

Sensitization of europium (Eu^{3+}) ions by terbium (Tb^{3+}) in ceramics based on yttrium stabilized cubic zirconium dioxide

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In this work, stabilized $f\text{-ZrO}_2$ ceramic samples with the compositions of $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Eu}_{0.09})\text{O}_{1.91}$, $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Tb}_{0.09})\text{O}_{1.91}$ and $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Eu}_{0.045}\text{Tb}_{0.045})\text{O}_{1.91}$ were studied. The elemental composition was studied by electron probe microanalysis, and the luminescent properties were studied by local cathodoluminescence (CL). An analysis of the Eu^{3+} CL spectra confirmed the stabilization of the cubic phase in ceramics at room temperature. The study of the obtained CL spectra, the $^5D_4\text{--}^7F_5\text{Tb}^{3+}$ band luminescence decay kinetics, CL images and excitation spectra showed europium sensitization by terbium in $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Eu}_{0.045}\text{Tb}_{0.045})\text{O}_{1.91}$.

Keywords: $f\text{-ZrO}_2$, Eu^{3+} , Tb^{3+} , Ceramics, Sensitization, Cathodoluminescence

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1. Introduction

The development of materials that efficiently convert high-energy radiation into visible light is an important practical problem. Such substances, called as scintillators, are widely used as part of high-energy radiation detectors in such fields as industrial dosimetry, medicine, geology and science [1,2].

One of the most famous scintillators are wide-band-gap oxide materials (matrices) activated by rare-earth ions (REI) [3]. REIs in them act as luminescence centers [4]. Ceramic cubic zirconia has high mechanical, chemical strength and radiation stability [5], widely used as a refractory structural material [6]. Such properties make it a promising matrix for creating a scintillator capable of operating effectively in extreme conditions. However, the cubic $f\text{-ZrO}_2$ phase is unstable at room temperature. To stabilize it, rare earth ion oxide R_2O_3 is added to zirconium oxide, for example Y_2O_3 [7].

Trivalent europium ions [8] are often used to activate oxide matrices. Eu^{3+} makes it possible to obtain a material with high-intensity luminescence in the red region of the spectrum, to which industrial radiation detectors are most sensitive [9]. In some cases, an analysis of the shape of the emitted spectrum of Eu^{3+} makes it possible to estimate the local environment of this ion and, consequently, the symmetry of the matrix in which it is included [10]. Nevertheless, such an activator in the $f\text{-ZrO}_2$ matrix has a rather low luminescence intensity [11]. The phenomenon of sensitization can be used to increase this intensity. For Eu^{3+} the most famous and effective sensitizer is Tb^{3+} [12]. The transfer of excitation energy between terbium and europium in $f\text{-ZrO}_2\text{:Eu}^{3+}\text{Tb}^{3+}$ has not been studied before.

The purpose of this work was to study the process of europium sensitization by terbium in ceramics based on stabilized cubic zirconia.

2. Samples and study methods

In the present work, one studied three ceramic samples based on cubic zirconia stabilized with yttrium oxide and activated with rare earth ions: europium (Eu^{3+}) (sample 1-Eu $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Eu}_{0.09})\text{O}_{1.91}$), terbium (Tb^{3+}) (sample 2-Tb $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Tb}_{0.09})\text{O}_{1.91}$) and $\text{Eu}^{3+}/\text{Tb}^{3+}$ (sample 3-Eu/Tb $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Eu}_{0.045}\text{Tb}_{0.045})\text{O}_{1.91}$).

The planned yttrium content for all samples was 0.09 form.un. (formula units), which was sufficient to stabilize the cubic phase [7]. The planned contents of europium and terbium in the 1-Eu and 2-Tb samples were 0.09 form. un each. for each REI. Such concentrations were close to optimal for maximizing the luminescence yield (before concentration quenching) of Eu^{3+} [13,14] and Tb^{3+} [15].

The feed stock for obtaining ceramics was synthesized by co-precipitation from a common aqueous solution. This method was chosen as one of the cheapest and most promising for industrial production. For the synthesis were obtained individual aqueous solutions $\text{Zr}(\text{NO}_3)_4$, $\text{Y}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$. They were filtered and calibrated to determine the concentration of oxides ZrO_2 , Y_2O_3 , Eu_2O_3 , Tb_2O_3 . Then the resulting solutions were mixed in the calculated proportions. Co-precipitation in the mixture was performed by adding an excess of 25% aqueous ammonia solution NH_4OH in a ratio of 1:2. The resulting precipitate was filtered in a paper filter and then

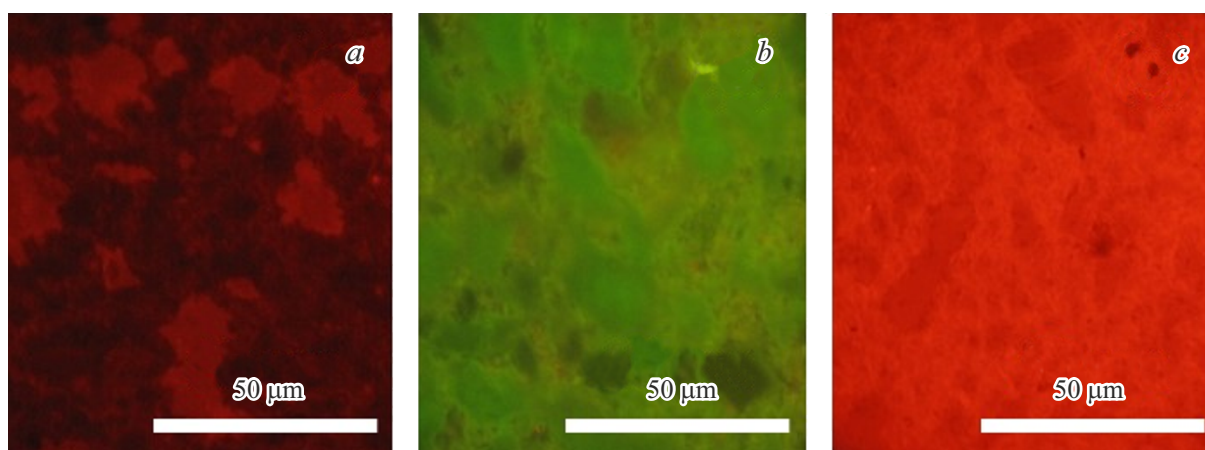


Figure 1. CL images of samples: (a) 1-Eu, (b) 2-Tb, (c) 3-Eu/Tb.

washed with distilled water to get rid of ammonium nitrate residues. Then the precipitate was dried at 150°C for 12 h and calcined at temperature of 800°C for 2.5 h.

The feed stock obtained, mixed with a liquid plasticizer (3% aqueous solution of polyvinyl alcohol), was ground manually in an agate mortar. Then it was pressed into tablets with a diameter of 8 mm under a pressure of 10 MPa. The tablets were annealed at 1600°C in air for 3 h.

The elemental composition of the obtained samples was studied by electron probe microanalysis (EPMA) on a CAMEBAX electron probe microanalyzer equipped with four X-ray spectrometers. The energy of the electron beam was $U = 20$ keV, the value of the absorbed current was $I = 15$ nA, the beam diameter was $d = 2$ μm. For analysis, the analytical line $L\alpha$ was chosen for all elements. Pure zirconium (for zirconium) and the following compounds were used as standards: EuPO_4 (for europium), TbPO_4 (for terbium), $\text{Y}_3\text{Al}_5\text{O}_{12}$ (for yttrium). The oxygen content was calculated based on stoichiometry. The elemental composition was measured at several randomly selected points of the sample and then averaged.

The luminescent properties were studied by the method of local cathodoluminescence (CL) using the same CAMEBAX analyzer, additionally equipped with visible range spectrometer [16]. The CL spectra and kinetic curves were obtained at beam energy $U = 20$ keV, absorbed current $I = 15$ nA, and beam diameter $d = 2$ μm. The CL spectra for all samples were measured under the same conditions at room temperature in the wavelength range 460–660 nm. CL images were obtained in a defocused electron beam with a diameter of $d = 100$ μm. Measurements of the CL decay kinetics were carried out in the mode of electron beam deflection.

To ensure electrical conductivity, the samples were additionally coated with a carbon film on a JEE-4C universal vacuum station.

The excitation spectra were recorded using the equipment of the Joint Research Center of the Frumkin Institute

of Physical Chemistry and Electrochemistry RAS. The excitation spectra were obtained on a Fluorolog-3 „Horiba“ spectrofluorimeter with an R928 detector, 450 W xenon lamp was used as a source.

3. Results and discussion

3.1. Elemental composition

Average elemental composition of samples according to EPMA data is presented in Table 1. The obtained values for the activators corresponded to the planned ones, the maximum deviation from the average value over the sample surface did not exceed 6%. Insignificant increase in the yttrium content in the 1-Eu and 3-Eu/Tb samples was observed compared to the specified one.

3.2. CL studies

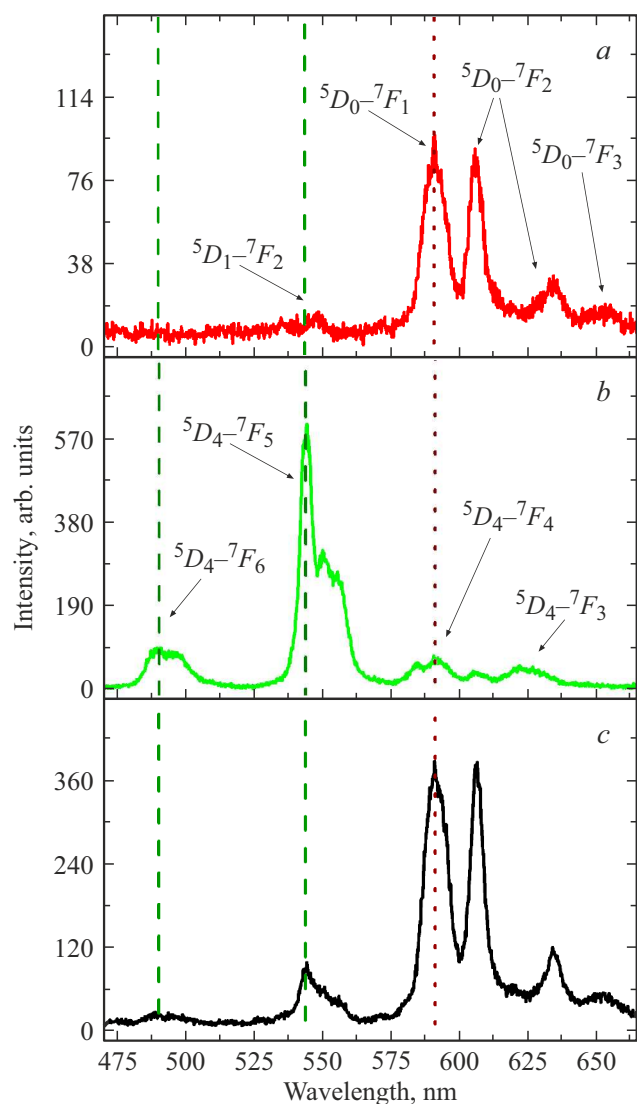
Color contrast was observed in CL images of all samples (Fig. 1). This contrast cannot be explained by the inhomogeneity of the samples in composition, since the EPMA showed that the samples were homogeneous. The contrast of CL images may be associated with the features of polishing materials.

The obtained CL spectra are presented in Fig. 2. The emission bands observed in the spectra were deciphered from the literature [8,11,17–19]. The spectrum of the 1-Eu sample exhibited bands associated with transitions from the 5D_0 Eu^{3+} levels to the $^7F_{1,2,3}$ and the transition band 5D_1 – 7F_2 . For the 2-Tb sample, lines appeared related to the transitions from the 5D_4 Tb^{3+} level to the $^7F_{3,4,5,6}$. The spectrum of the 3-Eu/Tb sample contained the emission bands of both REI e.i. Eu^{3+} and Tb^{3+} .

The number of splittings for the REI luminescence spectrum bands depends on the local environment of this ion [10]. On the basis thereof, the analysis of the luminescence spectra of samples containing europium made

Table 1. Average elemental composition of samples according to EPMA data

Sample	Planned composition	Element content (PCMA), formula units			
		Zr	Y	Eu	Tb
1-Eu	$(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Eu}_{0.09})\text{O}_{1.91}$	0.78 ± 0.01	0.13 ± 0.01	0.09 ± 0.003	0
2-Tb	$(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Tb}_{0.09})\text{O}_{1.91}$	0.86 ± 0.05	0.07 ± 0.03	0	0.07 ± 0.02
3-Eu/Tb	$(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Eu}_{0.045}\text{Tb}_{0.045})\text{O}_{1.91}$	0.79 ± 0.02	0.12 ± 0.01	0.04 ± 0.002	0.05 ± 0.003

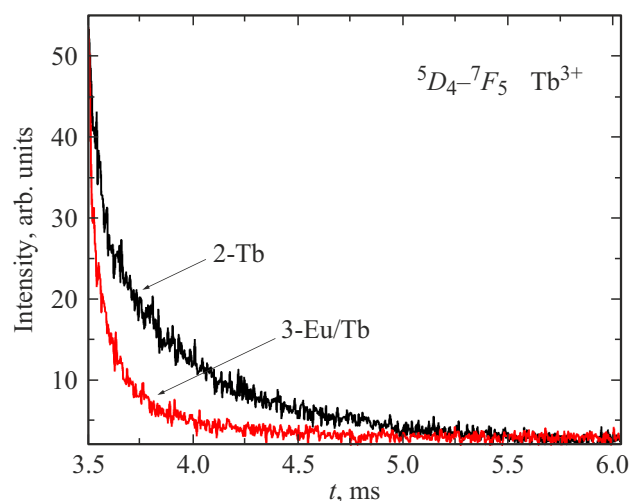
**Figure 2.** CL spectra of samples: (a) 1 — Eu, (b) 2 — Tb, (c) 3 — Eu/Tb.

it possible to confirm the stabilization of the $f\text{-ZrO}_2$ cubic phase. First of all, this was evidenced by the absence of splitting of the transition band $^5D_{0-7}F_2 \text{Eu}^{3+}$ [11].

A comparison of the brightest bands of the Eu^{3+} spectrum showed an increase in the europium luminescence intensity by a factor of four for the 3-Eu/Tb sample compared to the 1-Eu sample (Fig. 2, a, c). Increase in

Table 2. Band decay times $^5D_4\text{-}^7F_5 \text{Tb}^{3+}$

Sample	τ_1 , ms	A_1 , %	τ_2 , ms	A_2 , %
2-Tb	0.6	50	0.1	50
3-Eu/Tb	0.3	43	0.04	57

**Figure 3.** The CL decay kinetics of the band $^5D_4\text{-}^7F_5 \text{Tb}^{3+}$ for samples 2 — Tb and 3 — Eu/Tb.

brightness is also clearly seen when comparing CL images (Fig. 1, a, c). Also, the luminescence intensities of the bands associated with Tb^{3+} ions was compared, Their intensity decreased by a factor of 4.5 in the 3-Eu/Tb sample compared to the 2-Tb sample (Fig. 2, b, c). Such a redistribution of luminescence intensities may indicate the sensitization of europium by terbium.

For the band $^5D_4\text{-}^7F_5 \text{Tb}^{3+}$ ($\lambda = 545 \text{ nm}$) of the CL spectrum for 2-Tb and 3-Eu/Tb samples, the kinetics of CL decay was obtained (Fig. 3). The technique of kinetic measurements is described in detail in the work [19]. Each resulting curve was approximated by the sum of two exponents:

$$y = y_0 + A_1 \exp(-(t - t_0)/\tau_1) + A_2 \exp(-(t - t_0)/\tau_2).$$

The calculated decay times (τ) are presented in Table 2 (A_1 , A_2 are contributions of the first and second exponents, respectively).

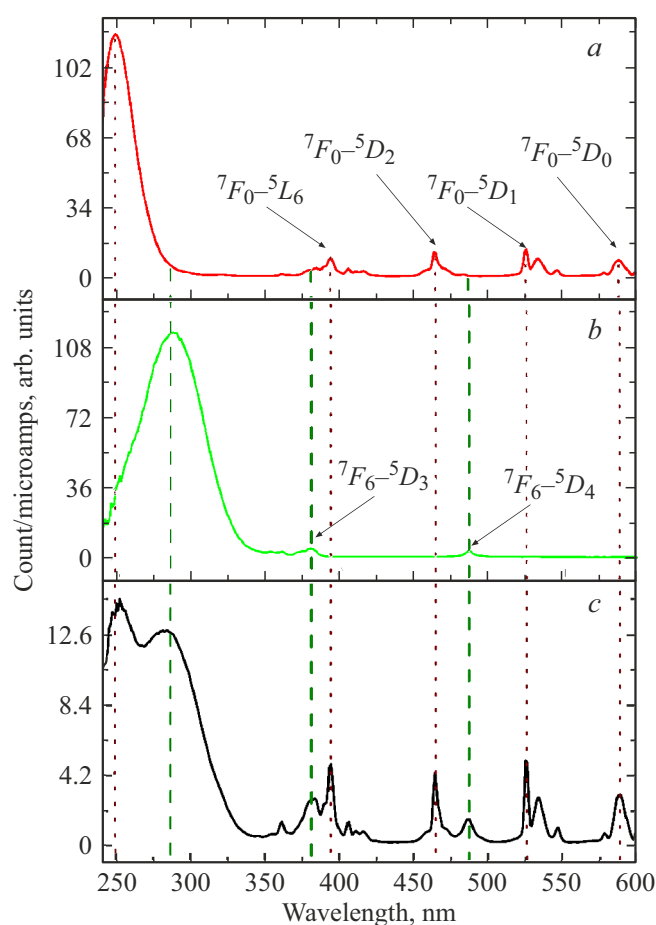


Figure 4. Sample excitation spectra: (a) 1 — Eu (band $^5D_0-^7F_2$ Eu^{3+} , $\lambda = 604$ nm), (b) 2 — Tb (band $^5D_4-^7F_5$ Tb^{3+} , $\lambda = 545$ nm), (c) 3 — Eu/Tb (band $^5D_0-^7F_2$ Eu^{3+} , $\lambda = 604$ nm)

The presence of a shorter decay time may be due to the influence of the grain boundaries that make up the ceramic [19].

In the 3-Eu/Tb sample, the CL decay times of the $^5D_4-^7F_5$ Tb^{3+} band are halved compared to the 2-Tb sample, which indicates the appearance of an additional energy transfer channel from the excited level of terbium. This fact may indicate the transfer of excitation energy from terbium to europium.

3.3. Excitation spectra studies

Excitation spectra were obtained for the 1-Eu and 3-Eu/Tb samples at the emission wavelength $\lambda = 604$ nm (Eu^{3+} band $^5D_0-^7F_2$) and for the 2-Tb sample at a wavelength $\lambda = 545$ nm (band Tb^{3+} $^5D_4-^7F_5$) (Fig. 4). The lines corresponding to energy transitions in the excitation spectra were deciphered from the literature data [8,20].

Fig. 4, a shows that the excitation of the 5D_0 Eu^{3+} level in the 1-Eu sample, in addition to direct capture, occurred from levels 5D_1 , 5D_2 and 5L_6 . Excitation of the 5D_4 Tb^{3+} level in the 2-Tb sample occurred both directly and through

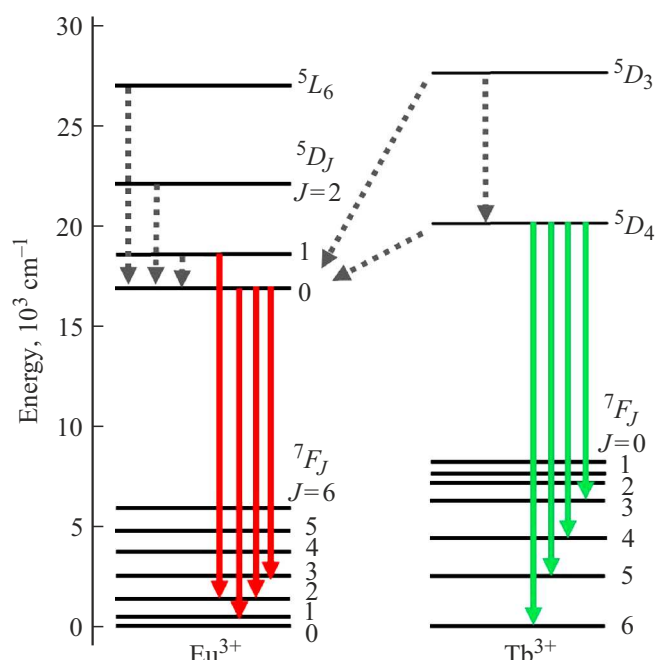


Figure 5. Scheme of energy transitions in the sample 3 — Eu/Tb. Solid lines are radiative transitions, dotted lines is non-radiative energy transfer.

the 5D_3 level (Fig. 4, b). The excitation spectrum of the 5D_0 Eu^{3+} level in the 3-Eu/Tb sample exhibited bands associated with energy transfer both from the Eu^{3+} levels, and from the levels Tb^{3+} (Fig. 4, c). This clearly demonstrated the sensitization of europium by terbium. The presence of broad bands in the excitation spectra requires a separate study.

The data obtained in the course of the work prove the sensitization of europium by terbium in cubic zirconia. On the basis of the obtained data, a scheme of energy transitions in $f\text{-ZrO}_2$ activated with Eu^{3+} and Tb^{3+} was constructed (Fig. 5).

4. Conclusions

In present work, ceramic samples of cubic zirconia of the following compositions were synthesized: $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Eu}_{0.09})\text{O}_{1.91}$, $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Tb}_{0.09})\text{O}_{1.91}$ and $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Eu}_{0.045}\text{Tb}_{0.045})\text{O}_{1.91}$. The average elemental composition of the samples corresponded to the specified one. An analysis of the Eu^{3+} CL spectra confirmed the stabilization of the cubic phase in ZrO_2 ceramics at room temperature.

It was shown that the Eu^{3+} CL intensity increased by a factor of 4, while the Tb^{3+} CL intensity decreased by a factor of 4.5 for the sample $(\text{Zr}_{0.82}\text{Y}_{0.09}\text{Eu}_{0.045}\text{Tb}_{0.045})\text{O}_{1.91}$ compared to the sample activated only with europium or terbium, respectively. In addition, the CL decay times of the $^5D_4-^7F_5$ Tb^{3+} band decreased by a factor of two for the sample containing both REIs compared to the material containing only Tb^{3+} . These facts, as well as an analysis

of the excitation spectra, confirmed the sensitization of europium by terbium in the obtained zirconium dioxide.

Further studies will be aimed at finding the optimal content of activator ions to maximize the Eu^{3+} luminescence intensity in the $f\text{-ZrO}_2$ matrix. Such studies will help in the creation of a scintillator that works effectively in extreme conditions.

Conflict of interest

The authors declare that they have no conflict of interest.

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