Upconversion luminescence of CaF$_2$-SrF$_2$-ErF$_3$ single crystals upon 1.5 µm laser excitation

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Abstract. In present work, the spectral-luminescent properties of CaF$_2$-SrF$_2$-ErF$_3$ (CaF$_2$-SrF$_2$:Er) single crystals were investigated. The upconversion luminescence (UCL) of CaF$_2$-SrF$_2$: Er in the visible and infrared spectral regions upon excitation of the $^4I_{13/2}$ level Er$^{3+}$ ions were studied for the first time. The absolute energy yields of the UCL upon laser excitation at 1.5 µm are determined for CaF$_2$-SrF$_2$:Er. The possible application of fluoride crystals for increasing the efficiency of solar cells was discussed.

1. Introduction
Today, photon upconversion is a rapidly developing area of photonic with a large direction of potential applications, for example, solid-state laser, laser beam visualizers, bioimaging, biometrics for laser scanning microscopy, temperature sensors, solar cell and etc [1-6]. In present paper we will focus on the investigation of UCL of fluoride crystals for application to enhance the efficiency of solar cells. For example, absorption threshold of the solar cell cannot allow to crystalline silicon solar cells utilized 20% of the energy incident from the sun [1, 7]. Upconversion materials can decrease these losses by generating one high-energy photon from two or three lower-energy photons. Previously UCL of fluorides MF$_2$ (M = Ca, Sr) doped with Er$^{3+}$ ions with fluorite-type structure upon 1.5 mcm laser excitation was investigated in different papers [8-15]. Fluoride materials have a high value of transmittance in a wide spectral range (from 0.16 to 11 microns), low phonon energy, clustering effect et al. Here we presented results of investigation UCL of mixed fluoride crystals CaF$_2$-SrF$_2$:Er upon excitation of $^4I_{13/2}$ level.

2. Experimental
CaF$_2$-SrF$_2$ single crystals with 0.5 mol%, 1 mol%, 1.5mol% and 2 mol% Er$^{3+}$ ions doping were grown by the vertical directed crystallization method (Bridgman method) (Table 1). Diameter and thickness of samples were 0.8 cm and 0.17 cm, respectively. Absorption spectra of single crystals were recorded with a Perkin–Elmer spectrophotometer Lambda 950. The luminescence of the Er$^{3+}$ ions excited by fiber laser at 1531.8 nm was recorded using a Horiba FHR1000 spectrometer. The focused excitation beam diameter on the samples was 212 µm. The integrating sphere method was used to measure the absolute
photoluminescence energy yield. The system consists of the OL IS-670-LED integrating sphere, an OL-770 UV/VIS (Gooch & Housego) spectroradiometer, and a monochromator-spectrograph M833 (Solar LS).

### Table 1. UCL energy yields, chromaticity coordinates and color temperatures of the luminescence of CaF<sub>2</sub>-SrF<sub>2</sub>:Er phosphors.

| Compositions | Contraction | B<sub>cmt</sub>, % | X    | Y    | T (K) |
|--------------|-------------|-----------------|------|------|-------|
| 0.6CaF<sub>2</sub>-0.39SrF<sub>2</sub>-0.005ErF<sub>3</sub> | CaF<sub>2</sub>-SrF<sub>2</sub>:Er(0.5%) | 5.1  | 0.5681 | 0.4195 | 1737 |
| 0.6CaF<sub>2</sub>-0.39SrF<sub>2</sub>-0.01ErF<sub>3</sub> | CaF<sub>2</sub>-SrF<sub>2</sub>:Er(1%) | 9.1  | 0.5073 | 0.4770 | 2585 |
| 0.6CaF<sub>2</sub>-0.385SrF<sub>2</sub>-0.015ErF<sub>3</sub> | CaF<sub>2</sub>-SrF<sub>2</sub>:Er(1.5%) | 9.9  | 0.4756 | 0.5067 | 3136 |
| 0.6CaF<sub>2</sub>-0.38SrF<sub>2</sub>-0.02ErF<sub>3</sub> | CaF<sub>2</sub>-SrF<sub>2</sub>:Er(2%) | 11.4 | 0.4331 | 0.5464 | 3904 |

3. Results

Upconversion materials can be used as materials for efficiency enhancement of solar cell. To develop UC phosphors for the above application field, the absorption properties, luminescence properties, photoluminescence energy yield and color temperature were investigated in present paper. Absorption spectra allow to estimate the spectral region of the potential upconversion of solar irradiance. Figure 1 presents the 300-K absorption spectra of the Er<sup>3+</sup> ion in the CaF<sub>2</sub>-SrF<sub>2</sub>:Er single crystal. The absorptions are due to the transitions from the <sup>4</sup>I<sub>15/2</sub> ground level to the <sup>4</sup>G<sub>11/2</sub>, <sup>4</sup>H<sub>9/2</sub>, <sup>4</sup>F<sub>5/2</sub>+, <sup>4</sup>F<sub>3/2</sub>, <sup>4</sup>F<sub>7/2</sub>, <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub>, <sup>4</sup>F<sub>9/2</sub>, <sup>4</sup>I<sub>9/2</sub>, <sup>4</sup>I<sub>11/2</sub>, <sup>4</sup>I<sub>13/2</sub> excited levels.

![Figure 1. Absorption spectra of CaF<sub>2</sub>-SrF<sub>2</sub>:Er(2%) in the spectral range 200-1800 nm.](image)

The spectral dependences of the absorption cross-sections for the transition <sup>4</sup>I<sub>15/2</sub>→<sup>4</sup>I<sub>13/2</sub> of Er<sup>3+</sup> ions were showed in Fig.2. The peaks absorption cross-sections of CaF<sub>2</sub>-SrF<sub>2</sub> crystals doped with 0.5 mol.%, 1 mol.%, 1.5 mol.% and 2 mol.% of Er<sup>3+</sup> ions at wavelength 1508 nm are 7.1×10<sup>-21</sup>, 6.0×10<sup>-21</sup>, 6.5×10<sup>-21</sup>, and 6.6×10<sup>-21</sup> cm<sup>2</sup>, respectively. Small difference in the absorption peaks can be explained by the accuracy of determining the concentration of Er<sup>3+</sup> ions. From analyses absorption of CaF<sub>2</sub>-SrF<sub>2</sub>:Er crystals and solar irradiance spectrum above atmosphere and at surface [16-19], we conclude that CaF<sub>2</sub>-SrF<sub>2</sub>:Er crystals potentially can convert low energy photons in wide spectral range 1450-1600 nm.
Figure 2. The spectral dependence of the absorption cross-sections for the transition $^4I_{15/2} \rightarrow ^4I_{13/2}$ of Er$^{3+}$ ions for CaF$_2$-SrF$_2$:Er crystals and solar irradiance spectrum above atmosphere (AM0 Solar spectrum) and at surface (AM1.5 Solar spectrum).

Upon 1531.8 nm laser excitation UCL of CaF$_2$-SrF$_2$:Er was observed in visible ($^2H_{9/2} \rightarrow ^4I_{15/2}$, $^3H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, $^2F_{9/2} \rightarrow ^4I_{15/2}$) and infrared ($^4I_{9/2} \rightarrow ^4I_{15/2}$, $^4I_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, $^5F_{9/2} \rightarrow ^4I_{15/2}$) spectral ranges. The most intensive luminescence was observed at around 980 nm which corresponding to the $^4I_{11/2} \rightarrow ^4I_{15/2}$ transition of Er$^{3+}$ ions. In the visible spectral range red luminescence dominates on the green and blue band for all samples. The intensity ratio of the UCL bands of CaF$_2$-SrF$_2$:Er has good agreement with the spectral sensitivity of silicon solar cells [20-21]. From Fig. 3a we can conclude that the spectral power of the UCL in range 360-1100 nm increases with the increase of the concentration of the Er$^{3+}$ ions until to 2%. The investigation of chromaticity coordinates showed that the UCL of CaF$_2$-SrF$_2$:Er crystals is characterized by color temperatures of 1737–3904 K at an incident power density of 283 W/cm$^2$ (Fig. 3b).

Figure 3. (A) Spectral power of UCL of CaF$_2$-SrF$_2$:Er crystals upon excitation at 1532 nm. (B) The CIE chromaticity diagram of CaF$_2$-SrF$_2$: Er.

Next we estimated efficiency of UCL of CaF$_2$-SrF$_2$:Er crystals (Table 1). The energy yield is defined as the UCL power per that of absorbed power by luminescence materials. The maximum energy yield of
the UCL in the spectral range of 380-1100 nm for the CaF$_2$-SrF$_2$:Er (2%) crystal was 11.4%. Interesting absorption and luminescence properties and high values of energy yields allow to us in the future investigate UCL of Er$^{3+}$ heavily doped CaF$_2$-SrF$_2$:Er single crystals.

4. Conclusion

In present paper spectral-luminescence properties of CaF$_2$-SrF$_2$:Er crystals were investigated. Wide absorption spectrum of CaF$_2$-SrF$_2$:Er crystals allows to upconvert radiation with a wavelength range 1450-1600 nm. Intensive UCL at around 980 nm and 650 nm good appropriate for spectral sensitivity of crystalline silicon cells. The investigated samples showed sufficiently high values of the UCL energy yields 11.4 %. The present results indicate that CaF$_2$-SrF$_2$:Er single crystals is a promising upconversion material for increasing the efficiency of crystalline silicon solar cells.

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