nucl. Sci.* 57 (2010) 1255.
- [189] Sunghwan Kim, Rooh Gul, H.J. Kim, Kim Wan, U. Hong, *IEEE Trans. Nucl. Sci.* 57 (2010) 1251.
- [190] G. Rooh, H. Kim, H. Park, S. Kim, *IEEE Trans. Nucl. Sci.* 57 (2010) 3836.
- [191] M. Zhuravleva, K. Yang, C.L. Melcher, *J. Cryst. Growth* 318 (2011) 809.
- [192] J.A. Mares, M. Nikl, Alena Beitlerova, Petr Horodysky, Karel Blazek, Karel Bartos, Carmelo D'Ambrosio, *IEEE Trans. Nucl. Sci.* 59 (2012) 2120.
- [193] W. Drozdowski, K. Brylew, A.J. Wojtowicz, J. Kisielewski, M. Swirkowicz, T. Lukaszewicz, J.T.M. de Haas, P. Dorenbos, *Opt. Mater. Expr.* 4 (2014) 1207.
- [194] G. Rooh, H.J. Kim, H. Park, S. Kim, *IEEE Trans. Nucl. Sci.* 59 (2012) 2248.
- [195] E. Rowe, P. Bhattacharaya, E. Tupitsyn, Michael Groza, Arnold Burger, Nerine J. Cherepy, Steve A. Payne, Benjamin W. Sturm, C. Pedrini, *IEEE Trans. Nucl. Sci.* 60 (2013) 1057.
- [196] Keiichiro Saeki, Yutaka Fujimoto, Masanori Koshimizu, Takayuki Yanagida, Keisuke Asai, *Appl. Phys. Express* 9 (2016) 042602.
- [197] Yuntao Wu, Hongliang Shi, Bryan C. Chakoumakos, Mariya Zhuravleva, Mao-Hua Duc, Charles L. Melcher, *J. Mater. Chem. C* 3 (2015) 11366.
- [198] N.V. Shiran, A.V. Gektin, Y. Boyarintseva, S. Vasyukov, A. Boyarintsev, V. Pedash, S. Tkachenko, O. Zelenskaya, N. Kosinov, O. Kisil, L. Philippovich, *IEEE Trans. Nucl. Sci.* 57 (2010) 1233.
- [199] F.G.A. Quarati, M.S. Alekhin, K.W. Krmer, P. Dorenbos, *Nucl. Instr. Meth. A* 735 (2014) 655.
- [200] P. Guss, Michael E. Foster, Bryan M. Wong, F. Patrick Doty, Kanai Shah, Michael R. Squillante, Urmila Shirwadkar, Rastgo Hawrami, Joshua Tower, Ding Yuan, *J. Appl. Phys.* 115 (2014) 034908.