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5*d*–4*f* Luminescence of Nd^{3+}, Gd^{3+}, Er^{3+}, Tm^{3+}, and Ho^{3+} Ions in Crystals of Alkaline Earth Fluorides

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Abstract—The vacuum ultraviolet emission spectra of alkaline-earth fluoride (CaF_2, SrF_2, BaF_2) crystals with rare earth impurity ions (Nd, Gd, Er, Tm, Ho) have been investigated. The main luminescence bands are described well by the transitions from the lowest excited 5*d* state to different 4*f* levels of rare earth ions.

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INTRODUCTION

The luminescence caused by the 5*d*–4*f* transitions of rare earth ions in ionic crystals has been intensively studied in the last decade [1–3]. For most ions, the luminescence was observed in the vacuum ultraviolet range (wavelengths below 200 nm); it can be used to develop lasers, scintillators, and phosphors with a quantum yield higher than unity. The $5d^14f^{n-1}$–$4f^n$ (for simplicity, 5*d*–4*f* below) luminescence of Ce^{3+} and Pr^{3+} ions lies in the ultraviolet region; it was investigated in detail for these ions incorporated in many matrices [4]. The luminescence of LaF_3 crystals containing Nd^{3+}, Tm^{3+}, and Er^{3+} ions in the vacuum ultraviolet region was found for the first time in [5]. Later the luminescence and excitation spectra of these ions in several fluoride matrices were investigated in detail in [6–8]. Along with the above-mentioned ions, the 5*d*–4*f* luminescence of Gd^{3+} and Lu^{3+} ions in crystals was also found [7], as well as the luminescence of Ho^{3+} and Tb^{3+} ions in $LiYF_4$ crystals [9, 10]. However, almost all measurements were performed on crystals with a relatively high content of rare earth ions (1% or more) [1, 2]. At the same time, the luminescence of aggregates of rare earth ions was observed in fluorine calcium crystals even at concentration of 0.1% and higher [11]. Therefore, to correctly study the spectra of single rare earth centers, it is necessary to use crystals with a relatively low impurity concentration [3]. In this paper, we report the results of studying the 5*d*–4*f* luminescence of single rare earth ions (Nd, Gd, Er, Tm, Ho) in CaF_2, SrF_2, and BaF_2 crystals.

EXPERIMENTAL

CaF_2, SrF_2, and BaF_2 crystals with a necessary concentration of MeF_3 impurity were grown by the Stockbarger method in graphite crucibles in vacuum. At the first stage, pure crystals were grown with the addition of some amount of CdF_2 to the raw material in order to remove oxygen. Then crystals with an impurity of rare earth fluorides (MeF_3) were grown from the crystalline raw material. The absence of oxygen in the final crystals was controlled by the absence of oxygen luminescence [12] under sample illumination by a DDS-30 UV deuterium discharge lamp.

The luminescence spectra were measured using a VM-4 vacuum monochromator with a detector based on a solar-blind FEU-142 photoelectron multiplier working in the counting mode. The luminescence in the crystals was excited by a KSR-2 xenon discharge lamp and a KRR-2 krypton lamp with the most intense lines at 146.96 and 123.58 nm, respectively. The typical spectral resolution was 0.4 nm.

The luminescence spectra were interpreted on the assumption that the radiative transition occurs from the lowest excited 5*d* state to the ground state and the first excited states of the 4*f* shell. The likely optical transitions for each case are shown in Figs. 1–4 (top). The strongest luminescence bands in the vacuum ultraviolet region were observed both at room and low temperatures. The xenon lamp line falls in the long-wavelength edge of exciton absorption in BaF_2; for this reason, some spectra exhibit the short-wavelength exciton luminescence edge (Figs. 1–3).

RESULTS

Nd^{3+} (f^3) *Luminescence*

The luminescence spectra of Nd^{3+} ions in the CaF_2 crystals contain three groups of bands, peaking at about 190, 240, and 270 nm (Fig. 1). In the spectra of the SrF_2 and BaF_2 crystals the bands are blueshifted. The mutual relative positions of the bands correspond to the values expected for the transitions from the 5*d* level to the ^4I, ^4F, and ^4G levels. In the BaF_2 crystals the 147-nm line excites also excitons, due to which the $5d$–$^4G_{5/2}$ band is eclipsed by the short-wavelength exciton luminescence edge (Fig. 1). Each group of the

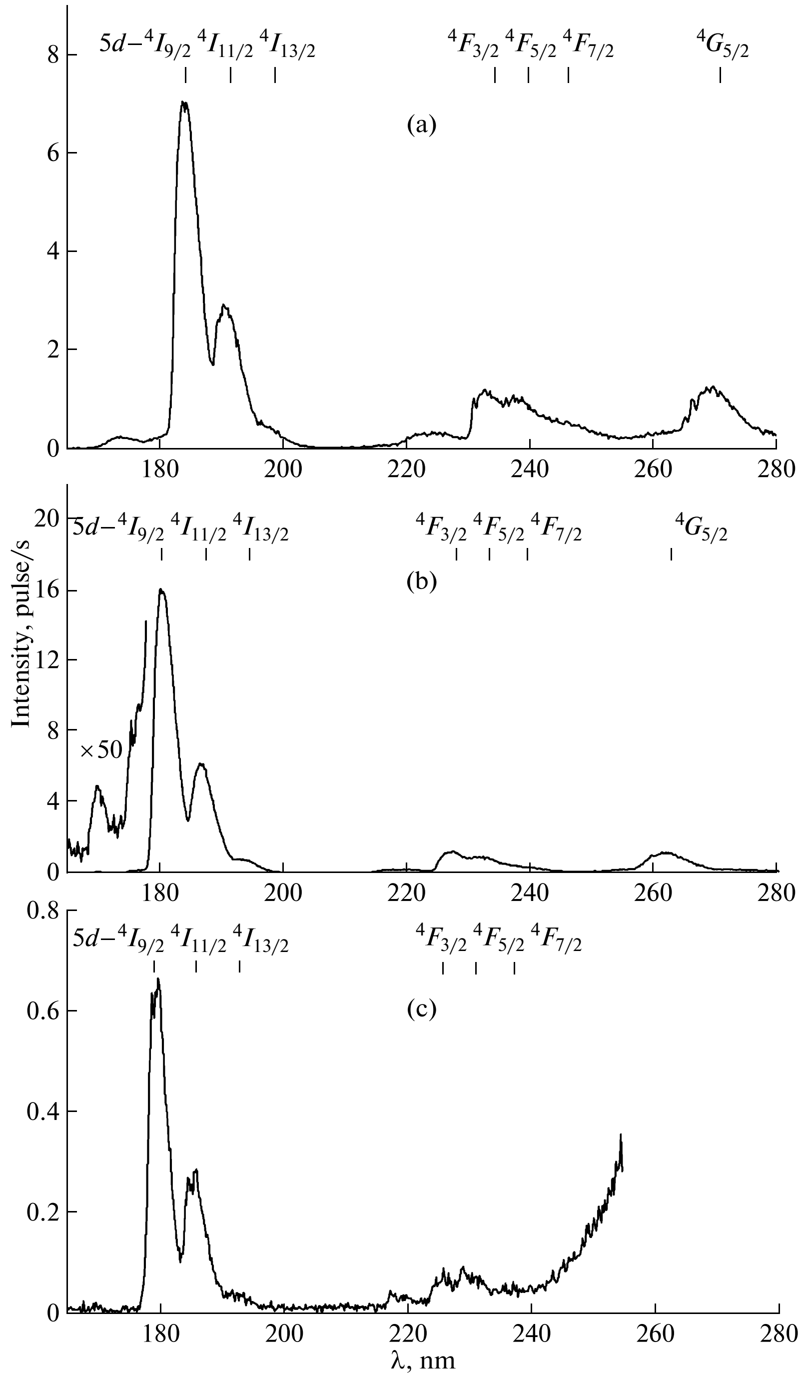

Fig. 1. Luminescence spectra of alkaline earth fluoride crystals with 0.01 mol % NdF_3 impurity, measured at a temperature of 78 K: (a) CaF_2, $\Delta E = 54\,300\ cm^{-1}$; (b) SrF_2, $\Delta E = 55\,500\ cm^{-1}$; and (c) BaF_2, $\Delta E = 55\,900\ cm^{-1}$; excitation wavelength is 147 nm.

luminescence bands in CaF_2–0.01%NdF_3 is accompanied by a short-wavelength satellite, which is much weaker and spaced from the main band by 2000–3000 cm^{-1}. In SrF_2 and, all the more, BaF_2 crystals, the short-wavelength satellites are even weaker (Fig. 1). These satellites can be due to both the structure of the excited 5*d* state and to another type of Nd^{3+} centers.

$Gd^{3+}(f^7)$ Luminescence

The 5*d*–4*f* luminescence of gadolinium ions in CaF_2 was revealed for the first time in [7]. A relatively weak luminescence band of Gd^{3+} ions, peaking at 129 nm, was observed by us at low temperatures in CaF_2 crystals with GdF_3 impurity concentrations from 0.01 to 1 mol % upon excitation by a krypton lamp.

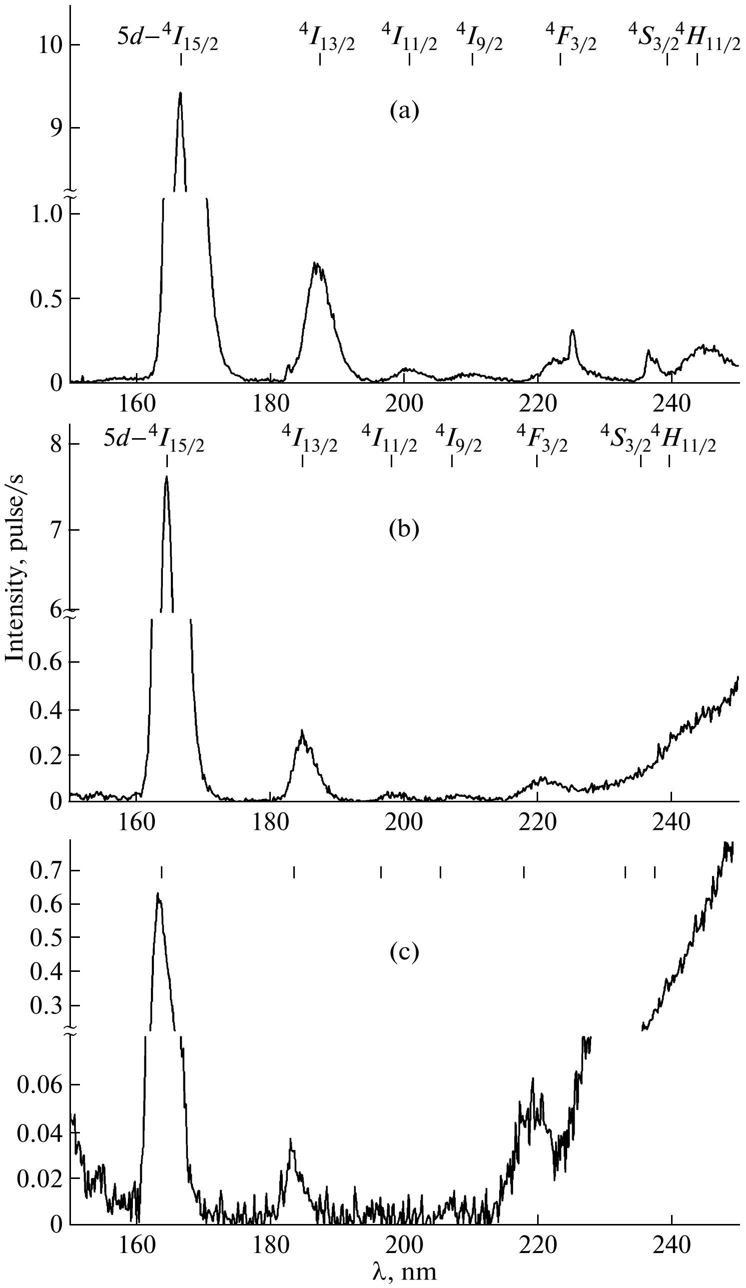

Fig. 2. Same as Fig. 1, but for crystals with 0.01 mol % ErF_3 impurity. Lower and upper parts of each plot are on different scales in order to visualize weak bands. ΔE = (a) 60000, (b) 60700, and (c) 61 100 cm^{-1}.

The luminescence band intensity monotonically increases with an increase in the GdF_3 concentration. The spectra of the SrF_2 and BaF_2 crystals did not contain this luminescence band. Obviously, the temperature quenching of the 5d–4f luminescence of Gd^{3+} ions in CaF_2 and the absence of luminescence in SrF_2 and BaF_2 crystals is explained by the proximity of the Gd^{3+} 5d level to the conduction band.

$Er^{3+}(f^{11})$ *Luminescence*

Along with the strongest band at 166.7 nm, the spectra of the CaF_2–0.01%ErF_3 crystals exhibit a series of weaker bands, which correspond well to the transitions from the 5d level to the excited 4f levels of erbium ions (Fig. 2). The relative intensity of these bands is lower in the spectra of SrF_2 and BaF_2. The narrow band at 225 nm and the doublet at 235 nm,

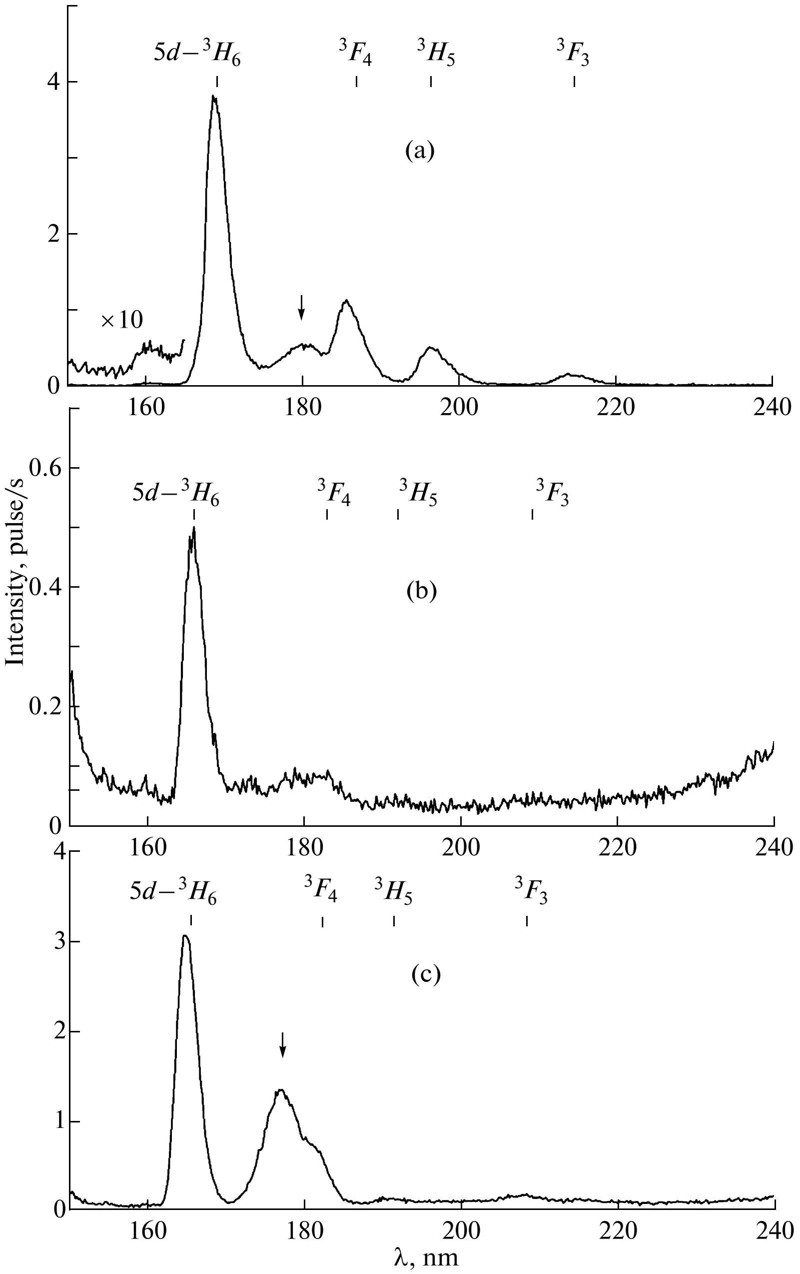

Fig. 3. Same as Fig. 1, but for the crystals with 0.01 mol % TmF_3 impurity. Arrows indicate bands due to aggregate centers (see text). ΔE = (a) 59 100, (b) 60 300, and (c) 60600 cm^{-1}.

which are present in the spectra of CaF_2 but absent in the spectra of SrF_2 and BaF_2, may be due to the transitions from the 4*f* shell (Fig. 2).

Tm^{3+} (f^{12}) *Luminescence*

The luminescence spectra of Tm^{3+} ions contain, along with the main $5d-{}^3H_6$ luminescence band, three more bands, which correspond well to the transitions from the 5*d* level to the ${}^3F_4$, ${}^3H_5$, and ${}^3F_3$ states (Fig. 3). Along with these bands, the spectra of all crystals contain a fairly strong band peaking at 178–180 nm (Fig. 3). The relative intensity of this band sharply increases with an increase in the thulium concentration, which indicates that this band is due to aggregate centers. Excitation of CaF_2–0.01% TmF_3 by a krypton lamp (123.6 nm) also yields pronounced luminescence bands at 146.4 and 159.5 nm, which are obviously due to the transitions from the higher excited states of the 5*d* shell to the ${}^3H_6$ ground state of the Tm^{3+} ion.

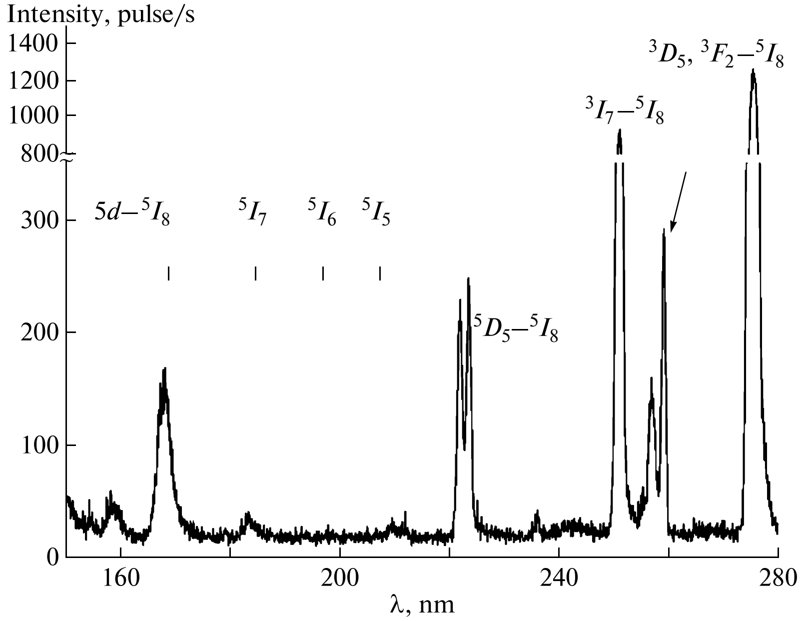

Fig. 4. Luminescence spectra of CaF_2 crystals with 0.01 mol % HoF_3 impurity, measured at 78 K; excitation wavelength is 147 nm. Arrow indicates second-order lamp line (129.6 nm).

$Ho^{3+}(f^{10})$ Luminescence

Weak luminescence in the vacuum ultraviolet region was revealed for the CaF_2–HoF_3 crystals (Fig. 4). The band at 168.1 nm is due to the $5d$–$^5I_8$ transition and the weak band at 183.8 nm corresponds to the $5d$-$^5I_7$ transition. The luminescence bands with wavelengths above 220 nm are obviously due to the $4f$–$4f$ transitions. The band near 224 nm is related to the $^1D_2$–$^5I_8$ transition [8].

DISCUSSION

The strongest luminescence bands of Nd, Er, and Tm ions in alkali-earth fluoride crystals are similar to the luminescence bands observed for $LiYF_4$ crystals [2]. The strong luminescence bands observed by us in the spectra of SrF_2–0.01 mol % ErF_3 or TmF_3 are similar to the bands recorded previously for SrF_2–1% MeF_3 crystals [6]. These bands are characterized by relatively slow luminescence decay times and are due to the transitions from the high-spin $5d^14f^{n-1}$ state to the low-spin ground state [2, 6]. For the heavy lanthanide ions with the number of electrons in the f shell above 7, each electronic configuration may exist in two states, the total spin of which differs by unity. These states are denoted as high and low spin. The ground state is low spin, while the lowest excited state is high spin. As a result of the exchange interaction the electrons in the high-spin state are more spatially spaced and undergo a weaker repulsion. Due to this, the high-spin state is a low-order excited state. The energy gap between the high- and low-spin states in $LiYF_4$ was determined from the excitation spectra to be 3460 cm^{-1} for Ho^{3+}, 3330 cm^{-1} for Er^{3+}, and 2070 cm^{-1} for Tm^{3+} [13]. The luminescence spectra of Er^{3+} and Tm^{3+} ions in some crystals ($LiYF_4$, YF_3) also contained relatively strong short-wavelength bands characterized by fast (nanosecond) decay, which were assigned to the transitions from the low-spin excited $5d^14f^{n-1}$ state [2]. Apparently, the 159-nm luminescence band of CaF_2–HoF_3 crystals (Fig. 4), which is spaced from the strongest 168.4-nm band by 3700 cm^{-1}, is due to the transitions from the low-spin state. Note that in the Tm–Er–Ho series the Ho^{3+} ion is characterized by the largest gap between the low- and high-spin excited states; therefore, one would expect the lowest probability of nonradiative transition between these states. The probability of nonradiative multiphonon transitions decreases exponentially with an increase in the energy gap between the states. In alkaline earth fluoride crystals the radiative transitions of Er and Tm ions from the low-spin state have a rather low intensity (see also [6]); the transition intensity decreases in the series from CaF_2 to BaF_2 (Figs. 2, 3).

The luminescence spectra of Nd^{3+} ions in alkali-earth fluoride crystals contain short-wavelength satellites of $5d$–$4f$ luminescence bands (Fig. 1). Satellites are observed for all groups of the $5d$–^4I, ^4F, ^4G transitions (Fig. 1). Since the Nd^{3+} ion is assigned to light lanthanides, its ground state, in contrast to heavy lanthanides, must be classified as high-spin. The short-wavelength satellites may be due to the transitions from the excited low-spin state to the ground high-spin state. Unlike the case of heavy lanthanides, the optical transitions for the short-wavelength luminescence bands must be spin-forbidden.

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