Radiation Measurements 90 (2016) 157–161

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Effects of Na and K co-doping on growth and scintillation properties of Eu:SrI$_2$ crystals

Tomoki Ito [a, *], Yuui Yokota [b], Shunsuke Kurosawa [a, b], Robert Kral [c], Jan Pejchal [b, c], Yuji Ohashi [a], Kei Kamada [b, d], Martin Nikl [c], Akira Yoshikawa [a, b, d]

[a] Institute for Materials Research, Tohoku University 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan
[b] New Industry Creation Hatchery Center (NICHe), Tohoku University 6-6-10, Aramaki, Aoba, Aoba-ku, Sendai, Miyagi, 980-8579, Japan
[c] Institute of Physics AS CR 10 Cukrovarnicka, Prague 6, 16200 Czech Republic
[d] C&A Corporation 6-6-40, Aramaki, Aoba, Aoba-ku, Sendai, Miyagi, 980-8579, Japan

HIGHLIGHTS

- Na or K co-doped Eu:SrI$_2$crystals were grown by the modified μ-PD method.
- The milky parts were generated in the Na5.0% and K5.0%,Eu:SrI$_2$crystals.
- The light yield of Eu:SrI$_2$was decreased by the Na or K co-doping.
- The decay times of Eu:SrI$_2$were almost constant by the Na or K co-doping.
- The non-proportionalitywas improved in the low energy region by the K co-doping.

ARTICLE INFO

Article history:
Received 25 October 2015
Received in revised form
20 January 2016
Accepted 21 January 2016
Available online 25 January 2016

Keywords:
Eu:SrI$_2$
Scintillator
Single crystal
Alkali metal
Light yield
Non-proportionality

ABSTRACT

We grew Na and K co-doped Eu:SrI$_2$ [Na,Eu:SrI$_2$ and K,Eu:SrI$_2$] crystals by a modified micro-pulling-down method to reveal the co-doping effects on the crystal growth and scintillation properties. The non-codoped, Na0.5%, Na1.0%, K0.5% and K1.0%,Eu:SrI$_2$ crystals indicated high transparency while the milky parts were generated in the Na5.0% and K5.0%,Eu:SrI$_2$ crystals. The light yields of Na,Eu:SrI$_2$ and K,Eu:SrI$_2$ crystals under γ-ray irradiation were decreased by the Na and K co-doping. On the other hand, there was a small change within 940–1020 ns in the decay times by the Na and K co-doping. In the light yield proportionality under γ-ray irradiation, the non-proportionality in the low energy region was improved by Na and K co-doping.

© 2016 Published by Elsevier Ltd.

1. Introduction

Eu doped SrI$_2$ [Eu:SrI$_2$] scintillator crystal has high light yield (~80,000 ph/MeV) and high energy resolution (~3%) due to the small band-gap. Therefore, it is expected to be applied for next-generation radiation detector (Cherepy et al., 2008; Belli et al., 2012; Glodo et al., 2010; Cherepy et al., 2009; Hawrami et al., 2013; Gahane et al., 2009). The light yield proportionality of Eu:SrI$_2$ single crystal has been measured in the previous reports (Cherepy et al., 2008) and the Eu:SrI$_2$ single crystal indicated excellent light yield proportionality compared to the other scintillators as represented by Tl:NaI, Ce:LaBr$_3$ and Ce:Y$_3$Al$_5$O$_{12}$. In our previous report [Yokota et al., 2013, Nishimoto et al., 2014], the light yield proportionality of La co-doped Eu:SrI$_2$ crystals was measured and the non-proportionality became worse especially in the low energy region (<200 keV) by the La co-doping. On the other hand, there is a previous report about the effects of alkali metal (Na$^+$) or alkali earth metal (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) doping on the non-proportionality of the CeBr$_3$ scintillator crystal and the non-proportionality in the low energy region was improved by the doping (Quarati et al., 2014). According to the previous report, the improvement of the non-proportionality by the alkali metal or

---

* Corresponding author.
E-mail address: tomoki@imr.tohoku.ac.jp (T. Ito).

http://dx.doi.org/10.1016/j.radmeas.2016.01.025
1350-4487/© 2016 Published by Elsevier Ltd.

alkali earth metal doping is originated from a more efficient e-h pair creation and/or energy transfer from the e-h pairs to the luminescent centers at energy below 100 keV. However, there is no report about the effects of alkali metal (Na^+ and K^+) co-doping to Eu:SrI_2 crystals on the optical and scintillation properties. According to the result of $CeBr_3$ crystal, the improvement of the non-proportionality is also expected for the Eu:SrI_2 crystal by the alkali metal.

On these backgrounds, in this study, we grew Na and K co-doping Eu:SrI_2 crystals with various Na and K concentrations and measure the optical and scintillation properties to reveal the effects of the alkali metal co-doping on the optical and scintillation properties and improve the non-proportionality of Eu:SrI_2.

2. Experimental procedure

We grew the $\{(Sr_{1-x}A_x)_{0.925}Eu_{0.075}\}I_2$ [A,Eu:SrI_2, A = Na, K] crystals by a modified micro-pulling-down [μ-PD] method (Totsuka et al., 2012; Kral et al., 2013). Detail of the crystal growth procedure was described in the previous reports (Yokota et al., 2011). Mixed powders of the $\{(Sr_{1-x}A_x)_{0.925}Eu_{0.075}\}I_2$ with $x = 0.00$, 0.005, 0.01, and 0.05 were prepared from the starting materials of SrI_2 (4N), EuI_2 (5N), NaI (4N), and KI (4N) in the glove box filled with Ar (oxygen and moisture concentrations <1 ppm). By the modified μ-PD method, we grew the Non-doped, Na,Eu:SrI_2 and K,Eu:SrI_2 fiber crystals in high-purity Ar gas (99.9999%) at ~0.05 mm/min growth rate using a Pt–Rh wire as a seed without rotation. Polished specimens with 1 mm thickness were prepared from the first half parts of the grown fiber crystals by cutting and polishing in a mineral oil for measurements of optical and scintillation properties.

Parts of the grown crystals were ground in the globe box for X-ray diffraction [XRD] measurement by using an X-ray diffractometer (BRUKER, D8 DISCOVER) and a sealed sample chamber with no diffraction peak in the 2θ range of 20–70°. The configuration of the sealed sample chamber was a 51.5 mm outer diameter half-sphere made of polystyrol and polymethyl methacrylate. The X-ray source was Cu–K_α with accelerating voltage of 40 kV and beam current of 40 mA). The Inductively Coupled Plasma [ICP] analysis (Thermo Fisher Scientific, IRIS Advantage DIO) of the as-grown crystals was performed to identify the actual chemical compositions.

Room temperature emission and excitation spectra of the polished specimens were measured by using a spectrophotometers A10094 and Hamamatsu KK (Kurosawa et al., 2014). Pulse-height spectra and the decay curves of the specimens under γ-ray excitation from ^{137}Cs radiation source were measured to estimate their light yields and decay times using a photomultiplier [PMT](HAMAMATSU, R7600U-200), multi-channel analyzer (AMPTEK CO. Pocket MCA 8000A) and an oscilloscope (TEKTRONIX, TBS1102). The measurements were performed in the grove box filled with Ar atmosphere, where the specimens and PMT were set. The shaping time was 2 μs in the pulse-height spectra measurements. The Ce 1 mol% doped Gd_2SiO_5 [Ce:GSO] single crystal with the light yield of 11,000 ph/MeV was used as a reference to estimate the light yields of the specimens. To evaluate the non-proportionality of the specimens, pulse-height spectra were measured with various γ-ray excitation sources (^{22}Na, ^{54}Mn, ^{60}Co, ^{133}Ba, ^{137}Cs, and ^{152}Eu). The non-proportionality of the Tl:NaI was also measured for the reference.

3. Results and discussions

Non-codoped Eu:SrI_2 and Na,Eu:SrI_2 and K,Eu:SrI_2 crystals with various Na and K concentrations were grown by the modified μ-PD method. It is shown in Fig. 1(a) that the as-grown and polished crystals. All as-grown crystals were approximately ϕ2 mm in diameter and more than 15 mm in length. No visible cracks and inclusions were observed in the polished non-codoped Eu:SrI_2, Na0.5% and 1.0%,Eu:SrI_2, and K0.5% and 1.0%,Eu:SrI_2 crystals and these crystals showing high transparency. On the other hand, milky parts in the polished Na5.0%,Eu:SrI_2 and K5.0%,Eu:SrI_2 crystals were present. It is shown in Fig. 1(b) that the powder XRD patterns of the as-grown crystals were measured for the phase identification. All diffraction peaks in the XRD patterns of the all crystals except for K5.0%,Eu:SrI_2 and Na5.0%,Eu:SrI_2 were identified by the SrI_2 crystal structure (Orthorhombic, Pnma). On the other hand, the additional diffraction peaks of secondary phases were observed in the XRD pattern of the K5.0%,Eu:SrI_2 and Na5.0%,Eu:SrI_2 crystals. The secondary phases of K5.0%,Eu:SrI_2 crystal were considered to be KSr_2I_5 and KI while the secondary phase(s) in the Na5.0%,Eu:SrI_2 crystal was not identified. According to the ICP analysis, the actual Na and K concentrations of Na5.0%, K1.0% and K5.0%,Eu:SrI_2 crystals were 1.3%, 0.3% and 2.7%, respectively. The actual Na and K concentrations of Na0.5%, Na1.0% and K0.5%,Eu:SrI_2 crystals were the below the limit of detection as it is shown in Table 1. In the Na,Eu:SrI_2 and K,Eu:SrI_2 crystals, the actual Na and K concentrations were lower than the nominal composition due to the difference of the valences and ionic radius between Sr^{2+} and, Na^+ and K^+ ions. Therefore, another co-doping of the trivalence cation as represented by Y and La could be effective to improve the segregation of Na^+ and K^+.

We measured the room temperature photoluminescence spectra of the polished specimens (Fig. 2). In the emission spectra performed 410 nm excitation (Fig. 2(a)), an emission peak around 435 nm originated from 5d to 4f transitions of Eu^{2+} ion was observed for all crystals except for K5.0%,Eu:SrI_2. The emission peak for K5.0%,Eu:SrI_2 crystal was shifted to higher wavelength by the K co-doping. However, the reason is not clear now. In the excitation spectra monitored at 435 nm, the excitation peak was observed around 422 nm for all crystals. In addition, a broad excitation peak appeared around 315 nm for K5.0%,Eu:SrI_2 crystal. Probably originating from the secondary phase of Eu:KI (Aceves et al., 2005).

It is shown in Fig. 3 that the pulse-height spectra and decay curves of the non-codoped Eu:SrI_2, Na,Eu:SrI_2 and K,Eu:SrI_2 specimens under γ-ray irradiation. In the pulse-height spectra, clear photo-peaks were observed for the non-codoped, Na0.5%, Na1.0%, K0.5%, and K1.0%,Eu:SrI_2 specimens whereas there was no photo-peak in the Na5.0% and K5.0%,Eu:SrI_2 crystals. The light yields of the specimens were estimated by using the Ce:GSO crystal (11,000 ph/MeV) as a reference (Fig.3(a)). The estimated light yields of the non-codoped,, K0.5%, K1.0%,Eu:SrI_2 specimens and Na0.5%, Na1.0%,Eu:SrI_2 specimens were 70,000, 46,000, 48,500, 53,500 and 49,000 ph/MeV, respectively, and the light yield of the Eu:SrI_2 was decreasing by the Na and K co-doping. In addition, the estimated energy resolutions of the non-codoped, K0.5%, K1.0%,Eu:SrI_2 specimens and Na0.5%, Na1.0%,Eu:SrI_2 specimens were 11.3, 34.8, 11.6, 20.0 and 39.1%, respectively. The energy resolutions were relatively worse than previous reports about Eu:SrI_2. The results are considered to be due to the degradation of the surface for the polished specimens. The scintillation decay curves were fitted by the single exponential decay function (Fig. 3(b)) and the decay times were estimated. The decay times of all crystals were ranging from 940 to 1000 ns and there were few effects on the decay time with the Na and K co-doping as it was observed for the light yield evaluation as it is shown in Table 1.

The light yield proportionalities of the non-codoped Eu:SrI_2 and Na1.0%,Eu:SrI_2 and K1.0%,Eu:SrI_2 specimens were measured using various radiation sources emitting γ-ray as it is depicted in Fig. 4. Comparing to the result of non-codoped Eu:SrI_2, the non-proportionalities of Na1.0%,Eu:SrI_2 and K1.0%,Eu:SrI_2 improved in the low energy region (<200 keV). Especially, the effect of the improvement on the non-proportionality in the low energy region

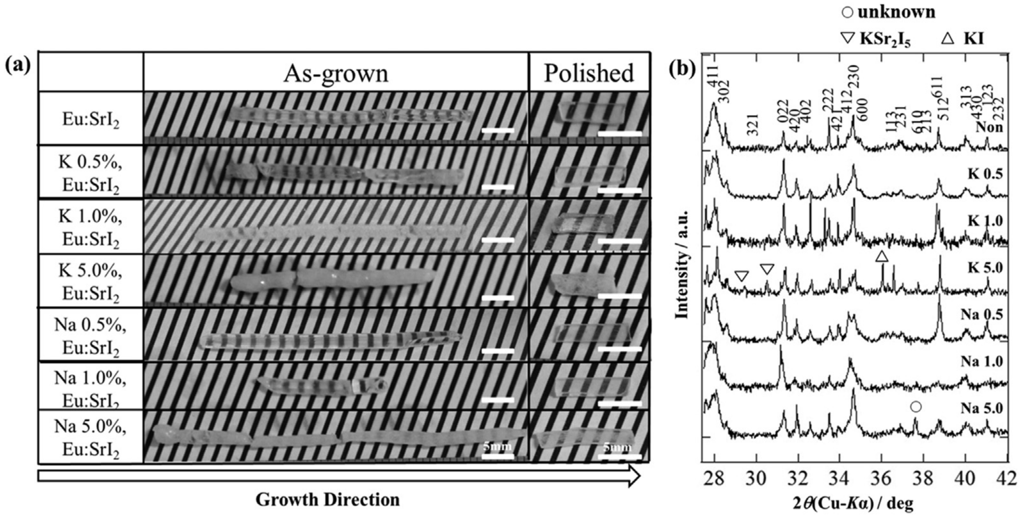

Fig. 1. (a) Non-codoped, Na,Eu:SrI$_2$ and K,Eu:SrI$_2$ crystals grown by the μ-PD method. (b) Powder XRD patterns of the non-codoped, Na,Eu:SrI$_2$ and K,Eu:SrI$_2$ crystals.

Table 1
Summary of chemical composition, and optical and scintillation properties for the Na,Eu:SrI$_2$ and K,Eu:SrI$_2$ crystals.

Co-dopant	Nominal concentration of co-dopant/mo%	Actual concentration of co-dopant/mol% (measured by ICP)	Emission wavelength/nm	Excitation wavelength/nm	Light yield/ photons$^+$ MeV^{-1}	Energy resolution/%	Decay time/ns
K	0	<0.1	435	420	70,000	11.3	959
	0.5	<0.1	435	422	46,000	34.8	947
	1.0	0.3	436	421	48,500	11.6	941
	5.0	2.7	435	310,424	–	–	968
Na	0.5	<0.1	435	421	53,500	20.0	968
	1.0	<0.1	435	422	49,000	39.1	1020
	5.0	1.3	435	424	–	–	947

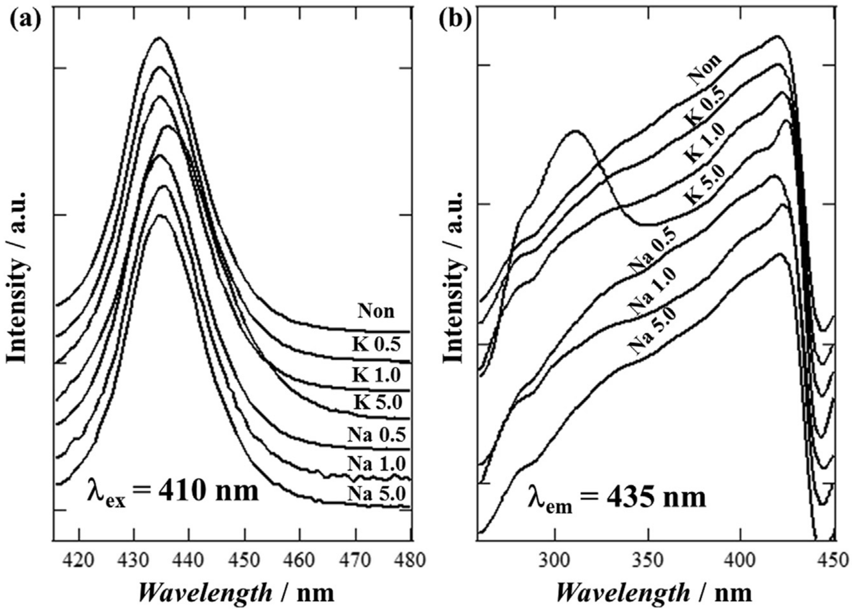

Fig. 2. (a) Emission and (b) excitation spectra of the non-codoped, Na,Eu:SrI$_2$ and K,Eu:SrI$_2$ specimens.

by the K co-doping was larger than that of the Na co-doping. The results suggest that alkali metal co-doping made the e-h pair cr1eation and/or energy transfer from the e-h pairs to the luminescent centers at energy below 100 keV more efficient and the effect is dependent on the ionic radius of co-dopant.

4. Conclusions

We grew the Na and K co-doped Eu:SrI$_2$ crystals by the modified μ-PD method and their optical and scintillation properties were measured. The grown non-codoped Eu:SrI$_2$, Na,Eu:SrI$_2$ and

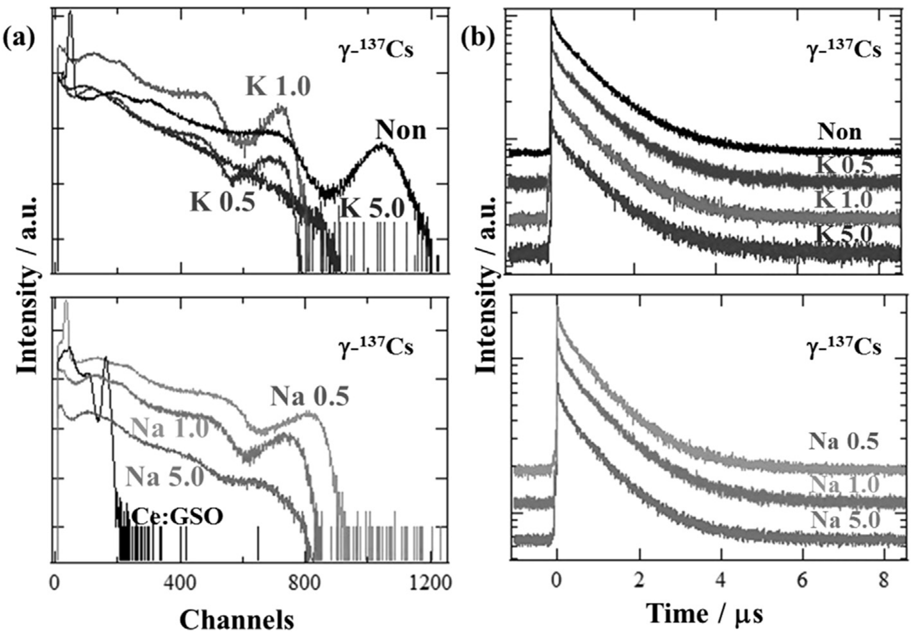

Fig. 3. (a) Pulse-height spectra and (b) decay curves of the non-codoped, Na,Eu:SrI_2 and K,Eu:SrI_2 specimens under γ-ray irradiation.

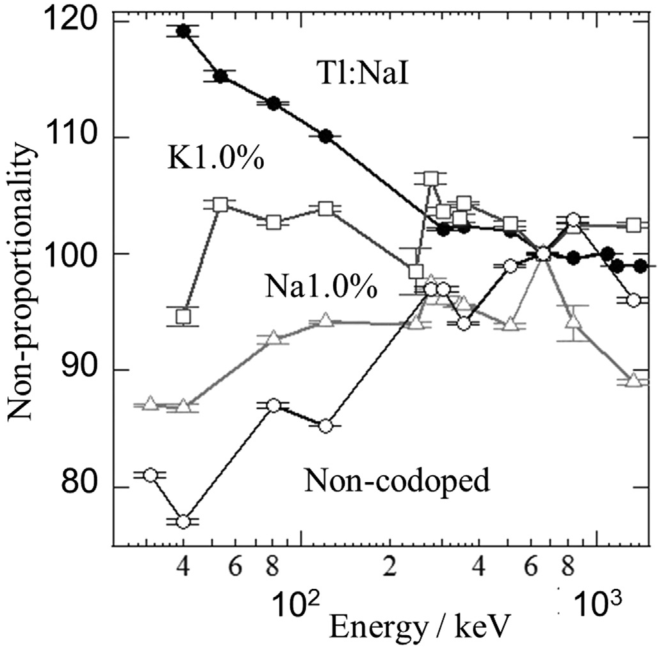

Fig. 4. Light yield proportionality of the non-codoped, Na,Eu:SrI_2 and K,Eu:SrI_2 specimens under γ-ray irradiation.

K,Eu:SrI_2 crystals except for the Na5.0% and K5.0%,Eu:SrI_2. Grown crystals indicated high transparency while the milky parts were generated in the Na5.0% and K5.0%,Eu:SrI_2 crystals as indicated by presence of secondary phases in the powder XRD patterns. In the photoluminescence spectra, emission and excitation peaks were observed around 435 nm and 422 nm respectively for all specimens except for K5.0%,Eu:SrI_2. On the other hand, K5.0%,Eu:SrI_2 showed the emission peak at the longer wavelength and the additional excitation peak around 330 nm which was considered to be attributable to the secondary phases. In the pulse-height spectra, the light yield of the Eu:SrI_2 was decreased by the Na and K co-doping whereas the decay times were almost constant (940–1020 ns). Meanwhile, the non-proportionality of the Eu:SrI_2 was improved in the low energy region (<200 keV) by the Na and K co-doping and the K1.0%,Eu:SrI_2 crystal showed the most excellent non-proportionality.

Acknowledgments

This work is partially supported by the New Energy and Industrial Technology Development Organization (NEDO), the Japan Society for the Promotion of Science (JSPS) Research Fellowships for Grant-in-Aid for Young Scientists, Bilateral AS CR-JSPS Joint Research Project, MEYS, KONTAKT II, no. LH14266, Japan Science and Technology Agency (JST) Adaptable & Seamless Technology Transfer Program through Target-driven R&D (A-STEP). In addition, we would like to thank following person for the support: Mr. Tetsuya Ashio in Analytical Research Core for Advanced Materials, Tohoku University.

References

Aceves, R., Piters, T.M., Zazu bovich, S., 2005. Luminescence of excitons and Eu^{2+} V_c^- centres on KI: Eu^{2+} crystals. Phys. Stat. Sol. 242, 2121–2128.

Belli, P., Bernabei, R., Cerulli, R., Danevich, F.A., Galenin, E., Gektin, A., Incicchitti, A., Isaienko, O., Kobychev, V.V., Laubenstein, M., Nagorny, S.S., Podviyanuk, R.B., Tkachenko, S., Tretyak, V.I., 2012. Radioactive contamination of SrI_2(Eu) crystal scintillator. Nucl. Instrum. Methods A 670, 10–17.

Cherepy, N.J., Hull, G., Drobshoff, A., Payne, S.A., van Loef, E., Wilson, C., Shah, K., Roy, U.N., Burger, A., Boatner, L.A., Choong, W.-S., Moses, W.W., 2008. Strontium and barium iodide high light yeild scintilltors. Appl. Phys. Lett. 92, 083508.

Cherepy, N.J., Payne, S.A., Asztalos, S.J., Hull, G., Kuntz, J.D., Niedermayr, T., Pimputkar, S., Roberts, J.J., Sanner, R.D., Tillotson, T.M., van Loef, E., Wilson, C.M., Shah, K.S., Roy, U.N., Hawrami, R., Burger, A., Boatner, L.A., Choong, W.S., 2009. Scintillators with potential to supersede lanthanum bromide. IEEE Trans. Nucl. Sci. 56, 873–880.

Gahane, D.H., Kokode, N.S., Muthal, P.L., Dhopte, S.M., Moharil, S.V., 2009. Luminescence of Eu^{2+} in some iodides. Opt. Mater. 32, 18–21.

Glodo, J., van Loef, E.V., Cherepy, N.J., Payne, S.A., Shah, K.S., 2010. Concentration effects in Eu doped SrI_2. IEEE Trans. Nucl. Sci. 57, 1228–1232.

Hawrami, R., Glodo, J., Shah, K.S., Cherephy, N., Payne, S., Burger, A., Boatner, L., 2013. Bridgman bulk growth and scintillation measurements of SrI_2:Eu^{2+}. J. Cryst. Growth 379, 69–72.

Kral, R., Nitsch, K., Jary, V., Yokota, Y., Futami, F., Yoshikawa, A., Nikl, M., 2013. Preparation and characterization of pure and Pr(III)-doped lead chroride single crystals grown by modified micro-pulling-down method. J. Cryst. Growth 375, 57–31.

Kurosawa, S., Yokota, Y., Yanagida, Y., Pejchal, J., Yamaji, A., Shoji, Y., Kamada, K., Yoshikawa, A., 2014. Optical properties of a Nd-doped $SrBr_2$ crystal grown by the Bridgman technique. J. Cryst. Growth 393, 163–166.

Nishimoto, K., Yokota, Y., Kurosawa, S., Pejchal, J., Kamada, K., Chani, V., Yoshikawa, A., 2014. Effects of La, Gd, or Lu co-doping on crystal growth and scintillation properties of Eu:SrI_2 single crystals. J. Cryst. Growth 401, 484–488.

Quarati, F.G.A., Alekhin, M.S., Kramer, K.W., Dorenbos, P., 2014. Co-doping of $CeBr_3$ scintillator detectors for energy resolution enhancement. Nucl. Instrum. Methods A 735, 655–658.

Totsuka, D., Yanagida, T., Fujimoto, Y., Pejchal, J., Yokota, Y., Yoshikawa, A., 2012. Growth and scintillation properties of pure CsI crystals grown by micro-pulling-down method. Opt. Mater. 34, 1087–1091.

Yokota, Y., Kawaguchi, N., Fukuda, K., Yanagida, T., Yoshikawa, A., Nikl, M., 2011. Development of modified micro-pulling-down method for bromide and chloride single crystals. J. Cryst. Growth 318, 908–911.

Yokota, Y., Nishimoto, K., Kurosawa, S., Totsuka, D., Yoshikawa, A., 2013. Crystal growth of Eu:SrI_2 single crystals by micro-pulling-down method and scintillation properties. J. Cryst. Growth 375, 49–52.