

STRUCTURE AND SPECTRAL AND LUMINESCENT PROPERTIES OF $Y_3Al_5O_{12}$ CERAMICS CONTAINING Ce AND Cr

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$Y_3Al_5O_{12}:Ce^{3+}$ ceramics additionally doped with chromium from the gas phase were synthesized by a colloidal-chemical method. It was established that its luminescence spectrum included a broad poorly resolved band with a barycenter at 570 nm due to Ce^{3+} and narrow bands in the region 670–750 nm due to Cr^{3+} in $Y_3Al_5O_{12}$ and $YAlO_3$. The structure of Cr^{3+} optical centers in both subsystems, the kinetic properties of their luminescence, and the transfer between them of electron excitations were considered.

Keywords: oxide ceramics, luminescence, optical centers, electron excitation transfer.

Introduction. The development of highly efficient LEDs based on crystalline InGaN that emit at ~450 nm has stimulated the fabrication of luminophores capable of transforming this radiation into the long-wavelength region in order to produce quasi-white light. The most suitable luminophores for such LEDs are considered to be garnets activated by Ce^{3+} , in particular yttrium-aluminum garnet (YAG, $Y_3Al_5O_{12}$), which luminesces over a broad band at ~530 nm and has already been widely utilized [1, 2]. The three sublattices in the structure of these compounds enable ions of practically all groups of the Periodic Table to be incorporated and to have a significant effect on the energy-levels of the $4f^{05}d^1$ -shell of this activator that determine the luminescence characteristics. In principle, selection of appropriate dopants can shift the barycenter of the Ce^{3+} luminescence band in such luminophores into the red spectral region in order to provide “warm” quasi-white light from dual-component (LED-luminophore) light sources [3]. An alternative approach is to dope these luminophores with additional elements whose ions luminesce in the red spectral region. The simplest and cheapest way to achieve this goal is co-activation by Ce^{3+} and Cr^{3+} . Efficient transfer of excitation from Ce^{3+} to Cr^{3+} in $Y_3Al_5O_{12}:Ce,Cr$ and an increased fraction of red quanta emitted by such luminophores was reported [4]. However, the spectral and luminescent properties of $Y_3Al_5O_{12}$ ceramics co-activated by these ions have not been published. Also, this ceramic is characterized by increased stability of the luminescence intensity upon heating up to 180°C [5]. This gives it an advantage when used in powerful dual-component light sources. Closing this gap is the goal of the present work.

Experimental. Test samples were synthesized in stages consisting of mixing $Y(NO_3)_3$, $Al(NO_3)_3$, and $Ce(NO_3)_3$ in the stoichiometric ratio in H_2O ; precipitation using NH_4OH ; rinsing and drying the precipitate; adding a sintering agent; drying and calcination; grinding and pressing; and sintering. Chromium was doped from the gas phase by calcining the produced Ce-containing powders and sintering pellets in a furnace with lanthanum chromite heaters. All reagents were at least chemically pure. Formation of the YAG phase was monitored using a DRON-7 x-ray diffractometer and $Cu K_\alpha$ -radiation ($\lambda = 1.54184 \text{ \AA}$). Extraneous impurities and the activator concentration were monitored using an LSA-1 laser spectral analyzer.

Luminescence spectra (LS) and luminescence excitation spectra (LES) were recorded using an SDL-2 spectrofluorimeter, were corrected taking into account the spectral sensitivity of the recording system and the spectral distribution of the exciting radiation, and were expressed as the dependence of the number of quanta per unit wavelength, $dN/d\lambda$, vs. λ .

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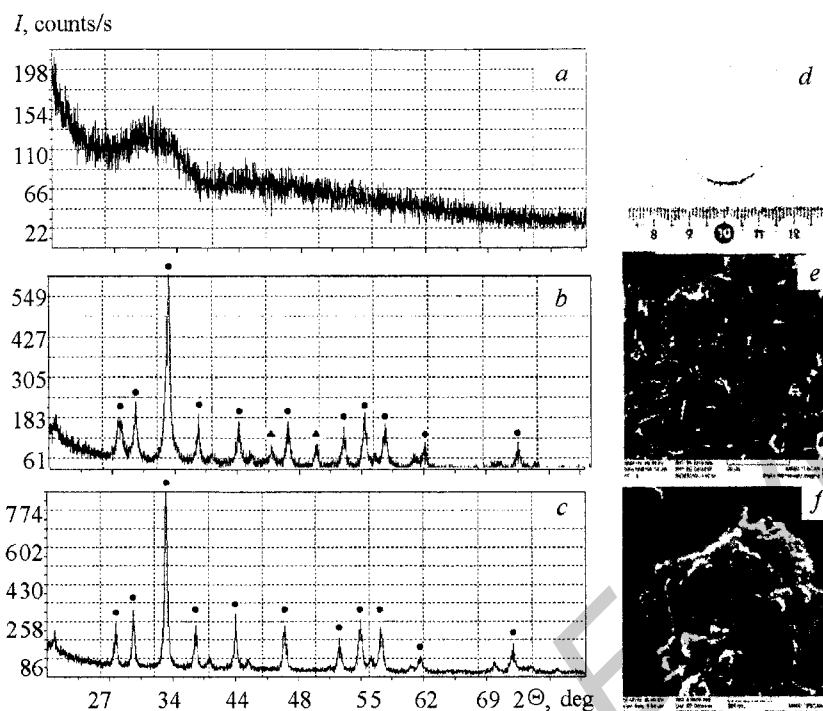


Fig. 1. X-ray powder patterns of ceramics containing Ce and Cr (a–c), photograph of the ceramic (d), and photomicrographs of a chip (e) and powder used for pressing (f); $T_{\text{ann}} = 800$ (a, f), 900 (b), and 1450°C (c–e); $\text{Y}_3\text{Al}_5\text{O}_{12}$ (●) and YAlO_3 (▲) reflections.

The luminescence kinetics and their instantaneous spectra were studied using an automated laser spectrometer with excitation by the second harmonic of a single-pulse tuned Ti:sapphire laser. The studied radiation was isolated by an MDR-23 grating monochromator and recorded by a photoelectric method using an analog-digital converter and data output to a computer. Signals were accumulated during recording of instantaneous spectra for $5 \mu\text{s}$ with various delay times t_{del} relative to the exciting pulse.

Results and Discussion. Figure 1 shows powder patterns of the precursor and the ceramic with $[\text{Ce}] \approx 5 \cdot 10^{19} \text{ cm}^{-3}$ and $[\text{Cr}] \leq 1 \cdot 10^{19} \text{ cm}^{-3}$ that was obtained at various annealing temperatures T_{ann} and a photograph and photomicrograph of a chip from the ceramic sample and the powder used for pressing. It can be seen that the precursor was amorphous (Fig. 1a) and became crystalline with noticeably broadened reflections after annealing at 900°C (Fig. 1b). This indicated that the component particles were nano-sized. According to the JCPDS-1996 catalog (PDF 16-0219 and 33-0040), Bragg reflections denoted by ● corresponded in intensity and position to YAG of cubic space group $1a3d$; by ▲, to the perovskite-like phase (YAlO_3). This phase did not appear in the diffraction pattern of the ceramic sample (Fig. 1c). It can also be seen that the individual grains of the powder used for pressing were $\sim 50 \text{ nm}$ in size (Fig. 1f); of the ceramic sample, $\sim 5\text{--}10 \mu\text{m}$ (Fig. 1e).

Figure 2 shows the LS of the ceramics containing Ce and Ce and Cr. It can be seen that the singly doped sample was characterized by a broad band with a barycenter at $\sim 570 \text{ nm}$ upon excitation at $\lambda_{\text{ex}} = 460 \text{ nm}$ (curve 1) whereas a series of relatively narrow spectral bands with $\lambda_{\text{max}} = 694 \text{ nm}$ (curve 2) appeared on the long-wavelength tail of this band for the sample doped with both activators. The broad luminescence band practically disappeared and the relative intensities of the narrow bands redistributed considerably for $\lambda_{\text{ex}} = 400 \text{ nm}$ (curve 3).

Figure 3 shows the LES of the ceramic containing Ce and Cr at recording wavelengths λ_{rec} corresponding to the maxima of the strongest luminescence bands. It can be seen that the excitation spectrum of the broad luminescence band contained a strong band with $\lambda_{\text{max}} \approx 460 \text{ nm}$ and a weak band with $\lambda_{\text{max}} \approx 340 \text{ nm}$ (curve 1). Luminescence spectra of the narrow band could be divided arbitrarily into two groups characterized by the greatest similarity in the visible spectral region. The first group included spectra obtained with $\lambda_{\text{rec}} = 688$ and 707 nm ; the second, $\lambda_{\text{rec}} = 694, 725, \text{ and } 750 \text{ nm}$. Spectra of the second group differed considerably in the UV region.

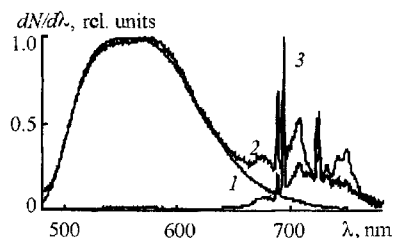


Fig. 2. Luminescence spectra of ceramics containing Ce (1) and Ce and Cr (2, 3) with $\lambda_{\text{exc}} = 400$ (3) and 460 nm (1, 2); $\Delta\lambda_{\text{exc}} = 4$ nm, $\Delta\lambda_{\text{rec}} = 0.6$ nm.

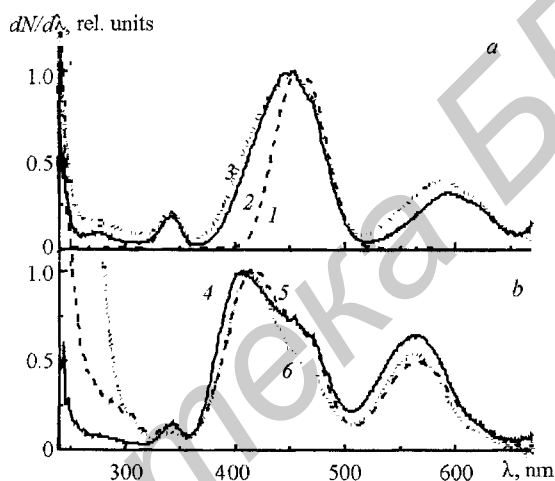


Fig. 3. Luminescence excitation spectra of ceramics containing Ce and Cr with $\lambda_{\text{rec}} = 600$ (1), 688 (2), 707 (3), 694 (4), 725 (5), and 750 nm (6); $\Delta\lambda_{\text{rec}} = \Delta\lambda_{\text{exc}} = 2$ nm.

Figure 4 shows the decay kinetics of the narrow-band luminescence of the ceramic containing Ce and Cr and its instantaneous LS. The kinetics were measured with a delay $t_{\text{del}} = 200$ ns from the time of excitation in order to avoid superimposing the Ce^{3+} luminescence with a moderate lifetime $\tau \approx 60$ ns [3]. It can be seen that the luminescence decay for $\lambda_{\text{rec}} = 694$ nm was close to exponential (Fig. 4a, curve 1) with $\tau \approx 3.4$ ms. The decay was clearly not exponential and the kinetic curve (curve 2) could be deconvoluted into two exponents for $\lambda_{\text{rec}} = 725$ nm. The initial curve had $\tau \approx 3$ ms; the latter one, $\tau \approx 36$ ms. It can also be seen that instantaneous spectra taken with $t_{\text{del}} = 1$ and 25 ms (Fig. 4b) differed radically.

The radical difference in the instantaneous LS of Cr^{3+} led to the conclusion that these ions were situated in two different subsystems in the synthesized ceramic. An analysis of the observed Stark splitting of the Cr^{3+} terms argued in favor of this conclusion. In fact, assuming that these ions replaced Al^{3+} in octahedral positions with a trigonal distortion of the local cubic symmetry, a Hamiltonian with approximate C_{3V} symmetry could be used to describe the experimental splittings:

$$H_{CF} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_3^4 (C_3^4 - C_{-3}^4), \quad (1)$$

where B_q^k are the crystal-field parameters; C_q^k , a spherical tensor acting on the angular variables of the d -electrons.

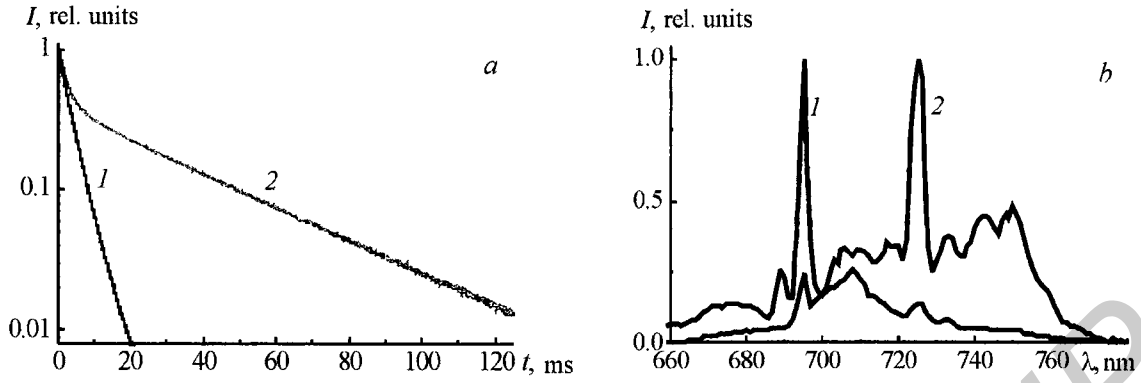


Fig. 4. Decay kinetics (a) and instantaneous luminescence spectra (b) of ceramics containing Ce and Cr with $\lambda_{\text{ex}} = 410$ nm; $\lambda_{\text{rec}} = 694$ (1) and 725 nm (2), $t_{\text{del}} = 200$ ns (1, 2) (a); $t_{\text{del}} = 1$ (1) and 25 ms (2) (b).

The crystal-field effect at cubic centers is usually described by the parameter $10Dq$ and trigonal distortion parameters v and v' . The crystal-field parameters can be expressed in terms of these parameters [6]:

$$B_0^2 = \frac{\sqrt{2}}{2} (\sqrt{2}v - 4v'), \quad (2)$$

$$B_0^4 = -\frac{\sqrt{2}}{30} (21\sqrt{2} \cdot 10Dq - 20\sqrt{2}v - 60v'), \quad (3)$$

$$B_3^4 = -\frac{\sqrt{70}}{30} (6 \cdot 10Dq + 2v + 3\sqrt{2}v'). \quad (4)$$

The energy of the 4T_2 level is equal to $10Dq$; its splitting in a trigonal field, $v/2$. The energy of the 4T_2 level depends on $10Dq$ and Racah parameter B ; its splitting is approximately equal to $v/2 + v'$. Furthermore, the energies of lower spin doublets depend strongly on v and v' .

Table 1 lists the experimental energies of the Stark components that were obtained by deconvoluting the spectra into Lorentzian curves. It also gives the calculated parameters in Eqs. (2)–(4) and the energies of the Stark components. An analysis of the tabulated results led to the following conclusions. The $10Dq$ values were close to those observed for Cr^{3+} in octahedral positions, which confirmed that the starting assumptions were correct. Racah parameters B differed greatly. Therefore, it could be supposed that Cr^{3+} characterized by the first and second groups of spectra were located in different matrix phases. The values of parameters v and v' indicated that the trigonal distortion of the local symmetry of the optical centers in these phases was different.

According to the literature, typical luminescence lifetimes of Cr^{3+} at room temperature in lightly doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ polycrystals and YAlO_3 single crystals are ~ 4 ms [7] and 31–35 ms [8]. Therefore, the first group of narrow luminescence bands with a maximum at 694 nm could be assigned to Cr^{3+} substituting for Y^{3+} in YAG, the group of bands with a maximum at 725 nm, in YAlO_3 . These assignments were confirmed by the satisfactory agreement of the LS and LES with the literature data for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Cr}^{3+}$ [4, 7] and $\text{YAlO}_3:\text{Cr}^{3+}$ [8]. The small difference in the emission rates for $\lambda_{\text{rec}} = 694$ nm that was indicated in the description of Fig. 4 and in the initial stage of this process for $\lambda_{\text{rec}} = 725$ nm suggested that this stage was due to luminescence of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Cr}^{3+}$ because of the superposition of its spectrum in the recording region (Fig. 4b). In such an instance, Cr^{3+} luminescence in YAlO_3 was quenched exponentially with $\tau \approx 36$ ms. The small deviation from exponential decay of metastable Cr^{3+} in $\text{Y}_3\text{Al}_5\text{O}_{12}$ and the exponential decay in YAlO_3 led to the conclusion that the Cr^{3+} luminescence had a rather high quantum yield. In fact, considering the low concentration of these ions and the small oscillator strengths of the interacting transitions, concentration luminescence quenching in each subsystem and also the occurrence of kinetic quenching leading to exponential luminescence quenching were improbable. The comparable luminescence intensities of

TABLE 1. Crystal Field Parameters and Spectroscopic Characteristics of Cr³⁺ Ions

Band	First group of spectra $A = 0, B = 625.0,$ $C = 3100.0, 10Dq = 16,500.0, v = -1100.0,$ $v' = -440.0$ $B_0^2 = 144.6, B_0^4 = -25,811.0, B_3^4 = -26,476.0$			Second group of spectra $A = 0, B = 535.0, C = 3350.0, 10Dq = 16,300.0,$ $v = 1000.0, v' = 600.0$ $B_0^2 = -697.0, B_0^4 = -19,790.0, B_3^4 = -28,543.0$		
	Symmetry	Theory, cm ⁻¹	Experiment, cm ⁻¹	Symmetry	Theory, cm ⁻¹	Experiment, cm ⁻¹
1	⁴ A ₂	0	0	⁴ A ₂	0	0
2	² E(² E)	14,199	14,124	² E(² E)	13,594	13,800
3	² E(² T ₁)	14,350	14,400	² A ₂ (² T ₁)	14,404	14,400
4	² A ₂ (² T ₁)	14,593	14,500	² E(² T ₁)	14,629	–
5	⁴ A ₁ (⁴ T ₂)	16,152	16,109	⁴ E(⁴ T ₂)	16,095	16,310
6	⁴ E(⁴ T ₂)	16,643	16,975	⁴ A ₁ (⁴ T ₂)	16,665	17,228
7	² E(² T ₂)	17,017	–	² E(² T ₂)	18,267	–
8	² A ₁ (² T ₂)	20,682	–	² A ₁ (² T ₂)	20,627	–
9	⁴ A ₂ (⁴ T ₁)	22,086	22,179	⁴ E(⁴ T ₁)	21,585	21,092
10	⁴ E(⁴ T ₁)	23,276	23,490	⁴ A ₂ (⁴ T ₁)	22,661	22,609
11	² A ₁ (² A ₁)	28,298	–	² A ₁ (² A ₁)	28,503	–
12	² E(² T ₂)	29,993	–	² E(² T ₂)	29,857	–

Cr³⁺ in Y₃Al₅O₁₂ and YAlO₃ (Fig. 2, curves 2 and 3) without distinct reflections of YAlO₃ in the diffraction patterns (Fig. 1c) could be explained by relatively efficient excitation transfer from Cr³⁺ in the first subsystem onto the same ions in the second because of the small energy gap (~320 cm⁻¹) between ²E metastable states in both subsystems (Table 1). Judging from the magnitude of the contribution from the Ce³⁺ luminescence excitation band at 460 nm to Cr³⁺ LES in Y₃Al₅O₁₂ (Fig. 3a), Cr³⁺ luminescence was efficiently sensitized by Ce³⁺. However, the insignificant intensity of this band in the Cr³⁺ LES with λ_{rec} = 750 nm (Fig. 3b, curve 6), where the overlap of the Cr³⁺ luminescence bands in YAlO₃ and Y₃Al₅O₁₂ was minimal (Fig. 4b, curves 1 and 2), led to the conclusion that excitation transfer from Ce³⁺ in Y₃Al₅O₁₂ to Cr³⁺ in YAlO₃ was much less efficient.

Conclusions. The synthesized ceramic included cubic Y₃Al₅O₁₂ of space group *Ia3d* and an insignificant impurity of orthorhombic YAlO₃. It was characterized by a noticeable sensitization of Cr³⁺ luminescence by Ce³⁺ in Y₃Al₅O₁₂ and rather efficient excitation transfer from Cr³⁺ in Y₃Al₅O₁₂ to the same ions in YAlO₃, which was characterized by no noticeable luminescence quenching, for low concentrations of Ce³⁺ and Cr³⁺ (≈5·10¹⁹ and ≤1·10¹⁹ cm⁻³). This allowed co-activation of the YAG ceramic by Ce³⁺ and Cr³⁺ to be considered one of the possible pathways for increasing substantially the fraction of red quanta in its luminescence spectrum upon excitation by radiation from crystalline InGaN LEDs.

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