Characterization of CsSrCl$_3$:Ce Crystalline Scintillator

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We report on the photoluminescence and scintillation characterizations of a new CsSrCl$_3$:Ce (0.5 mol%) crystalline scintillator grown by the vertical Bridgman method. The fluorescence quantum efficiency (QE) for the Ce^{3+} 5d–4f allowed transitions at around 365–425 nm was 90% under excitation of 315 nm light. The photoluminescence decay time of Ce^{3+} was approximately 28 ns. When X-rays excited the crystal, intense emission bands were observed at 350–400 nm, which could be attributed to the Ce^{3+} characteristic emission. The scintillation light yield of the developed crystal was ~8600 photons/MeV compared with a NaI:Tl commercial scintillator, and the principal scintillation decay time was approximately 626 ns plus two fast components of around 3.8 and 57 ns.

1. Introduction

A scintillation detector based on a scintillator that is optically coupled to a photosensitive detector is one of the most common techniques for detecting and measuring ionizing radiation. The detection technique plays an important role in various fields such as high-energy physics,[1] medical imaging,[2] well logging,[3] crystallography,[4] and national security.[5] The advancement of detector's performance has been realized through the discovery of new superior scintillators and the improvement of existing scintillators. Actual requirements for the scintillator are high light yield with an excellent energy resolution, fast decay time, and good linearity. Other factors are also important to consider when choosing a scintillator for a particular application. These include low hygroscopy, high radiation hardness, low production cost, matching of the wavelength of the scintillation light from the scintillator with the sensitive wavelength region of the photosensitive detector, and the refractive index of the scintillator. In order to realize the development of an advanced detector, there have been a number of halide-based scintillators developed in past research.

The perovskite chloride crystals with the structural composition of ABCl$_3$ (with A = Cs, Rb, K; B = Ba, Sr, Ca, Mg) are investigated in numerous synthesis, structural, magnetic, optical, and scintillation characteristic studies. Auger-free luminescence (AFL), that is, radiative electric transition from the valence band to the outermost core band, in undoped CsMgCl$_3$, CsCaCl$_3$, and CsSrCl$_3$ crystals have been intensely studied because of their interesting characteristics such

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as fast decay times with high thermal stability.[6–9] The rare-earth-, transition-metal-, and s^2-ion-doped perovskite chloride crystals have attracted the most attention as the phosphor,[10–15] magnetic material,[16–19] and scintillator,[19–23] and then their crystal growth and characterizations have been reported by some researchers. Among the rare-earth-doped crystals, $CsCaCl_3$:Eu and $CsSrCl_3$:Eu are proposed to be promising X-ray and gamma-ray scintillators because of their high light yield (~18000 photons/MeV) owing to a 5d–4f allowed transition of Eu^{2+}.[20,21] In addition to the excellent scintillation characteristics, these perovskite chloride host crystals require no special handling or packaging techniques because they are less hygroscopic than commercial halide scintillators such as NaI:Tl and SrI_2:Eu. Recently, we reported the characterization of a $CsCaCl_3$:Ce crystalline scintillator. The crystal shows an interesting scintillation performance, including a moderate light yield and a faster decay time than $CsCaCl_3$:Eu.[22] Thus, we focus on $CsSrCl_3$:Ce (0.5 mol%) because the crystal is expected to have both higher atomic number and higher density than that of $CsCaCl_3$. Although some researchers reported that various strontium-containing halide crystalline scintillators activated with Ce^{3+} showed a high light yield and fast response,[24,25] to our best knowledge, no other study on crystal growth, photoluminescence, and scintillation properties of the $CsSrCl_3$:Ce has been reported so far. In this paper, we report the photoluminescence and scintillation characterizations of the $CsSrCl_3$:Ce crystal grown by the vertical Bridgman method.

2.   Experimental Procedure

We used the vertical Bridgman technique to prepare the $CsSrCl_3$:Ce (0.5 mol%) crystal sample. A mixture of CsCl (99.999%), $SrCl_2$ (99.9%), and $CeCl_3 \cdot 7H_2O$ (99.9%) raw materials in stoichiometric ratio was used for the crystal growth. The mixture was dried in vacuum at 623 K for 72 h in order to expel water. The crystal growth of $CsSrCl_3$:Ce (0.5 mol%) was carried out under vacuum in a sealed quartz ampoule by the vertical Bridgman method. The ampoule was pulled down at a rate of 1.0 mm/h from top to bottom in a gradient temperature zone. The temperature of the upper and lower zones in the vertical furnace was 1273 and 1073 °C, respectively.

After the crystal growth process, powder X-ray diffraction (XRD) analysis of part of an as-grown crystal was performed in the 2θ range from 5 to 80° using an Ultima IV diffractometer (Rigaku). The X-ray source was CuK_α with an accelerating voltage of 40 kV and a tube current of 40 mA. Another part of an as-grown crystal was cut and polished into dimensions of $3.0 \times 3.0 \times 1.0$ mm^3 to be used in photoluminescence and scintillation measurements. We demonstrated the measurements under air atmosphere because visual observation indicated that the crystal is less hygroscopic than SrI_2:Eu and $LaBr_3$:Ce crystals.

The emission and excitation spectra were measured using a Hitachi high-tech fluorescence spectrophotometer (F-7000). The fluorescence quantum efficiency (QE) value was estimated using a Quantaurus-QY (Hamamatsu Photonics K.K.) spectrofluorometer.

The photoluminescence decay curve was obtained with a DeltaFlex (Horiba) system equipped with a light-emitting diode (LED) with an emission wavelength of 320 nm as the excitation source.

The scintillation spectrum was measured by exciting the crystal with X-rays from a Spellman X-ray generator (XRB80P Monoblock) at power settings of 80 kV and 2.5 mA. The scintillation light was detected with an R163i-UV spectrometer (Andor) combined with a DU920P CCD detector (Andor) that was cooled to 210–230 K by a Peltier module.[26]

The scintillation decay time profile was obtained using a customized-setup, pulsed X-ray-induced scintillation characterization system (Hamamatsu).[27]   Pulsed X-rays were generated by combining the pulsed LED light source and X-ray tube. The scintillation light was measured with a Hamamatsu R7400P-06 photomultiplier tube (PMT).

The ^{137}Cs-gamma-ray-induced pulse height spectrum was measured with the crystal optically coupled to a Hamamatsu R7600-200 PMT. The experimental details were reported in an earlier study.[28]   The bias voltage across the PMT was set to −600 V. The PMT was connected to an ORTEC 113 preamplifier, an ORTEC 572 shaping amplifier, and an Amptec 8000A multichannel analyzer (MCA). The spectrum was recorded with a 6 μs shaping time. The spectrum of a NaI:Tl commercial scintillator (light yield = ~40000 photons/MeV) was also measured for the estimation of the scintillation light yield for the CsSrCl$_3$:Ce (0.5 mol%) crystal.

3.   Results and Discussion

An as-grown crystal sample of CsSrCl$_3$:Ce (0.5 mol%) is shown in Fig. 1(a), and the analyzed powder XRD patterns are shown in Fig. 1(b). The crystal sample is not fully transparent, which indicates that the crystal quality can be further improved by optimizing the crystal growth condition. A similar result was also observed for CsSrBr$_3$ crystals,[29] Gokhale *et al*. suggested that the poor optical quality may be caused by the volatilization of CsBr during synthesis and crystal growth. Thus the poor optical transparency of the grown CsSrCl$_3$:Ce crystal may be due to the volatilization of CsCl during the crystal growth process. In the XRD patterns of CsSrCl$_3$:Ce, the main peaks of α-SrCl$_2$ were weak, indicating that the grown crystal contained a slight α-SrCl$_2$ crystalline phase. From the result, we speculate that the contamination of a slight α-SrCl$_2$ crystalline phase is caused by the volatilization of CsCl during crystal growth, resulting in the cloudy appearance of the grown crystal. Moreover the contamination of the secondary phase may act as an electron (or hole)-trapping center that decreases the scintillation light yield and delays the scintillation decay time.

Figure 2 illustrates the obtained excitation and emission spectra of CsSrCl$_3$:Ce (0.5 mol%). The characteristic Ce^{3+} 5d^1–4f (^{2}F$_{5/2}$, ^{2}F$_{7/2}$) emission peaking at 365–400 nm was observed upon 315 nm excitation. When monitoring emission at 365 nm, at least four excitation bands in the

(a)   (b)
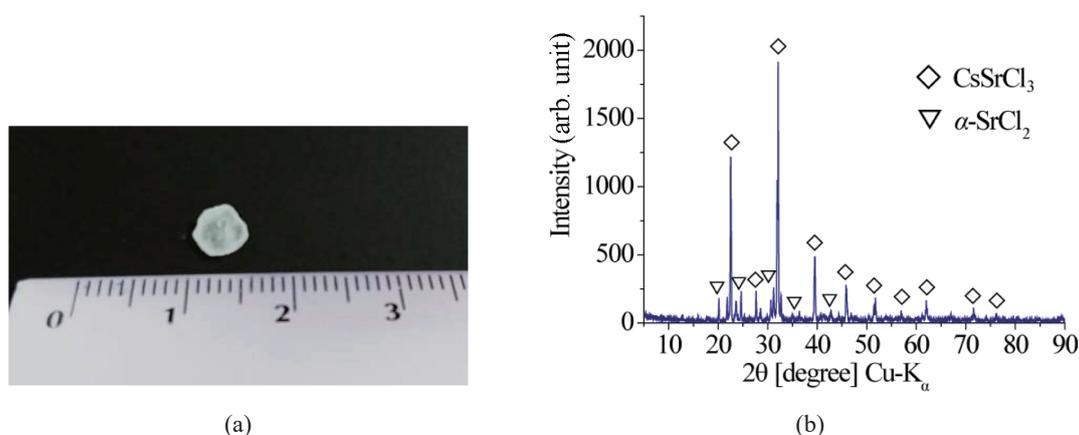
Fig. 1.   (Color online) (a) An as-grown CsSrCl$_3$:Ce crystal and (b) XRD patterns of the crystal.

wavelength range from 200 to 320 nm were observed. These excitation bands correspond to the transitions from 4f ground states to $5d^4$ (~210 nm), $5d^3$ (~225 nm), $5d^2$ (~263 nm), and $5d^1$ (~315 nm) excited states of Ce^{3+}. The fluorescence QE for the Ce^{3+} $5d^1$–4f emissions was calculated to be about 90% under excitation of 315 nm light using the integrating sphere in the Quantaurus-QY spectrofluorometer.

The photoluminescence decay curve of $CsSrCl_3$:Ce (0.5 mol%) is shown in Fig. 3. The decay time was calculated by fitting a single-exponential equation with a deconvolution of instrumental response. From the calculation, the decay time was found to be approximately 28 ns, which is close to the value for $CsCaCl_3$:Ce (τ = ~32 ns) reported in a previous study.[22]

Figure 4 illustrates the scintillation spectrum of $CsSrCl_3$:Ce (0.5 mol%). The spectrum shows intense emission bands peaking at 360 and 385 nm, and can be assigned to the transitions from the $5d^1$ excited state to the 4f ($^2F_{5/2}$, $^2F_{7/2}$) ground states owing to the Ce^{3+}. In addition, a weak emission band peaking at 300 nm was observed, which appears to be similar to that of $CsCaCl_3$:Ce reported previously.[22] Macdonald *et al.* studied the intrinsic luminescence properties including radiative core–valence luminescence (CVL) in an undoped $CsSrCl_3$ crystal. They observed the intrinsic emission peaking at 250–400 nm under excitation by X-rays.[6] Referring to the previous
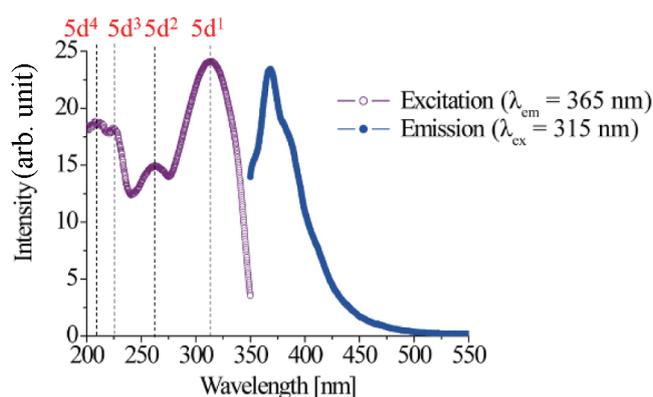
Fig. 2. (Color online) Excitation and emission spectra of the $CsSrCl_3$:Ce crystal.
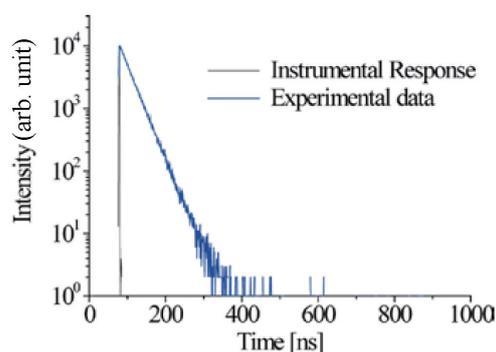
Fig. 3. (Color online) Photoluminescence decay time profile of the $CsSrCl_3$:Ce crystal. (λ_{ex} = 320 nm, λ_{em} = 365 nm)
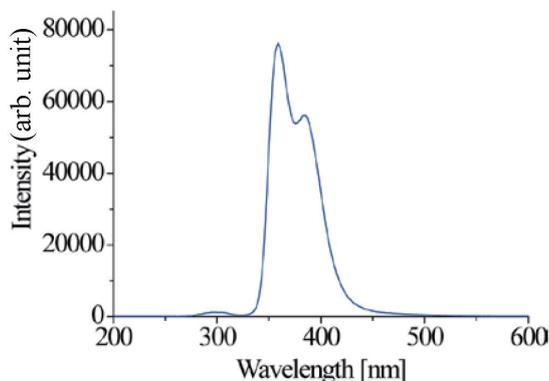
Fig. 4. (Color online) X-ray-induced scintillation spectrum of the $CsSrCl_3$:Ce crystal.
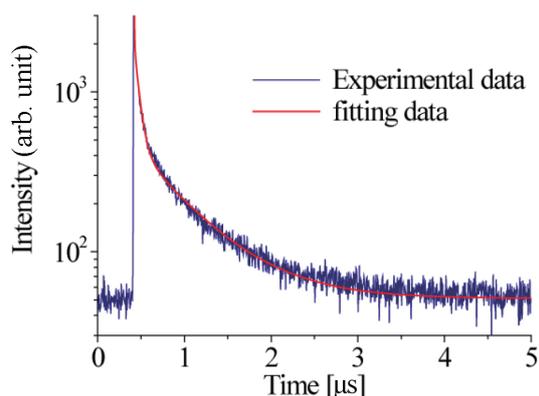
Fig. 5. (Color online) Pulsed-X-ray-induced scintillation decay time profile of the CsSrCl$_3$:Ce crystal.
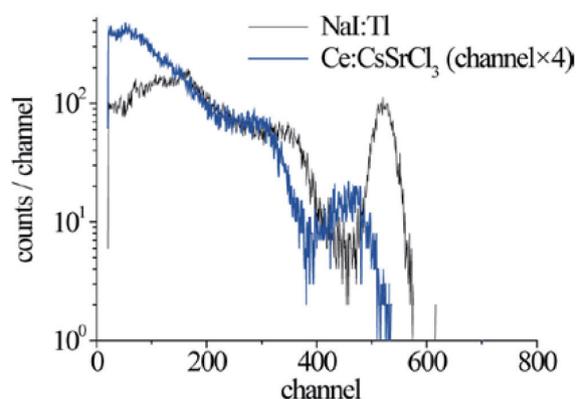
Fig. 6. (Color online) ^{137}Cs-gamma-ray-induced pulse height spectra for CsSrCl$_3$:Ce and the NaI:Tl commercial scintillator.

study on the CsCaCl$_3$:Ce and undoped CsSrCl$_3$, we speculate that the unidentified emission band was due to the distorted intrinsic emission of the undoped crystal.

The scintillation decay time profile of CsSrCl$_3$:Ce (0.5 mol%) is shown in Fig. 5. The decay curve can be fitted by a tri-exponential function. There are initially two fast components with decay times of 3.8 ns (23%) and 57 ns (23%). A slower component with a decay time of 626 ns (54%) dominates the scintillation light. The result is similar to the decay components for Cs$_2$LiYCl$_6$:Ce, Cs$_2$LiYBr$_6$:Ce, and CsCaCl$_3$:Ce.[22,30] Thus, it is suggested that the two fast components with a decay time of 3.8 and 57 ns are due to intrinsic luminescence such as CVL and self-trapped excitons (STEs) from the CsSrCl$_3$ host and typical Ce^{3+} 5d^1–4f emissions, respectively. The delay of the Ce^{3+} emissions with respect to the photoluminescence may be caused by the above-mentioned retrapping of the charge carriers at the defect-related traps during their transport to the Ce^{3+} emission centers. The slower component with 626 ns may be caused by the delayed transfer from STE to Ce^{3+} ions, which are common for Cs$_2$LiYCl$_6$:Ce, Cs$_2$LiYBr$_6$:Ce, and CsCaCl$_3$:Ce. Further experimental investigations are required for the confirmation of the proposed scintillation mechanisms behind the decay time.

Figure 6 illustrates the ^{137}Cs-gamma-ray-induced pulse height spectra for CsSrCl$_3$:Ce (0.5 mol%) and the NaI:Tl commercial scintillator. The scintillation light yield is determined by the photo-peak channel with 662 kV gamma rays and the QE of the PMT at the scintillation wavelength. The light yield for CsSrCl$_3$:Ce (0.5 mol%) was calculated to be approximately 8600 photons/MeV on the basis of a comparison of the NaI:Tl. The energy resolution (FWHM) of the 662 keV photo-peak is approximately 7.2%. From the measurement, the CsSrCl$_3$:Ce crystal was found to show higher light yield than that of the previously studied CsCaCl$_3$:Ce crystal in spite of the fact that our developed CsSrCl$_3$:Ce crystal contained a slight amount of the secondary phase. Future efforts toward growing high-quality crystals with no secondary phase are expected to further improve the scintillation efficiency.

4. Conclusions

We reported on the photoluminescence and scintillation characterizations of a new CsSrCl$_3$:Ce (0.5 mol%) crystalline scintillator grown by the vertical Bridgman method. The grown crystal had

a low hygroscopic property, therefore all the measurements were performed in air atmosphere. We demonstrated interesting properties in the crystal, such as moderate light yield (~8600 photons/ MeV) with an energy resolution of 7.2% at 662 keV and a relatively fast decay time (~626 ns). Among them, the better light yield performance than that of the previously studied $CsCaCl_3$:Ce crystal was especially interesting because of the α-$SrCl_2$ phase that contaminates $CsSrCl_3$:Ce. We speculate that the scintillation characteristics will further improve with the improvement of the optical crystalline quality owing to the optimization of crystal growth conditions.

Acknowledgments

References

1 S. Kishimoto, F. Nishikido, R. Haruki, K. Shibuya, and M. Koshimizu: Hyperfine Interact. **204** (2012) 101.
2 D. Totsuka, T. Yanagida, Y. Fujimoto, Y. Yokota, F. Moretti, A. Vedda, and A. Yoshikawa: Appl. Phys. Express **5** (2012) 052601.
3 T. Yanagida, Y. Fujimoto, S. Kurosawa, K. Kamada, H. Takahashi, Y. Fukazawa, M. Nikl, and V. Chani: Jpn. J. Appl. Phys. **52** (2013) 076401.
4 K. J. Gofron and A. Joachimiak: J. Syst. Cybern. Inf. **9** (2011) 87.
5 M. E. Ellis, K. Duroe, and P. A. Kendall: Int. J. Mod. Phys. Conf. Ser. **44** (2010) 1660214.
6 M. A. Macdonald, E. N. Mel'chakov, I. H. Munro, P. A. Rodnyi, and A. S. Voloshinovsky: J. Lumin. **65** (1995) 19.
7 Y. Chornodolskyy, G. Stryganyuk, S. Syrotyuk, A. Voloshinovskii, and P. Rodnyi: J. Phys.: Condens. Matter **19** (2007) 476211.
8 S. H. Doh, S. Kim, S. Ra, H. Kim, H. D. Kang, and M. Y. Oh: J. Korean Sens. Soc. **16** (2007) 337.
9 M. Koshimizu, N. Yahaba, R. Haruki, F. Nishikido, S. Kishimoto, and K. Asai: Opt. Mater. **36** (2014) 1930.
10 J. Grimm, J. F. Suyver, E. Beurer, G. Carver, and H. U. Güdel: Phys. Chem. B **115** (2006) 2093.
11 J. Grimm, E. Beurer, P. Gerner, and H. U. Güdel: Chem. Eur. J. **13** (2007) 1152.
12 A. Wolfert and G. Blasse: J. Solid State Chem. **55** (1984) 344.
13 T. C. Vanoy and G. L. Mcpherson: Chem. Phys. Lett. **143** (1988) 51.
14 U. Oetliker, and H. U. Güdel: J. Lumin. **58** (1993) 350.
15 M. Suta, W. Urland, C. Daul, and C. Wickleder: Phys. Chem. Chem. Phys. **18** (2016) 13196.
16 T. C. Vanoy and G. L. Mcpherson: Solid State Commun. **74** (1990) 5.
17 H. Takeuchi and H. Tanaka: J. Phys.: Condens. Matter **4** (1992) 10071.
18 H. Takeuchi, H. Tanaka, and M Arakawa: J. Phys.: Condens. Matter **5** (1993) 9205.
19 H. Takeuchi, H. Tanaka, M. Arakawa, and H. Ebisu: J. Phys.: Condens. Matter **17** (2005) 1375.
20 M. Zhuravleva, B. Blalock, K. Yang, M. Koschan, and C. L. Melcher: J. Cryst. Growth **352** (2012) 115.
21 V. L. Cherginets, A. Y. Grippa, T. P. Rebrova, Y. N. Datsko, T. V. Ponomarenko, N. V. Rebrova, N. N. Kosinov, O. A. Tarasenko, Y. I. Dolzhenko, and O. V. Zelenskaya: Funct. Mater. **19** (2012) 187.
22 Y. Fujimoto, K. Saeki, H. Tanaka, T. Yahaba, T. Yanagida, M. Koshimizu, and K. Asai: Phys. Scr. **91** (2016) 094002.
23 E. V. van Loef, C. M. Wilson, N. J. Cherepy, G. Hull, S. A. Payne, W.-S. Choong, W. W. Moses, and K. S. Shah: IEEE Trans. Nucl. Sci. **56** (2009) 869.
24 R. Shendrik, E. A. Radzhabov, and A. I. Nepomnyashchikh: Radiat. Meas. **56** (2013) 58.
25 M. Tyagi, M. Zhuravleva, and C. L. Melcher: J. Appl. Phys. **113** (2013) 203504.
26 Y. Fujimoto, T. Yanagida, M. Koshimizu, and K. Asai: Sens. Mater. **27** (2015) 263.
27 T. Yanagida, Y. Fujimoto, T. Ito, K. Uchiyama, and K. Mori: Appl. Phys. Express **7** (2014) 062401.
28 Y. Fujimoto, M. Koshimizu, T. Yanagida, G. Okada, K. Saeki, and K. Asai: Jpn. J. Appl. Phys. **55** (2016) 090301.
29 S. S. Gokhale, L. S. A. Lindsey, M. Koschan, M. Zhuravleva, and C. L. Melcher: J. Cryst. Growth **445** (2016) 1.
30 E. V. D. van Loef, P. Dorenbos, C. W. E. van Eijk, K. W. Kramer, and H. U. Güdel: J. Phys.: Condens. Matter **14** (2002) 8481.