

VUV Spectroscopy of Ce³⁺-Doped Na_{0.4}Lu_{0.6}F_{2.2} Single Crystals

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Abstract—The short-wave transmission spectrum of Na_{0.4}Lu_{0.6}F_{2.2} with the visible/ultraviolet transmission edge of 8 eV was studied. Absorption spectra of the 4*f*–5*d* transitions of the Ce³⁺ ion in the region of 4–8 eV were studied in Ce³⁺-doped Na_{0.4}Lu_{0.6}F_{2.2} single crystals. Luminescence spectra in the ultraviolet and visible spectral regions, luminescence decay kinetics and reflection and luminescence excitation spectra in the visible/ultraviolet and ultraviolet regions (4–20 eV) were investigated at helium and room temperatures.

Key words: 5*d*–4*f*-luminescence, trivalent cerium, fluoride crystals.

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INTRODUCTION

Na_{0.4}Lu_{0.6}F_{2.2} crystals are of interest as promising luminescence materials to be used as the active media of solid-state lasers [1]. In addition, the broadband fluoride matrices may be used as scintillators because doping with Ce³⁺ ions provides effective and fast luminescence.

EXPERIMENTAL METHODS

Experiments were carried out on samples obtained in the A.V. Shubnikov Institute of Crystallography of the Russian Academy of Sciences (Moscow). Single crystals of the pure Na_{0.4}Lu_{0.6}F_{2.2} matrix and Ce³⁺-doped Na_{0.4}Lu_{0.6}F_{2.2}: Ce³⁺ ($C_{\text{Ce}^{3+}} = 0.5, 2, 5, \text{ and } 20 \text{ mol.}\%$) were grown by the Bridgman method in a graphite oven in an active fluorine atmosphere. The crystals were a chaotic solid solution of cubic symmetry (*fm3m*) with a fluorite structure in which cations with different charges (Lu³⁺ and Ce³⁺) occupy the same positions in the points of the crystalline lattice. Initial reagents were highly pure NaF and LuF₃ powders preliminary annealed in vacuum (about 10^{–2} Pa) and fused in the fluorine atmosphere to purify them from the oxygen-containing admixtures. Multicellular graphite crucibles were used as containers for the synthesis. The following growth parameters were used: the thermal gradient in the growth zone was about 80 K/cm; the crucible pulling velocity was 3–10 mm/h; the cooling rate was 200 K/h. According to the method described in [2], optical-quality crystals with diameters of 6–12 mm and

lengths of 30–85 mm without the cellular substructure and light-dispersing admixtures were obtained. In the present paper Na_{0.4}Lu_{0.6}F_{2.2} crystals with the Ce concentration $C_{\text{Ce}^{3+}} = 0.05, 2, 5 \text{ and } 20 \text{ mol.}\%$ were studied. The density of Lu³⁺ ions in the Na_{0.4}Lu_{0.6}F_{2.2} crystal is $1.45 \times 10^{22} \text{ cm}^{-3}$. Transmission spectra were measured on samples with a plane-parallel polished surface 0.5–1 mm thick and a diameter of 10 mm. Luminescence, luminescence excitation, decay and reflection kinetics spectra were measured on the polished surface and the curvilinear cleavage surface. The crystallographic axes of the crystal were not oriented specifically with respect to the polarization vector of the synchrotron irradiation.

The reflection, luminescence excitation, luminescence and luminescence decay kinetics spectra of the Na_{0.4}Lu_{0.6}F_{2.2}: Ce³⁺ ($C_{\text{Ce}^{3+}} = 2, 5, \text{ and } 20 \text{ mol.}\%$) were measured on a SUPERLUMI setup (HASYLAB, Hamburg, Germany) [3]. The samples were irradiated with synchrotron irradiation pulses of a DORIS storage device in the range of 60–320 nm at 10 and 300 K. The spectral resolution of the primary monochromator is less than 0.4 nm. The luminescence spectra in the ultraviolet (UV) and visible ranges were recorded on a SpectraPro-308 monochromator-spectrograph (Action Research Corporation) with a Czerny–Turner optical scheme supplied with a CCD detector (Princeton Instruments, Inc.) cooled by liquid nitrogen. The spectral resolution of the recording monochromator with a grating of 300 grooves/mm is

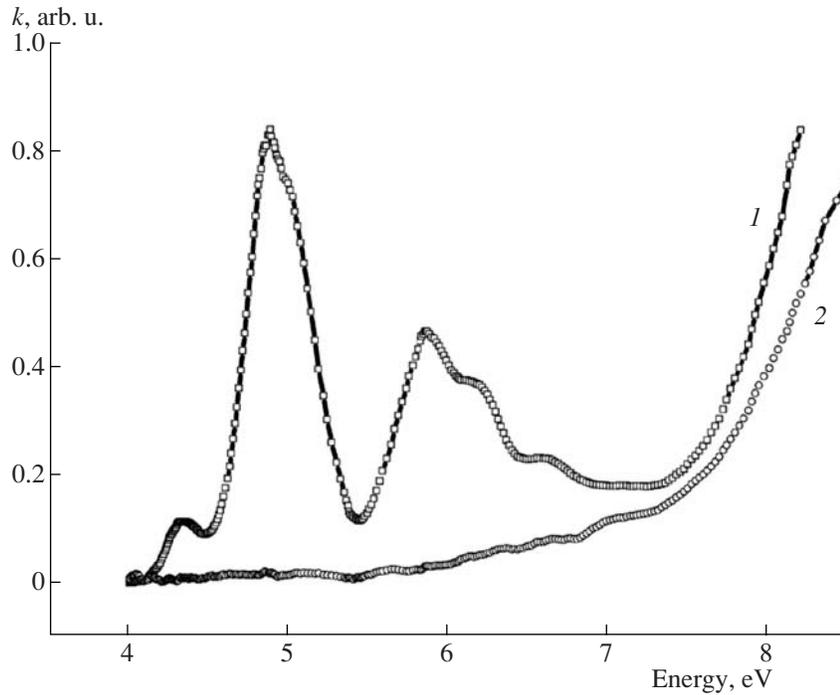


Fig. 1. Absorption spectra of $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}:\text{Ce}^{3+}$ concentration ($C_{\text{Ce}^{3+}} = 0.05$ mol.%) (curve 1) and $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$ matrix (curve 2) in the UV and VUV spectral regions.

about 1 nm. The luminescence spectra were not normalized to the spectral sensitivity of the registering system. The luminescence excitation and decay kinetics spectra were registered on a Hamamatsu R6358P photomultiplier.

The transmission spectra of $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$ and $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}:\text{Ce}^{3+}$ ($C_{\text{Ce}^{3+}} = 0.05, 2, 5,$ and 20 mol.%) single crystals in the range of 120–300 nm were measured on a vacuum VMR-2 monochromator (the inverse linear dispersion of 1.66 nm/mm) with the grating of 600 grooves/mm at room temperature. A homebuilt hydrogen lamp with a MgF_2 window was used as a radiation source. The study samples were plane-parallel

Positions of maxima of the $4f-5d$ absorption bands ν_{max} and the oscillator forces of the transitions for the rare-earth element (REE) Ce^{3+} in the $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$ (concentration ($C_{\text{Ce}^{3+}} = 0.05$ mol %)

REE	$\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$	
	$\nu_{\text{max}}, \text{cm}^{-1}$	$f \times 10^{-2}$
Ce^{3+}	35000	0.064
	39525	0.874
	47260	0.760
	50000	
	53190	

plates with polished surfaces 0.5–1 mm thick cut from the portion of $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$ single crystals that were central with respect to their length.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum of the $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}:\text{Ce}^{3+}$ ($C_{\text{Ce}^{3+}} = 0.05$ mol.%). All $5d$ -configurations of the Ce^{3+} ion are observed. If compared with the free Ce^{3+} ion [4], the position of the first maximum of the $5d$ -configuration in the $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$ matrix is lowered by 14700 cm^{-1} .

For the experimental $4f-5d$ bands the oscillator forces of the transitions were calculated according to

$$f = \frac{mc^2}{\pi e^2 \rho \bar{\lambda}^2} \frac{9n}{(n^2 + 2)^2} \int k(\lambda) d\lambda,$$

where m is the electron mass, e is the electron charge, c is the velocity of light in vacuum, n is the refraction index, $\bar{\lambda}$ is the mean line width of the transition and ρ is the Ce^{3+} concentration. Table presents the values of the oscillator forces. The integration was carried over the whole absorption band. Figure 2 shows the luminescence excitation and reflection spectra of the 330 nm line in $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}:\text{Ce}^{3+}$ ($C_{\text{Ce}^{3+}} = 2$ mol.%) at the helium temperature in the range of 4–18 eV from the plane-parallel polished sample surface.

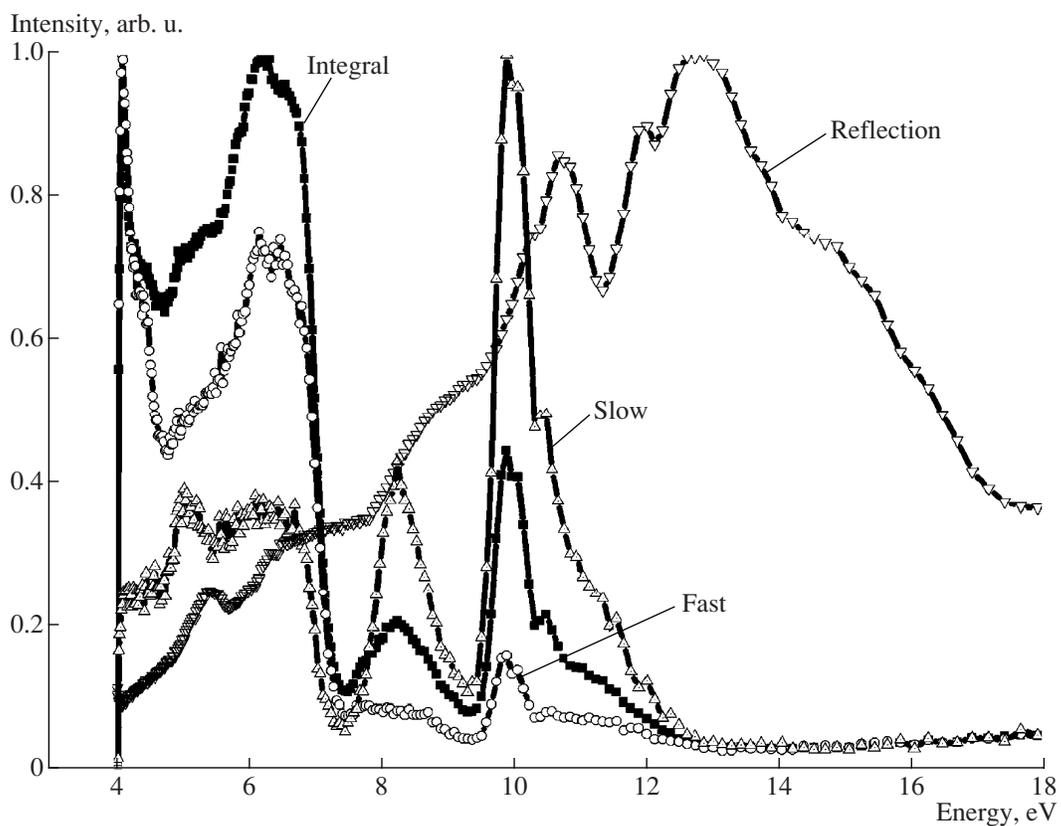


Fig. 2. Excitation and reflection spectra with time-resolved $4f-5d$ luminescence of the Ce^{3+} ion in $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2} : \text{Ce}^{3+}$ ($C_{\text{Ce}^{3+}} = 2$ mol.%) crystal at $T = 10$ K. Time gate width and delay with respect to the excitation pulse of the synchrotron radiation were 10 and 2 ns (to register “fast” component) and 40 and 130 ns (to register “slow” component), respectively.

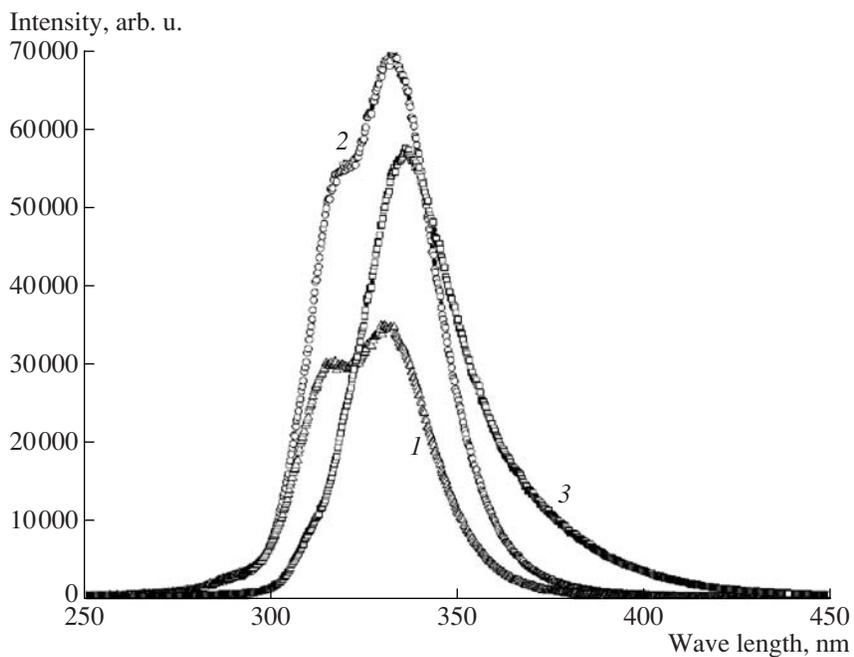


Fig. 3. Luminescence spectra of $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2} : \text{Ce}^{3+}$ ($C_{\text{Ce}^{3+}} = 2$ mol.%, curve 1; 5 mol.%, curve 2; 20 mol.%, curve 3). $h\nu_{\text{ex}} = 6.7$ eV; $T = 300$ K.

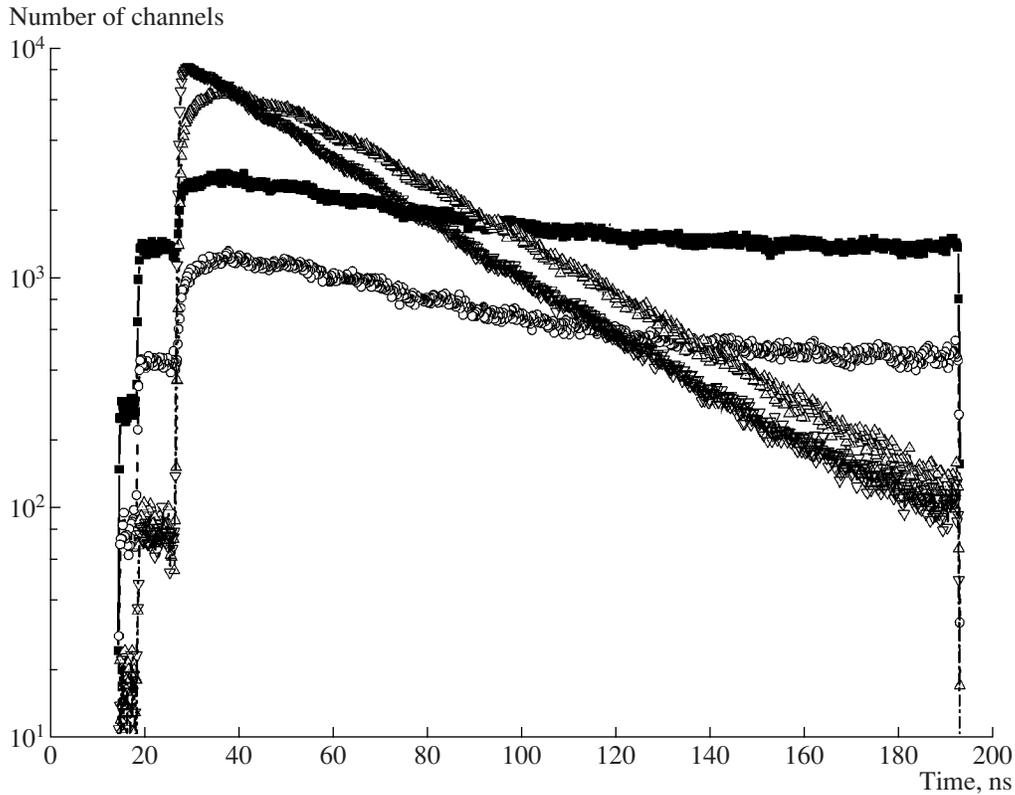


Fig. 4. $4f-5d$ luminescence decay spectra of Ce^{3+} in $Na_{0.4}Lu_{0.6}F_{2.2} : Ce^{3+}$ ($C_{Ce^{3+}} = 2$ mol.%), $\lambda_{em} = 335$ nm, $T = 10$ K. $h\nu_{ex} = \nabla$, 4.1 eV; \triangle , $h\nu_{ex} = 6.9$ eV; \circ , $h\nu_{ex} = 8.3$ eV; \blacksquare , $h\nu_{ex} = 6.9$ eV.

The increase of the reflection index in the range of 8 eV corresponds to the end of the crystal transparency zone and the beginning of the fundamental absorption zone. The first intense reflection peak is situated at 10.8 eV. It has a doublet structure with a weak peak at 10.3 eV with the corresponding gaps in the excitation spectra. This structure is present in all luminescence excitation and reflection spectra. The gap in the excitation spectra at 10.3 eV shifts to the low-energy part as the temperature is increased as manifested by the measurements at the room and helium temperatures for all samples. It may be supposed that the peak at 10.3 eV is the exciton peak. In [6] it was shown that the absorption of Lu^{3+} ions starts from energies exceeding 10.1 eV (81000 cm^{-1}) and not 8 eV (64000 cm^{-1}) as supposed in [7]. In our case no fine structure in the luminescence excitation spectra $4f-5d$ of Ce^{3+} in the $4f^{14} \rightarrow 4f^{13}5d$ absorption region of Lu^{3+} ions (10–11 eV) was resolved. The beginning of the absorption by a matrix may be due to the inter-configuration $4f^{14} \rightarrow 4f^{13}5d$ transitions of the Lu^{3+} ions and the creation of the $F^{-}2p$ exciton. Optical measurements demonstrated that the transparency boundary of the $Na_{0.4}Lu_{0.6}F_{2.2}$ crystal is 130 nm. In the reflection spectrum a sharp increase after the exciton peak allowing one to estimate the width of the forbidden E_g band of the $Na_{0.4}Lu_{0.6}F_{2.2} : Ce^{3+}$ compound as 10.5 eV (84700 cm^{-1}) is observed. The slow-

component peak in the excitation spectrum in the region of 8.3 eV may be manifested due to the presence of defects in the crystal, in particular, to the presence of oxygen.

The luminescence spectra of the crystals have the Gaussian form. The own luminescence of $Na_{0.4}Lu_{0.6}F_{2.2}$ is slow with the duration of more than 1 μs . At the helium temperature a broadband weak luminescence with maxima at about 3.7 and 4.1 eV is observed. As the temperature is increased to the room temperature, the luminescence yield is decreased by more than an order of magnitude.

Figure 3 shows luminescence of the studied series $Na_{0.4}Lu_{0.6}F_{2.2} : Ce^{3+}$ ($C_{Ce^{3+}} = 2, 5,$ and 20 mol.%) at 300 K. The plot demonstrates the broad luminescence bands of Ce^{3+} at 315 and 330 nm due to the transitions from the low-lying $5d$ levels in the Ce^{3+} ions to the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ levels of the ground configuration split by the spin-orbit interaction. The energy difference between 315 and 330 nm lines corresponds to the value of the spin-orbit splitting (of the order of 2000 cm^{-1}) of the ${}^2F_{5/2, 7/2}$ ground state of the Ce^{3+} ion. As the Ce^{3+} concentration is increased from 2 to 5%, the luminescence yield of the long-wave component increases and a redistribution in intensities between the doublet lines in favor of the

long-wave component takes place. As the Ce^{3+} concentration is increased from 5 to 20%, a general decay of the luminescence yield occurs, with the general shift of maxima to the long-wave spectral region. In $Na_{0.4}Lu_{0.6}F_{2.2} : Ce^{3+}$ ($C_{Ce^{3+}} = 20$ mol.%) the concentration decay is observed and the short-wave doublet component disappears practically completely.

As the temperature is lowered from 300 to 4.2 K, in the luminescence spectra the redistribution of the luminescence intensity between the doublet bands occurs with the domination of the long-wave component at 330 nm. At 10 K the luminescence of $Na_{0.4}Lu_{0.6}F_{2.2} : Ce^{3+}$ ($C_{Ce^{3+}} = 20$ mol.%) is higher than that for the Ce^{3+} concentration of 2 and 5 mol.%. The locations of the maxima of $4f-5d$ absorption bands ν_{max} and values of oscillator forces of transitions for Ce^{3+} are presented in a table.

Figure 4 shows the decay kinetics of the $4f-5d$ transitions of the Ce^{3+} ion. The kinetics are exponential and the decay time of the $4f-5f$ luminescence is about 25 ns. The kinetics behavior at $h\nu_{ex} = 4.1$ eV shows the direct excitation of the Ce^{3+} centers in the region up to 6 eV. At energies higher than 7 eV the excitation of the Ce^{3+} centers occurs via the matrix defects, which transfer the excitation to Ce^{3+} as shown by the kinetics behavior at $h\nu_{ex} = 6.9$ eV with build-up. The further increase in the excitation energy and the type of kinetics at energies $h\nu_{ex} = 8.3$ and $h\nu_{ex} = 9.9$ eV indicate that the energy transfer to Ce^{3+} through the crystalline matrix is extremely ineffective.

CONCLUSIONS

Spectral characteristics in the short-wave spectral region of $Na_{0.4}Lu_{0.6}F_{2.2}$ crystals with the cerium concentration ($C_{Ce^{3+}} = 0.05, 2, 5,$ and 20 mol.%) were studied. $Na_{0.4}Lu_{0.6}F_{2.2} : Ce^{3+}$ may be considered as a promising material to be used in the UV and VUV spectral region. These crystals may be used in manufacturing filters, windows, luminophores with rare-earth dopants, and active laser media in the short-wave spectral region.

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