

New red phosphor: $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$ single crystal

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The first observation of absorption, red-orange luminescence, and decay kinetics of $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$ single crystal is reported. The emission spectrum of excited directly in absorption bands consists of narrow bands at ~590, 614 and 690 nm caused by ${}^5D_J \rightarrow {}^7F_J$ transitions typical of Eu^{3+} ion. The same luminescence was found under UV, X- and γ -excitation. The optical parameters of x-ray irradiated crystal remain unchanged at dose increasing up to 10^4 Gy. That is, the compound holds a high radiation damage threshold. It can be presumed that this multicomponent solid solution may be used as a converter of UV and ionizing radiation into visible photons with high quantum efficiency.

Впервые представлены данные о поглощении, красно-оранжевой люминесценции и кинетике высвечивания монокристаллов $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$. При возбуждении в полосах поглощения в спектре излучения проявляются узкие полосы с максимумами при ~590, 614 и 690 нм, обусловленные ${}^5D_J \rightarrow {}^7F_J$ переходами в ионах Eu^{3+} . Аналогичная люминесценция имеет место при УФ, рентгеновском- и γ -возбуждениях. При облучении рентгеновским излучением оптические параметры остаются неизменными до доз 10^4 Грей, что свидетельствует о высокой радиационной стойкости материала. Показано, что кристалл $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$ может быть использован в качестве эффективного конвертирующего материала для преобразования УФ и рентгеновского излучений в видимый свет.

Solid-state inorganic phosphors, in particular, lanthanide-doped materials, are used as X- or γ -radiation-to-light converters in medical diagnostic imaging detectors [1–4]. The main role of these phosphors is to reduce the exposure of the patient to X-rays, while preserving the quality of the X-ray image. Phosphor intensifying screens absorb, amplify, and convert X-ray photons into hundreds of visible photons that are then recorded by optical or electronic detectors (e.g. photographic films, photomulti-

pliers, or photodiodes) incorporated in diagnostic imaging systems. Presently, conventional medical screening and film imaging methods are among the most widely used and cost-effective diagnostic tools available in radiology.

Vacuum ultraviolet (VUV) transparency of CaF_2 crystals (up to 130 nm) makes them promising candidates as hosts for phosphors in mercury-free discharge lamps, converting the broad xenon discharge emission

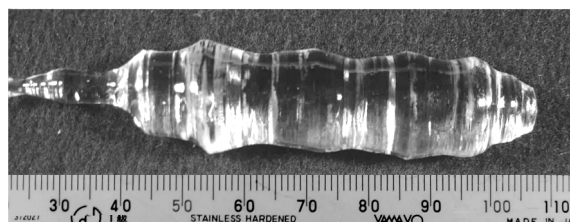


Fig. 1. As-grown $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$ single crystal.

(172 nm) into visible photons at a high quantum efficiency.

Bright blue emission (430 nm) resulting from $5d-4f$ transitions of Eu^{2+} ion is inherent in $\text{CaF}_2:\text{Eu}$ crystals used to detect β -rays and low-energy γ -quanta [5]. Obviously, during crystal growth and after the special treatment, a fraction of Eu ions enters the host in trivalent state (Eu^{3+}). In that case, the luminescence spectrum consists of the narrow lines located in the red-orange wavelength region resulting from the transitions of Eu^{3+} ion [2, 3, 6]. The excitation energy values typical of the $4f^6-4f^55d$ transitions in trivalent europium ion in fluorides lie in VUV (8.6–10.0 eV), UV (~5 eV) and VIS ranges [7]. Their positions agree closely with Eu^{3+} absorption.

Active optical media suitable in development of optical amplifiers in the red spectral region of the high sensitivity of photodiodes are now a subject of interest. This motivates the investigation of Eu^{3+} ions doped into CaF_2 crystals, providing strong spin-allowed $f-d$ absorption in VUV/UV and $f-f$ emission in the red-orange range. As far as we know, up to date, there is no published information devoted to luminescence of highly concentrated solid solution $\text{Ca}_{1-x}\text{Eu}_x\text{F}_{2+x}$ with $0.1 \leq x \leq 0.45$. In this article, we represent the results of $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$ single crystal study demonstrating the bright red emission under UV, X- and γ -rays excitations.

The crystals were grown in a Czochralski system with a 30 kW R.F.-generator. High purity powders (>99.99 %) of commercially available CaF_2 and EuF_3 powders were used. CaF_2 and EuF_3 were weighted and mixed in composition ratio $\text{Ca}:\text{Eu} = 0.65:0.35$ (at.%). The raw materials were purified in a glassy carbon crucible by heating at 800°C for 12 h under vacuum ($\sim 10^{-3}$ Pa). This vacuum level, obtained by a rotary pump and a diffusion one, was necessary to eliminate effectively the water and oxygen present in the chamber and raw materials, since even traces of those are well-known to be very

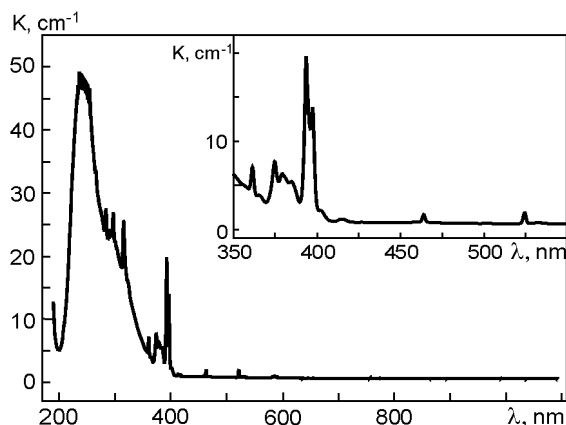


Fig. 2. Optical absorption spectrum of $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$ single crystal.

detrimental for the optical quality of fluoride crystals. Subsequently, high purity CF_4 gas (99.99 %) was slowly introduced into the furnace and the powders were melted. The growth temperature was approximately 1400°C . After seeding, the crystal rotation rate was fixed at 15 rpm, and the pulling rate was 2 mm/h. Crystals of 1 inch in diameter and several centimeters long were grown. Fig. 1 shows an as-grown $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$ single crystal. This crystal was yellowish in color and was transparent, free of bubbles and cracks. An inductively coupled plasma (ICP) technique was used to determine the chemical composition of the grown crystal. With this result, the effective segregation coefficient of Eu was determined to be 0.826.

A SPECORD M40 spectrophotometer used to measure the crystal optical absorption at 300 K in 190–1100 nm range. Photoluminescence and excitation spectra were studied using a setup described elsewhere [8]. To perform time-resolved measurements at photo-excitation, the VARIAN CARY ECLIPSE Fluorescence Spectrophotometer was employed. The stationary γ -luminescence was measured with ^{241}Am source. The luminescence kinetics under X-ray pulsed irradiation was measured using a setup described in [9]. Radiation damage experiments were performed with irradiation of samples by an X-ray pulse tube (160 kV, 10 Gy/min).

The absorption spectrum of $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$ crystal is shown in Fig. 2. The most intense wide band is in UV region with a maximum near 250 nm. Besides, there are several lines overlapping the main band and a number of distinct long-wave-

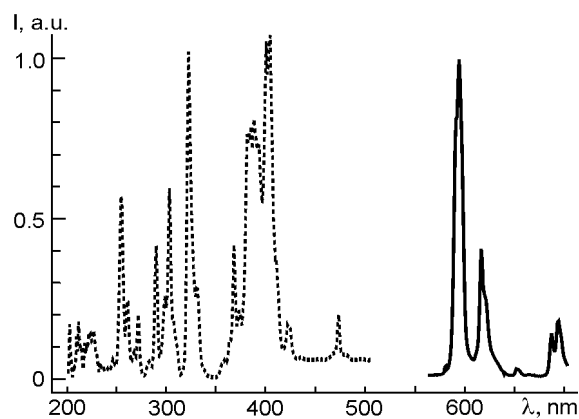


Fig. 3. Excitation spectrum of emission with maximum at 592 nm (left) and luminescence spectrum at excitation by 394 nm (right).

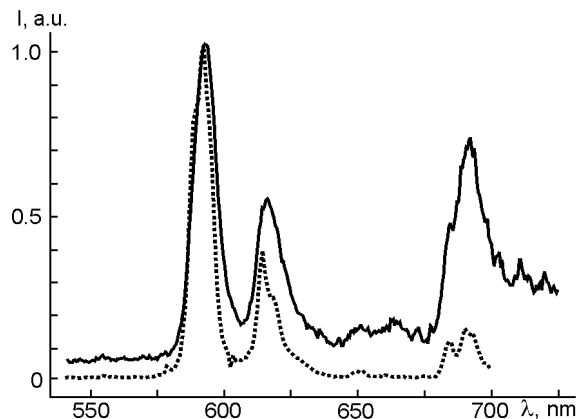


Fig. 4. Spectra of Ca_{0.65}Eu_{0.35}F_{2.35} emission excited by x- (dotted) and γ-(solid) rays.

length lines in the visible range. The line positions agree well with the known transitions in Eu³⁺ ion in different europium doped matrices [3, 6, 7]. The luminescence and excitation spectra are demonstrated by Fig. 3. The brightest duplicated emission lines take up the positions at 589–592 and 614–618 nm whereas less intensive ones are situated at 649–652 and 683–692 nm. The excitation is performed by lines located in 350–500 nm range and by light corresponding to the main UV absorption band as well.

As follows from the spectra represented, $^5D_0 \rightarrow ^7F_j$ ($j = 0-4$) optical transitions of Eu³⁺ ion are revealed in investigated samples. Unlike CaF₂:Eu crystal, the "blue" emission resulting from transitions of bivalent europium was not found in the multi-component compound studied.

The radioluminescence spectra of the Ca_{0.65}Eu_{0.35}F_{2.35} crystal under x- and γ-excitation exhibit the typical Eu³⁺ red-orange luminescence (Fig. 4). At the same time, the long-wavelength (680–700 nm) contribution is noticeably higher in γ-luminescence. The spectrum structure of x-ray emission is evidently similar to that at γ-irradiation. The line positions fit with those observed under direct photo-excitation. This means that in these crystals the recombination mechanism of the energy transfer from the host to the impurity RE ions can excite the Eu³⁺ to its $5d$ levels resulting in the appearance of $^5D_0 \rightarrow ^7F_j$ luminescence of the respective ion. The luminescence decay kinetic features under photo- and x-ray pulse excitation are shown in Fig. 5. Under the photo-excitation (394 nm) of Eu³⁺ ion emission, the leading decay time (τ) is equal to

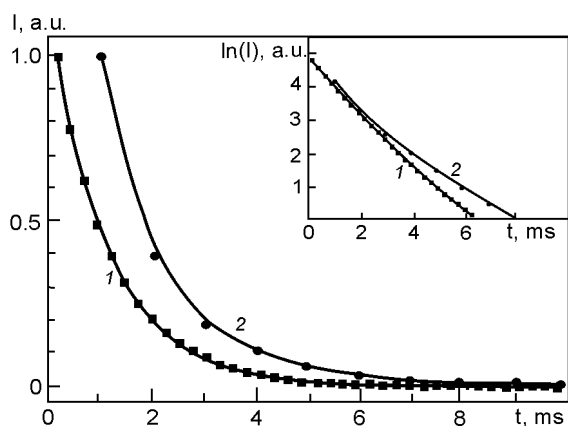


Fig. 5. Decay curves of Ca_{0.65}Eu_{0.35}F_{2.35} crystal emission excited by $\lambda = 394$ nm (1) and x-ray (2) pulses.

$\sim 1.34 \mu\text{s}$, while x-ray excitation gives rise to pulse with $\sim 1.64 \mu\text{s}$. These values agree approximately with the ordinary transition times of trivalent europium ions in different matrices [1, 6].

The radiation damage in Ca_{0.65}Eu_{0.35}F_{2.35} crystals was studied to provide data on light yield losses and color center formation. As was found, the optical transmission and luminescence spectra of samples remain unchanged at irradiation dose increasing up to 10^4 Gy.

Thus, the compound studied shows a sufficiently high radiation damage threshold and therefore is applicable in radiation environment. From the results obtained, it can be deduced that due to bright Eu³⁺ ion luminescence under UV and ionizing irradiations, the Ca_{0.65}Eu_{0.35}F_{2.35} single crystal is of good prospects as a red phosphor and display material. It is to note that the crys-

tal emission region is in good agreement with the photodiode detector sensitivity. It is known that the most effective excitation of the $4f^6-4f^55d$ transitions in Eu^{3+} ion take place in VUV range [7], it can be presumed that this multicomponent solid solution may be used not only in visualization and detection of x-rays, γ -quanta, and UV radiation, but for vacuum ultraviolet light as well. The $\text{Ca}_{1-x}\text{Eu}_x\text{F}_{2+x}$ crystal luminescence study of at VUV excitation is in progress.

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Новий червоний фосфор: монокристал $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$

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Уперше представлено дані про поглинання, червоно-жовтогарячу люмінесценцію й кінетику висвітлювання монокристалів $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$. При збудженні у смугах поглинання у спектрі випромінювання проявляються вузькі смуги з максимумами при ~590, 614 та 690 нм, обумовлені $^5D_J \rightarrow ^7F_J$ переходами в іонах Eu^{3+} . Аналогічна люмінесценція має місце при УФ, х- і γ -збудженнях. При опроміненні рентгенівським випромінюванням оптичні параметри залишаються незмінними до доз 10^4 Грей, що свідчить про високу радіаційну стійкість матеріалу. Показано, що кристал $\text{Ca}_{0.65}\text{Eu}_{0.35}\text{F}_{2.35}$ може бути використаний в якості ефективного матеріалу для перетворення УФ і рентгенівського випромінювань у видиме світло.