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VUV-spectroscopy of Ce^{3+} -doped crystals with fluorite-type structure

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Abstract. The spectral properties of two-component $Ca_{1-x}Sr_xF_2:Ce^{3+}$(0.05 mol%) (x = 0.75, 0.41, 0.25, 0.14) crystals in UV spectral region were investigated. It was shown that spectral properties of $Ca_{1-x}Sr_xF_2:Ce^{3+}$(0.05 mol%) in UV spectral region have intermediate position between those for pure CaF_2 and SrF_2 crystals. The optical constants were calculated from reflectance spectrum for CaF_2, SrF_2, $Ca_{1-x}Sr_xF_2:Ce^{3+}$(0.05 mol%) (x = 0.75, 0.25) crystals by use of Kramers-Kronig relations for complex reflection coefficient and Fresnel formulas.

1. Introduction

Two-component $Ca_{1-x}Sr_xF_2:Ce^{3+}$(0.05 mol%) (x = 0.75, 0.41, 0.25, 0.14) crystals were taken as the subject of this investigation. It is caused by interest to $Ca_{1-x}Sr_xF_2$ solid solution crystals as optical and laser materials, their possible application as scintillator materials and for study physical processes in mixed cation solutions.

Crystals CaF_2 and SrF_2 are used for many applications. A possible way of search for new materials with the required properties is a complication of their chemical composition. In binary systems MF_2-$M'F_2$ (M, M' – alkaline earth elements) the isovalent solid solutions are formed. As it was shown in [1] two-component crystals $Ca_{1-x}Sr_xF_2$ with definite x have mechanical and electrophysical properties improved in comparison with one-component CaF_2 and SrF_2. To be exact, they have lower melting temperature, lager mechanical strength and value of ionic conduction. It expands significantly the application area for these crystals.

2. Experimental

The crystals were grown by the vertical Bridgman method in the KPF system (Special Design Bureau, Institute of Crystallography of the Russian Academy of Sciences) [1]

Reflectivity and luminescence excitation spectra of $Ca_{1-x}Sr_xF_2$: Ce^{3+}crystals were measured at the SUPERLUMI station (HASYLAB, DESY, Hamburg, Germany) [2], luminescence spectra, decay kinetics of luminescence were recorded using SR from the BW3 beam-line (HASYLAB, DESY, Hamburg, Germany). The SR pulse width (FWHM) at DORIS is 130 ps and the repetition rate is 5

MHz. The reflection spectra (at fixed angle of 17.5°) were measured simultaneously with excitation spectra.

3. Results and discussion

Reflectance spectra of two-component $Ca_xSr_{1-x}F_2$ crystals are shown in figure 1 with spectra for pure CaF_2 and SrF_2 from [4]. Extinction coefficient k, refractive index n, real ε1 and imaginary ε2 parts of dielectric constant ε = ε1 + i·ε2 were calculated from reflectance spectra of investigated crystals with use of Kramers-Kronig relations for complex reflection coefficient $r(\omega) = \sqrt{R(\omega)} * \exp\left(i * \Theta(\omega)\right)$[3,5]:

$$\Theta(\omega) = \frac{\omega}{\pi} \int_0^{\infty} \frac{\ln\,[R(x)/R(\omega)]}{\omega^2 - x^2} dx$$

The spectra have been measured within a finite spectral range, so reflectance spectra have been complemented. For visible spectral region, reflection coefficient $R(\omega)$ for $Ca_{1-x}Sr_x F_2$ crystal was calculated from literature data of refractive index for pure CaF_2 n1(ω) and that one for SrF_2(n1(ω))[6] using formula:

$$R(\omega) = \left(\frac{n(\omega) - 1}{n(\omega) + 1}\right)^2$$

where $n(\omega) = x * n1(\omega) + (1 - x) * n2(\omega)$. Linear interpolation was used for long wavelength region. The $\Theta(\omega)$ was defined to be equal 0 for transparent region. In the high-energy region $R(x)/R(\omega)$was assumed to behave as ω^4/x^4[3]. Optical constants have been calculated in investigated area from $r(\omega)$ by use of Fresnel formulas [3] (see figure 1).

Luminescence peak (see figure 2) with maximum near 4.5eV in the emission spectra are attributed to self-trapped exciton emission [7, 8]. Doublets with splitting about 0.25 eV between components in crystals doped with Ce^{3+} ions (see figure 2) are attributed to transitions from lowermost 5d state to the splitted ^2F level of Ce^{3+} in 4f configuration.

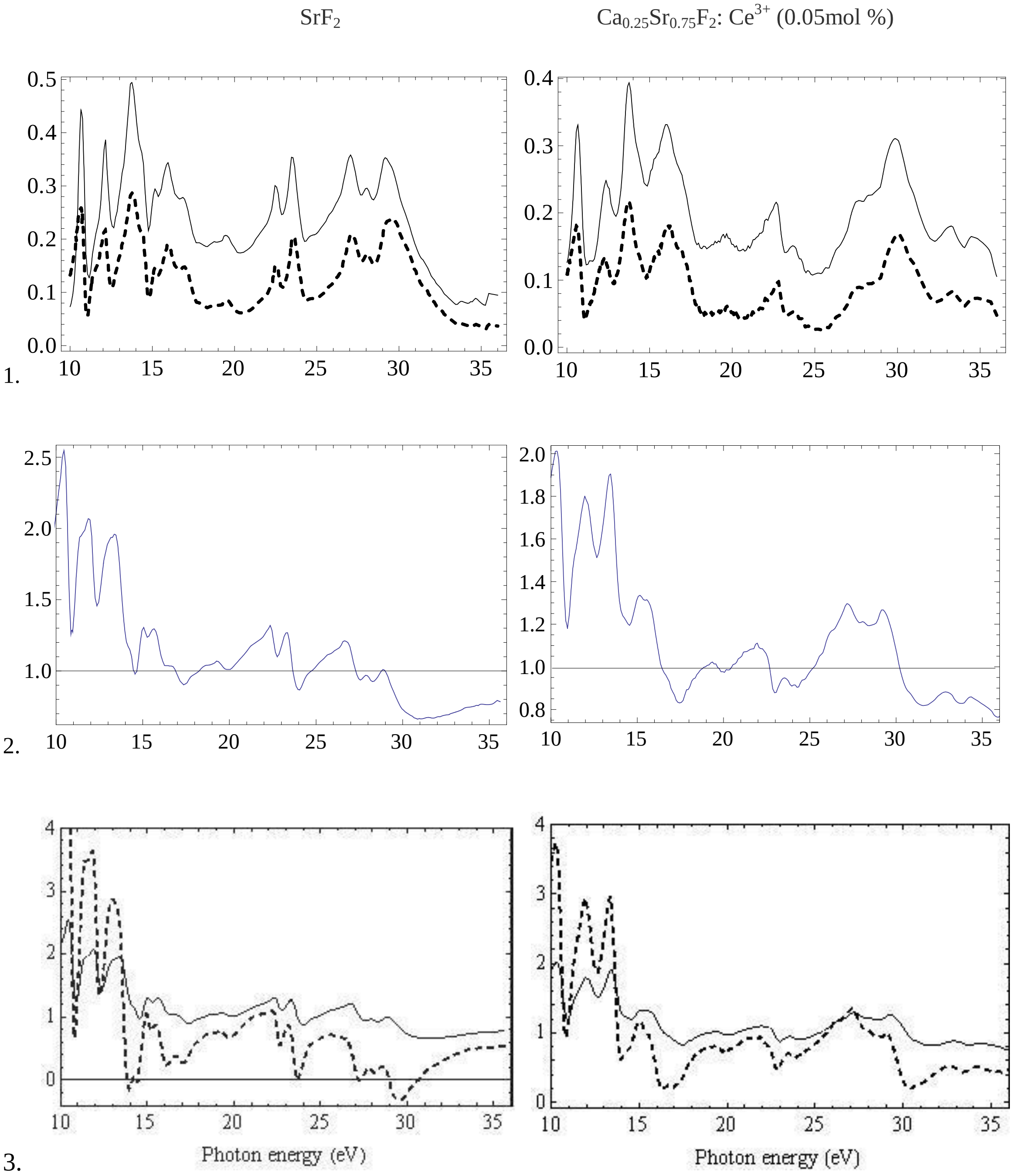
Different features in excitation spectra of emission peaked near 4.5 eV and 3.8 eV (see figure 3) confirm exciton character of the first one. The broad band in the luminescence excitation spectra around 6.2 eV is attributed to f-d absorption transitions in Ce^{3+} because of its location in the range of $Ca_{1-x}Sr_xF_2$ host transparency and relation with emission doublet near 3.9 eV.

Decay kinetics of luminescence from investigated crystals is presented in figure 4. There was no significant distinction observed in decay times as concentration x is changed.

At 100-ns timescale, fast and slow kinetics are observed. The slow decay correspond to the peak in emission spectra with maximum near 4.5 eV (slow), the fast one – 3.8 eV (fast). The temperature dependence of the scintillation decay time constants is observed similar to that one mentioned in [9].

4. Conclusions

Spectral properties of $Ca_{1-x}Sr_xF_2$:Ce^{3+}(0.05 mol%) in UV spectral region are intermediate between those for pure CaF_2 and SrF_2 crystals. Two-component $Ca_{1-x}Sr_xF_2$ with definite x values have mechanical and electrophysical properties improved in comparison with one-component compounds. These two-component systems are considered as prospective materials for optical applications.



SrF_2 $Ca_{0.25}Sr_{0.75}F_2$: Ce^{3+} (0.05mol %)

Figure 1 a. 1 - reflection coefficient R (ħω) (dashed line) and one third of extinction coefficient k(ħω)/3 (solid line), 2 - index of refraction, 3 - real ε1 (dashed line) and imaginary ε2 (solid line) parts of dielectric constant ε for SrF_2, $Ca_{0.25}Sr_{0.75}F_2$: Ce^{3+} (0.05mol %).

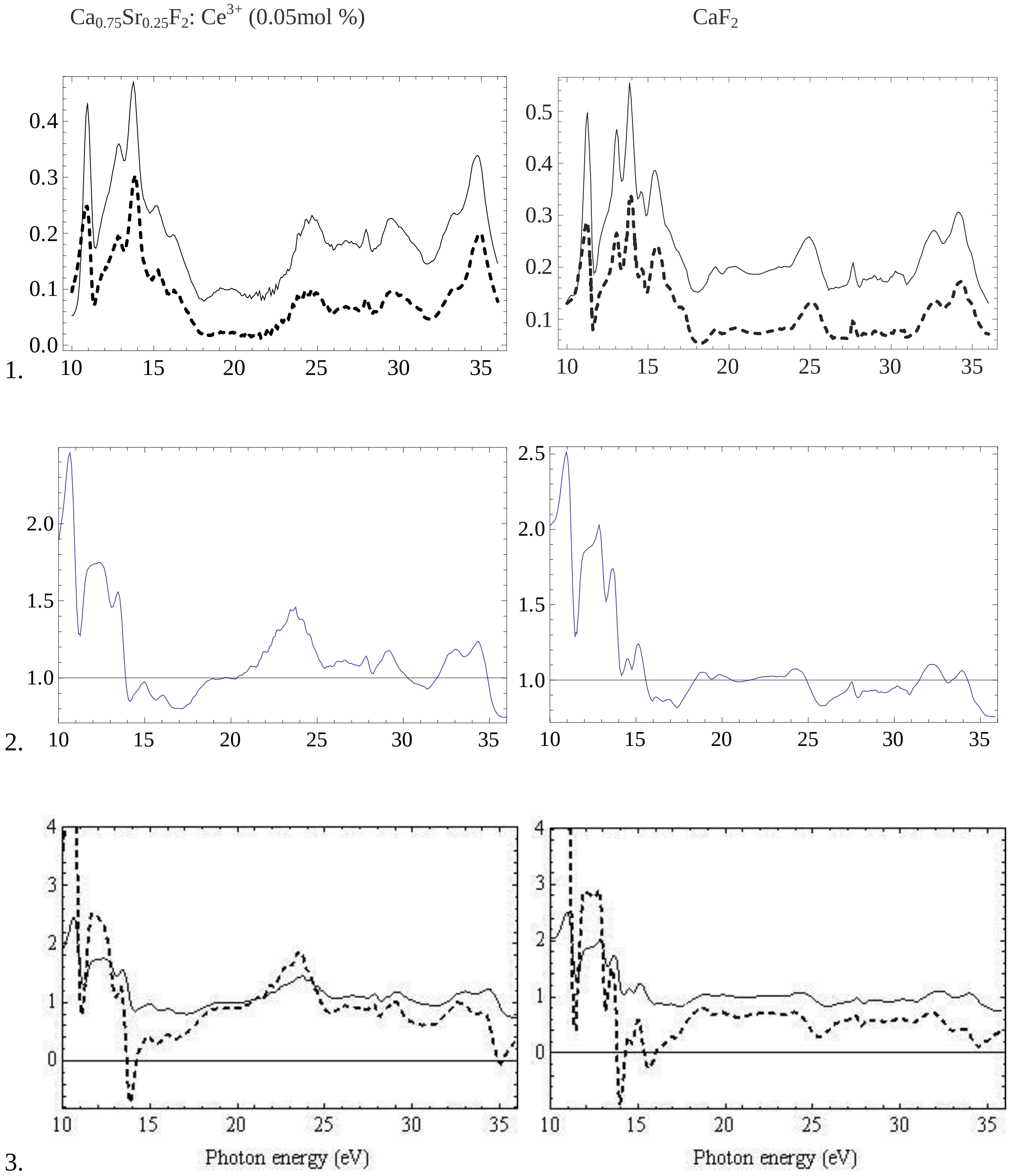
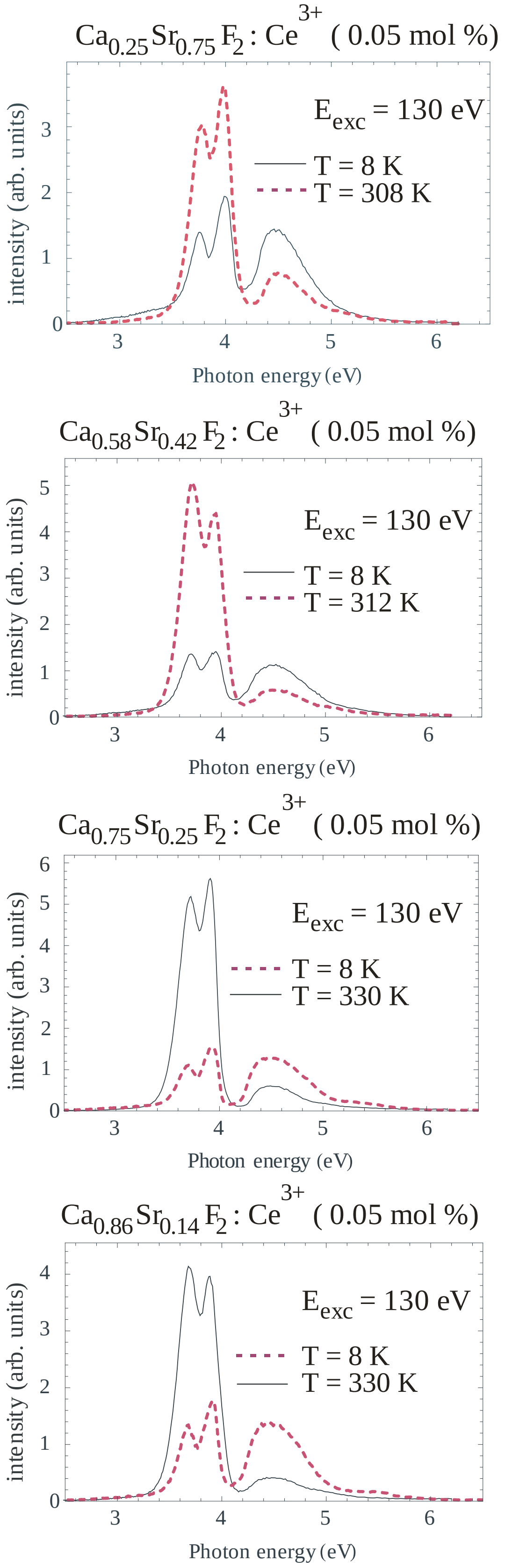


Figure 1 b. 1 - reflection coefficient R (ħω) (dashed line) and one third of extinction coefficient k(ħω)/3 (solid line), 2 - index of refraction, 3 - real ε1 (dashed line) and imaginary ε2 (solid line) parts of dielectric constant ε for $Ca_{0.75}Sr_{0.25}F_2$: Ce^{3+} (0.05mol %), CaF_2.



$Ca_{0.25}Sr_{0.75}F_2 : Ce^{3+}$ (0.05 mol %)

$Ca_{0.58}Sr_{0.42}F_2 : Ce^{3+}$ (0.05 mol %)

$Ca_{0.75}Sr_{0.25}F_2 : Ce^{3+}$ (0.05 mol %)

$Ca_{0.86}Sr_{0.14}F_2 : Ce^{3+}$ (0.05 mol %)

Figure 2. Emission spectra of $Ca_{1-x}Sr_xF_2$: Ce^{3+} (0.05mol %) (x = 0.75, 0.58, 0.25, 0.14).

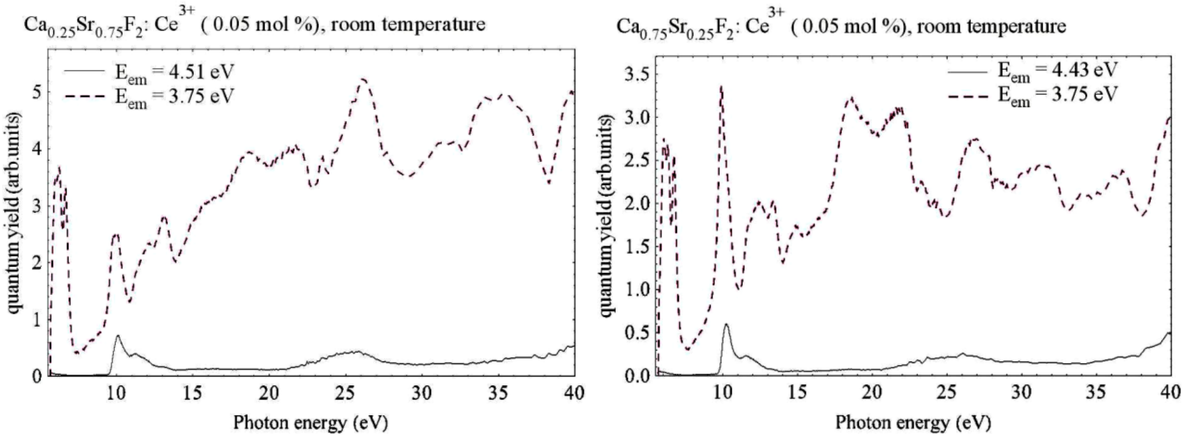


Figure 3. Excitation spectra of luminescence peaks with maximum near 4.5 eV and 3.8 eV for $Ca_{0.75}Sr_{0.25}F_2$: Ce^{3+} (0.05 mol %) and $Ca_{0.25}Sr_{0.75}F_2$: Ce^{3+} (0.05 mol %).

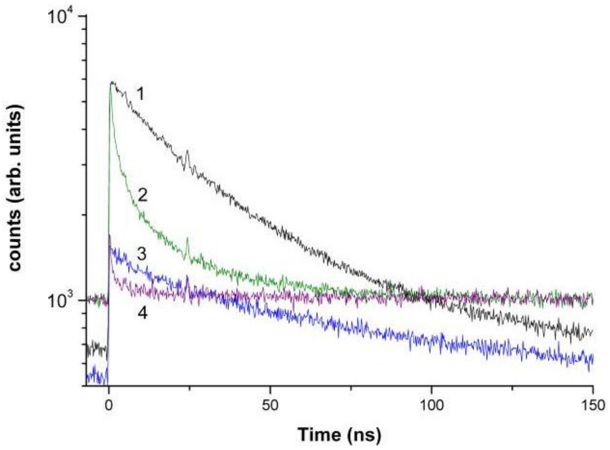


Figure 4. Luminescence decay kinetics for $Ca_{0.25}\,Sr_{0.75}\,F_2$: Ce^{3+}. Photon energy (excitation) = 130 eV.

Curve 1 – E_{em} = 3.65 eV, room temperature (RT). Decay time constant τ of major component $\approx$ 50 ns. (d-f luminescence of Ce^{3+})

Curve 2 – E_{em} = 3.75 eV, T = 8 K. $\tau \approx$ 10 ns

Curve 3 – E_{em} = 4.51 eV, RT. $\tau \approx$ 250 ns.

Curve 4 – E_{em} = 4.43 eV, T = 8 K. τ lies in microsecond region

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