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Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeasScintillation properties of pure and Ce³⁺-doped SrF₂ crystalsR. Shendrik^{a,b,*}, E.A. Radzhabov^{a,b}, A.I. Nepomnyashchikh^{a,b}^a Vinogradov Institute of Geochemistry SB RAS, Favorskogo 1a, Irkutsk 664033, Russia^b Physics Department of Irkutsk State University, Gagarina Blvd. 20, Irkutsk 664003, Russia

HIGHLIGHTS

- ▶ Scintillation properties of oxygen-free SrF₂–Ce crystals were measured.
- ▶ Light output of SrF₂ is 85% of the NaI–Tl output.
- ▶ Light output of SrF₂–Ce is 115% of the NaI–Tl output.
- ▶ Crystals SrF₂–0.3 mol% Ce³⁺ can be applied in well-logging scintillation detectors.
- ▶ Strontium fluoride crystals would be useful as newly perspective scintillator.

ARTICLE INFO

Article history:

Received 15 October 2012

Received in revised form

9 January 2013

Accepted 21 January 2013

Keywords:

Scintillator

Well-logging

Alkali-earth fluorides

Cerium doped crystals

ABSTRACT

In this paper results of scintillation properties measurements of pure and Ce³⁺-doped strontium fluoride crystals are presented. We measure light output, scintillation decay time profile and temperature stability of light output. X-ray excited luminescence outputs corrected for spectral response of monochromator and photomultiplier for pure SrF₂ and SrF₂–0.3 mol% Ce³⁺ are approximately 95% and 115% of NaI–Tl emission output, respectively. A photopeak with a 10% full width at half maximum is observed at approximately 84% the light output of a NaI–Tl crystal after correction for spectral response of photomultiplier, when sample 10 × 10 mm of pure SrF₂ crystal is excited with 662 keV photons. Corrected light output of SrF₂–0.3 mol% Ce³⁺ under 662 keV photon excitation is found at approximately 64% the light output of the NaI–Tl crystal.

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1. Introduction

The interest in new scintillation materials is promoted by an increasing number of new applications in medicine, science, and homeland security, which require ramp-up of material production. The most prospective scintillators are bromides and iodides doped with Ce³⁺ and Eu²⁺ ions, such as SrI₂–Eu and LaBr₃–Ce. These crystals have high light outputs (up to 100,000 photons/MeV for SrI₂–Eu), good energy resolution, and high proportionality (Dorenbos, 2010). Disadvantages of these scintillators are high hygroscopicity and price. In addition, SrI₂–Eu has temperature instability of light output observed by Alekhin et al. (2011).

For most applications a cheaper NaI–Tl scintillator has adequate properties (light output about 45,000 photons/MeV cited in Derenzo, 2012). Therefore, one of the ways in development of new

scintillators is to find new materials with similar to NaI–Tl properties but no hygroscopic. In this way advanced materials for new scintillators are alkali-earth fluorides doped with rare earth ions. Theoretical limit of light output for them is up to 50,000 photons/MeV (Dorenbos, 2010). If an efficient energy transfer is provided then alkali-earth fluorides will be promising scintillators. A real light output of CaF₂–Eu is 18,000–22,000 photons/MeV, but BaF₂ and BaF₂–Ce crystals demonstrate lower light output at about 10,000 photons/MeV (Visser et al., 1991). Scintillation properties of SrF₂ crystals have not been extensively investigated. Light output of SrF₂ was estimated about 10,000–12,000 photons/MeV by Schotanus et al. (1987), but direct measurements of SrF₂ light yield till now have not been made. Potential light output of SrF₂ can be higher. Also SrF₂ crystals doped with Ce³⁺ and Pr³⁺ demonstrate a temperature stability of light output in wide range (20 °C–200 °C) (Shendrik and Radzhabov, 2010). Therefore, SrF₂ can be a promising scintillator for well-logging. So, scintillation properties of strontium fluoride crystals are among the least studied of fluorides crystals, but these crystals have potential applications. Thus, the investigations of scintillation properties of strontium fluorides are

* Corresponding author. Vinogradov Institute of Geochemistry SB RAS, Favorskogo 1a, Irkutsk 664033, Russia. Tel.: +7 9149562136.

E-mail addresses: roshen@yandex.ru, r.shendrik@gmail.com, shendrik@ieee.org (R. Shendrik).

topical today. This paper describes the scintillation properties of pure and cerium doped strontium fluorides crystals.

2. Experimental methodology

Growing with addition of CdF_2 as an oxygen scavenger, oxygen-free crystals of pure SrF_2 and doped with different concentrations of Ce^{3+} ions were grown in a graphite crucible by the Stockbarger method. We applied several experimental techniques in measurements of scintillation properties of crystals. To determine light output, pulsed-height spectra under ^{137}Cs 662 keV gamma source excitation were measured with PMT FEU-39A, a homemade pre-amplifier and an Ortec 570A spectrometric amplifier. The crystals of 10×10 mm dimensions were polished and then covered with several layers of ultraviolet reflecting Teflon tape (PTFE tape). The shaping time of Ortec 570 spectrometric amplifier was set at 10 μs to better scintillator light collection.

X-ray excited luminescence was performed using X-ray tube with Pd anode operating at 35 kV and 0.8 mA. The spectra were recorded at photon-counting regime using PMT FEU-39A and vacuum grating monochromator VM-4. The spectral width of the monochromator slits was 7 nm. A spectral sensitivity of the VM-4 monochromator and PMT FEU-39A is shown in Fig. 1, dashed curve.

Scintillation decay time profiles under ^{137}Cs $E = 662$ keV gamma source excitation were recorded by 200 MHz oscilloscope Rigol DS-1202CA. To register decay curves in wide time interval, we used oscilloscope input resistance set at 50 Ω and 2.8 k Ω .

3. Experimental results and discussion

Fig. 1 shows spectra of X-ray luminescence of pure SrF_2 , NaI–Tl, SrF_2 -0.3 mol% Ce^{3+} , and CaF_2 -0.1 mol% Eu^{2+} corrected for the spectral sensitivity of the detection part of apparatus. In the spectrum of SrF_2 a wide band at 280 nm is attributed to self-trapped exciton (STE) emission. In SrF_2 doped with Ce^{3+} ions STE luminescence is quenched and vanished at concentrations Ce^{3+} ions higher than 1 mol%. The most intense bands in X-ray luminescence spectra of SrF_2 - Ce^{3+} crystals at 310 and 325 nm correspond to 5d–4f emission of Ce^{3+} ions.

Luminescence spectrum of CaF_2 - Eu^{2+} is shown in Fig. 1, curve 4. Its emission band is centred at 425 nm. This luminescence is due to 4f⁶5d¹–4f⁷ transitions in the Eu^{2+} ion (Kobayasi et al., 1980).

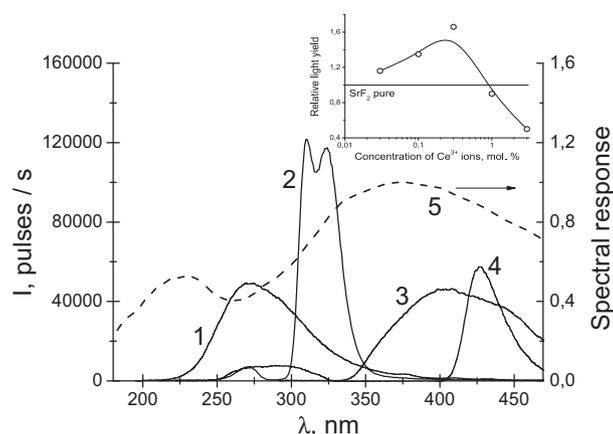


Fig. 1. Luminescence spectra of SrF_2 (curve 1), SrF_2 -0.3 mol% Ce^{3+} (curve 2), NaI–Tl (curve 3), and CaF_2 -0.1 mol% Eu^{2+} (curve 4) under X-ray excitation measured at room temperature. Dashed curve 5 is spectral sensitivity of the vacuum grating monochromator VM-4 and PMT detection part. The spectra were corrected for the spectral sensitivity of detection part of the apparatus. In the inset dependence of integral intensity of emission bands of Ce^{3+} ions versus Ce ions concentration is presented. A solid curve in the inset is b-spline smoothing of the data.

A dependence of integral intensity of Ce^{3+} ions emission bands on Ce ion concentration is shown in the inset to Fig. 1. The highest light output is demonstrated by the sample of SrF_2 -0.3 mol% Ce^{3+} .

X-ray excited luminescence output measured by integral intensity is compared with the one of NaI–Tl crystal (Table 1). Light output of NaI–Tl crystals is approximately 43,000 photons/MeV. Therefore, light output of the measured samples can be estimated. The data are shown in Table 1. Light output of CaF_2 -0.1 mol% Eu^{2+} is about 21,500 photons/MeV that is in accordance with known data for CaF_2 -Eu crystals given by Derenzo (2012). Pure SrF_2 has light output about 20,640 photons/MeV, doped with 0.3 mol% and 1 mol% crystals have the ones about 34,000 photons/MeV and 18,500 photons/MeV, respectively.

All integral intensities and light outputs are presented without correction for spectral response of detection channel. The spectral response curve is shown in Fig. 1, dashed line. The sensitivity of the PMT and monochromator system in SrF_2 and SrF_2 -Ce luminescence spectral range is lower than in NaI–Tl and CaF_2 -Eu emission region. After the correction, light output of pure SrF_2 luminescence is about 40,000 photons/MeV, and SrF_2 doped with 0.3 mol% and 1 mol% crystals have light outputs about 50,000 photons/MeV and 28,000 photons/MeV, respectively.

It should be noted, the comparison integral X-ray luminescence intensities with light output of NaI–Tl crystal in photons per MeV is given only for estimation of maximal light output of strontium fluoride crystals. A light output measured by pulse-height spectra could be lower due to the presence of slow components in luminescence. It is discussed below.

Temperature dependences of integral X-ray excited luminescence of SrF_2 -Ce are given in Fig. 2. Emission intensity does not depend on temperature in the range between -50 °C and $+50$ °C. At higher temperatures decrease of 5d–4f luminescence intensity is observed. At 170 °C light outputs of SrF_2 doped with 0.01 mol% and 0.1 mol% of Ce^{3+} ions decrease to 30% of the light output at room temperature. 25% and 15% decreases in integral emission are found in the SrF_2 crystals doped with 0.3 mol% Ce^{3+} and 1 mol%, respectively. Crystals of SrF_2 -0.3 mol% Ce^{3+} and SrF_2 -1 mol% Ce^{3+} demonstrate high temperature stability of light output in the region between -50 °C and 170 °C in comparison with NaI–Tl (see Fig. 2, solid line) and SrI_2 -Eu. For this reason, the SrF_2 - Ce^{3+} crystals would be promising scintillators for well-logging applications.

Fig. 3 shows pulse height spectra of SrF_2 , SrF_2 -0.3 mol% Ce^{3+} and NaI–Tl. The photopeak corresponding to the ^{137}Cs energy photon is seen in each curve in Fig. 3. Light outputs of SrF_2 and SrF_2 -Ce crystals were measured by comparing these response to 662 keV energy to the response of NaI–Tl crystal with known characteristics under the same conditions. The photopeak in pure SrF_2 is centred at a pulse height that is 42% of the 662 keV photopeak pulse height in NaI–Tl. Using the NaI–Tl light output of 43,000 photons/MeV, this implies that the light output of pure SrF_2 is approximately 18,000 photons/MeV that is similar to X-ray emission light output (see Table 1). The full width at half maximum (FWHM) in pure SrF_2 of the 662 keV photopeak is 10%. FWHM of NaI–Tl is 6.7%, which is

Table 1

Light output of SrF_2 , SrF_2 - Ce^{3+} , NaI–Tl and CaF_2 -0.1 mol% Eu^{2+} crystals measured under gamma and X-ray excitation at room temperature.

Crystal	Light output of X-ray excited luminescence spectra		Light output measured by pulse height spectra	
	rel. units	Photons/MeV	rel. units	Photons/MeV
NaI–Tl	1	43,000	1	43,000
CaF_2 -0.1 mol% Eu^{2+}	0.5	21,500	0.44	18,920
SrF_2	0.48	20,640	0.42	18,060
SrF_2 -0.3 mol% Ce^{3+}	0.79	33,970	0.32	13,760
SrF_2 -1 mol% Ce^{3+}	0.43	18,490	0.2	8600

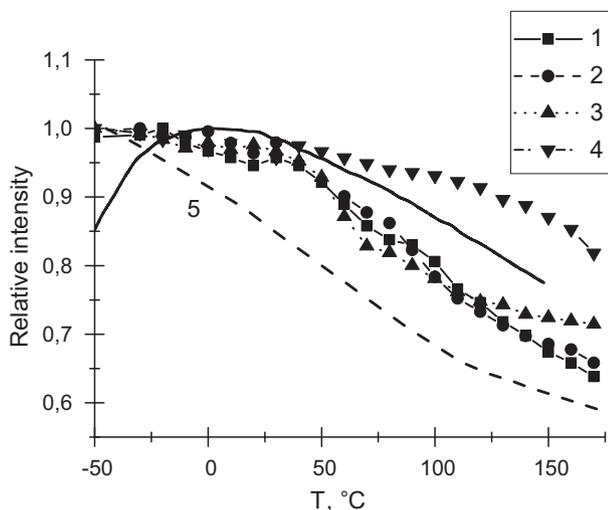


Fig. 2. Temperature dependences of relative light output of SrF₂ crystals doped with 0.01 mol% Ce³⁺ (curve 1); 0.1 mol% Ce³⁺ (curve 2); 0.3 mol% Ce³⁺ (curve 3) and 1 mol% Ce³⁺ (curve 4) in comparison with NaI–Tl (solid line) by Saint-Gobain (2012) and SrF₂–Eu (dashed curve 5) measured by Alekhin et al. (2011). All curves are normalized for maximal value.

consistent with known results given by scintillators database of Derenzo (2012).

Dependence of SrF₂–Ce relative light output versus concentration is demonstrated in the inset to Fig. 3. The best light output of the Ce-doped crystals is found for SrF₂–0.3 mol% Ce³⁺. Its photopeak is centred at a pulse height that is 32% of the 662 keV photopeak pulse height in NaI–Tl, this implies that the light output of SrF₂–0.3 mol% Ce³⁺ is approximately 14,000 photons/MeV. FWHM of the SrF₂–0.3 mol% Ce³⁺ is approximately 9.3%, which is lower than FWHM of pure SrF₂. This fact means that in spite of worse light output SrF₂–0.3 mol% Ce³⁺ crystal has better energy resolution in comparison with pure strontium fluoride.

All light outputs without any corrections are given in Table 1. Spectral sensitivity of S20 photocathode (PMT FEU–39A) is higher at CaF₂–Eu and NaI–Tl emission bands than in SrF₂ and SrF₂–Ce luminescence region (Flyckt and Marmonier, 2002). Corrected light outputs of pure SrF₂ is about 80% (36,000 photons/MeV) of

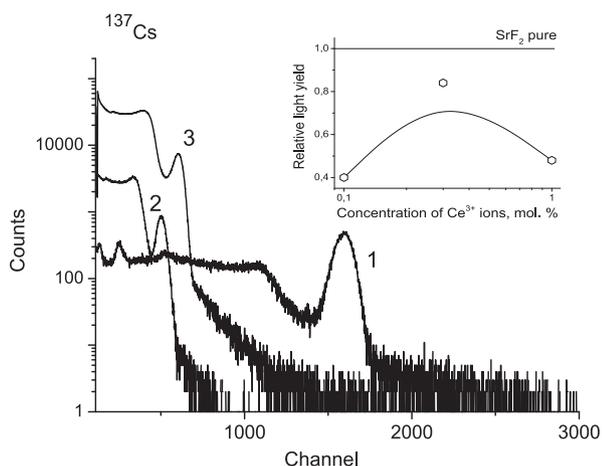


Fig. 3. Pulse height spectra of NaI–Tl (curve 1), SrF₂–0.3 mol% Ce³⁺ (curve 2) and SrF₂ (curve 3) under gamma-source ¹³⁷Cs ($E = 662$ keV) excitation measured at room temperature. In the inset dependence of relative light outputs of SrF₂–Ce crystals versus Ce concentration is presented. A solid curve in the inset is b-spline smoothing of the data.

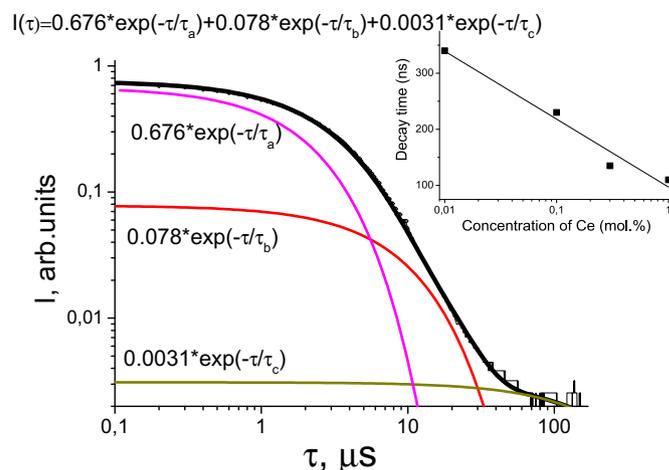


Fig. 4. Scintillation decay time profile of SrF₂–0.3 mol% Ce³⁺ crystal measured under gamma-source ¹³⁷Cs excitation ($E = 662$ keV) at room temperature. Exponential components of total decay curve are presented separately ($\tau_a = 2.8$ μs, $\tau_b = 9$ μs and $\tau_c = 280$ μs). In the inset dependence of shortest decay time component on Ce³⁺ ions concentration is shown.

NaI–Tl and SrF₂–0.3 mol% of Ce³⁺ – about 60% (26,000 photons/MeV) of NaI–Tl.

Scintillation decay time profile of SrF₂–0.3 mol% Ce³⁺ is shown in Fig. 4. Resistance of oscilloscope input was 2.6 kΩ for registering of long time decay components in Ce³⁺ emission. The decay time is described by a sum of exponents. First component (2.8 μs) in Ce³⁺ decay is integrated short components. Lifetime of the shortest one equals 130 ns at 50 Ω input resistance in SrF₂–0.3 mol% Ce³⁺ and it becomes longer with decrease of Ce concentration. Decay constants of this component in dependence on Ce ions concentration are presented in the inset of Fig. 4.

Contribution of slow components to scintillation time profile is estimated. In Fig. 4 exponential components of total decay curve are shown separately. There are two long time components in SrF₂–0.3 mol% Ce³⁺ emission. 20% of the light is emitted with a 9 μs time constant, and 25% of the light is emitted with a 280 μs time constant.

Emission decay time of cerium doped alkaline-earth fluorides under optical excitation at lowest energy absorption bands is estimated about 30 ns (Visser et al., 1993; Radzhabov and Kurobori, 2004; Wojtowicz et al., 2000). Under vacuum ultraviolet excitation at exciton and higher energies regions the decay of Ce-doped fluorides became nonexponential (Wojtowicz et al., 2000). The decay curves under X-ray excitation are also nonexponential (Fig. 4). Therefore, the whole decay curve can be described by several processes. Fast stage, its decay constant is longer than decay time of direct 5d–4f recombination in cerium ions, could be ascribed to resonance energy transition in nearest pairs of exciton and cerium ion. This energy transfer mechanism was investigated by Visser (1993) in BaF₂–Ce crystals and in Ce-doped fluorides by Radzhabov and Nepomnyaschikh (2012). In the inset of Fig. 4 concentration dependence of these decay constants is presented. If described above energy transfer mechanism takes place then the decay will become shorter with increasing Ce³⁺ ions concentration due to reduction of distance between exciton and activator ion with increase of cerium ions concentration.

In SrF₂–Ce crystals thermoluminescence glow peaks at 200–250 K were found (Radzhabov, 2001; Maghrabi and Townsend, 2001). Broad glow peaks at higher temperatures are shifted to lower temperature with increasing concentration of Ce³⁺ ions in the SrF₂ crystal (Maghrabi and Townsend, 2001). Long stages in scintillation time profile can be attributed to thermoactivated

processes related to electron or hole delayed transfer to the activator ion. A similar energy transfer mechanism has been observed in SrF₂ doped with Pr (Shendrik and Radzhabov, 2012).

The difference in light outputs measured from X-ray luminescence and pulse height spectra is explained by presence of intensive slow components in cerium ions luminescence (see Fig. 4). They give a large contribution to total light output. Shaping time of pulse height spectrum measurement is 10 μs, and a large part of emitted light is not registered whereas a rate of X-ray excited luminescence spectra registration is amount about 1 s⁻¹ that leads to collect much more light registration.

Light output of SrF₂-Ce³⁺ samples can be increased by decreasing of slow component contribution in Ce³⁺ luminescence. It might be possible by co-doping these crystals with Ga³⁺, In³⁺ or Cd²⁺ ions to change band gap in SrF₂-Ce crystal and, consequently, reducing the role of traps in scintillation energy transfer. This idea has been made in garnets by Fasoli et al. (2011). However, Cd²⁺ ions bring to STE suppressing in alkali-earth fluorides (Radzhabov and Kirm, 2005; Radzhabov et al., 2005). Consequently, Cd²⁺ co-doping leads to suppression of efficient resonance exciton energy transfer mechanism and following light output reducing. Therefore, Cd²⁺ co-doping is not eligible way for increasing light output of SrF₂-Ce scintillator. A role of Ga³⁺ and In³⁺ impurities in STE suppressing has not yet been investigated and follow-up study of the crystals doped with Ga³⁺ and In³⁺ ions is required.

4. Conclusion

The SrF₂ crystals are well suited for use as gamma radiation detector. It has a higher (4.18 g/cm³) than NaI-Tl (3.67 g/cm³) density, comparable light output, and it is no hygroscopic. Taking into account that crystals SrF₂-0.3 mol% Ce³⁺ and SrF₂-1 mol% Ce³⁺ have a high temperature stability of light output in the temperature interval from -50 °C to 200 °C, these materials can be applied in well-logging scintillation detectors. The presence of long decay components is a huge lack of these scintillators. Consequently, the contribution of the slow components in the Ce³⁺ luminescence should be decreased for real scintillation applications of SrF₂-Ce crystals. The work in this direction is in progress. Summarizing the experimental results we conclude that strontium fluoride crystals would be useful as promising scintillator.

Acknowledgement

This work was partially supported by The Ministry of Education and Science of Russian Federation and Russian Foundation for Basic

Research (RFBR). Authors are thankful to V. Kozlovskii for growing the crystals investigated in this work.

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