Vacuum-ultraviolet interconfigurational $4f^3 \rightarrow 4f^25d$ absorption and emission studies of the Nd^{3+} ion in KYF, YF, and YLF crystal hosts

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The laser-induced vacuum-ultraviolet fluorescence spectra of $KY_3F_{10}:Nd^{3+}$ (KYF:Nd) and $YF_3:Nd^{3+}$ (YF:Nd) single crystals pumped by a pulsed-discharge molecular F_2 laser at 157 nm were obtained. A number of new fluorescence peaks were observed and were assigned to the $4f^25d \rightarrow 4f^3$ dipole-allowed transitions of the Nd^{3+} ion. The absorption spectra of $LiYF_4:Nd^{3+}$ (YLF:Nd), KYF:Nd, and YF:Nd crystal samples in the vacuum-ultraviolet spectral regions were also obtained. Finally, the splitting of the states of the $4f^25d$ configuration of the Nd^{3+} ion, which is due to the crystal field, was observed in all the crystal samples.

1. INTRODUCTION

The broadband emission features of the $4f^N \rightarrow 4f^{N-1}5d$ transitions of the rare-earth trivalent ions in dielectric crystal hosts suggest that these materials could be used as active media for tunable solid-state lasers.[1] This idea is attractive because of the relative simplicity of this method for generating coherent vacuum-ultraviolet (VUV) and UV radiation in comparison with the existing nonlinear methods. The first laser action in the VUV region from a solid-state dielectric crystal ($LaF_3:Nd^{3+}$) was reported by Waynant[2] and by Waynant and Klein.[3] Laser action from the same solid-state active medium at 172 nm has since been obtained as well, after pumping of the $LaF_3:Nd^{3+}$ crystal with a pulsed-discharge molecular F_2 laser operating at 157 nm.[4,5]

In this paper we report on the VUV absorption and emission spectra of the Nd^{3+} ion in KYF, YF, and YLF dielectric crystal hosts. The absorption spectra were obtained by means of a hydrogen lamp at room temperature. The absorption features of the crystal samples in the VUV region are due to the transitions from the $^4I_{9/2}$ ground state of the Nd^{3+} ion of the $4f^3$ configuration to the states of the $4f^25d$ configuration. The electric crystal field is responsible for the Stark effect and splits all the levels of the ground and the excited configurations. The number and the spacing of the components depend on the symmetry and the intensity of the crystal field. We found that the $4f^25d$ levels of the Nd^{3+} ion split into four, five, and five components in KYF, YF, and YLF hosts, respectively, as manifested by the observed peaks in their corresponding absorption spectra. The edge of the $4f^25d$ band of the Nd^{3+} ion in KYF, YF, and YLF crystals was found to be at 61 061 cm^{-1} (163.7 nm), 59 554 cm^{-1} (167.9 nm), and 55 640 cm^{-1} (179.7 nm), respectively. Furthermore, we report on the $4f^25d \rightarrow 4f^3$ VUV fluorescence features of the KYF:Nd and the YF:Nd crystals as they are deexcited, after their excitation with a pulsed-discharge molecular F_2 laser operating at 157 nm.

2. EXPERIMENTAL

The KYF:Nd, the YF:Nd, and the YLF:Nd monocrystal samples that were used for this study were grown from carbon crucibles by the Bridgman–Stockbarger method. The concentration of Nd^{3+} ions for these crystal samples was 0.1%, 1%, and 1%, respectively. The samples were optically polished disks having a diameter of 5 mm and a thickness of 1.4, 0.4, and 0.6 mm, respectively. The experimental setup is presented in Fig. 1. It consists mainly of a pulsed-discharge molecular F_2 laser, a hydrogen lamp, and an extreme UV–VUV monochromator (Acton VM502) with the related electronics for detecting and recording the absorption spectra. The laser pumping source was a homemade molecular F_2 laser that was been described previously.[4] It delivers 12 mJ/pulse and only 1 mJ/pulse after focusing was used to excite the crystal samples. The spectra were detected with a resolution of better than 0.5 nm. The optical paths were within a stainless-steel vacuum chamber of 10^{-5} mbar background pressure, achieved with turbomolecular pumps.

3. RESULTS AND DISCUSSION

A. KYF:Nd

The intense structure in the absorption spectrum shown in Fig. 2, which extends in the spectral range from 61 061 cm^{-1} (163.7 nm) to 86 652 cm^{-1} (115.4 nm), can be attributed to the Nd^{3+}-ion manifold of the $4f^25d$ configuration situated in this energy region.[6]

From this spectrum it seems that the crystal field splits the $4f^25d$ configuration into four components, with the

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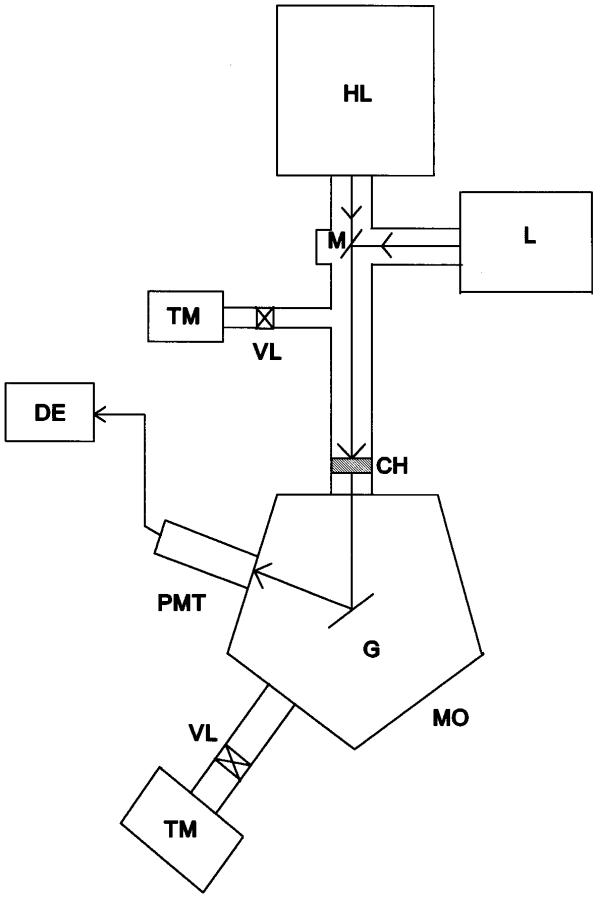

Fig. 1. Experimental setup for obtaining the absorption and the laser-induced fluorescence spectra of KYF:Nd, YF:Nd, and YLF:Nd crystals: HL, hydrogen lamp; L, pulse-discharged molecular F_2 laser; M, mirror; VL, stainless-steel vacuum lines; CH, crystal holder; G, grating; MO, VUV monochromator; TM, turbomolecular pump; PMT, solar-blind or scanning electron microscope photomultiplier; DE, detection electronics.

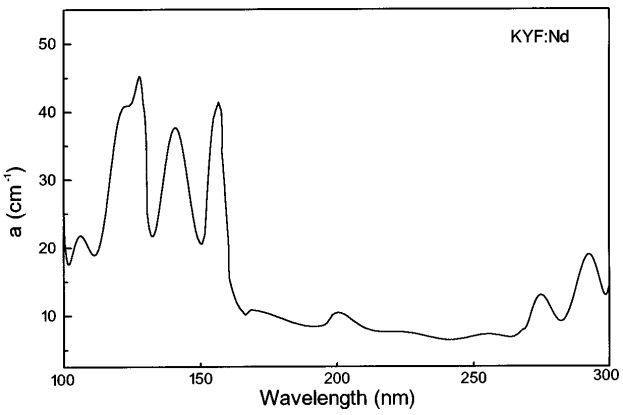

Fig. 2. Absorption spectrum of the KYF:Nd crystal in the spectral region from 100 to 300 nm.

maximum of their absorption at 63 773 cm^{-1} (156.8 nm), 70 515 cm^{-1} (141.8 nm), 77 512 cm^{-1} (129 nm), and 81 758 cm^{-1} (122.3 nm), correspondingly. The far edge of the levels of the $4f^25d$ configuration extends down to 61 061 cm^{-1} (163.7 nm).

The fluorescence spectrum of the Nd^{3+} ion in KYF dielectric crystal hosts depends strongly on the excitation wavelength. As can be seen from the fluorescence spectrum shown in Fig. 3, a broad emission band appears in the spectral region between 60 239 cm^{-1} (166 nm) and 56 495 cm^{-1} (177 nm). The peaks near 62 498 cm^{-1} (160 nm), 59 169 cm^{-1} (169 nm), 58 137 cm^{-1} (172 nm), and 57 469 cm^{-1} (174 nm) were assigned to the dipole-allowed transitions between the $4f^25d$-configuration levels of the Nd^{3+} ion, which occupy the spectral region from 63 773 to 61 061 cm^{-1}, and the $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$ levels of the $4f^3$ configuration (see Fig. 4) as follows:

$$4f^25d \rightarrow {}^4I_{9/2}\ (160\ \text{nm}),$$
$$4f^25d \rightarrow {}^4I_{11/2}\ (169\ \text{nm}),$$
$$4f^25d \rightarrow {}^4I_{13/2}\ (172\ \text{nm}),$$
$$4f^25d \rightarrow {}^4I_{15/2}\ (174\ \text{nm}).$$

As we can see from Fig. 3, a peak near 65 059 cm^{-1} (153.7 nm) appears in the excitation spectrum. The presence of this peak can be explained if we consider

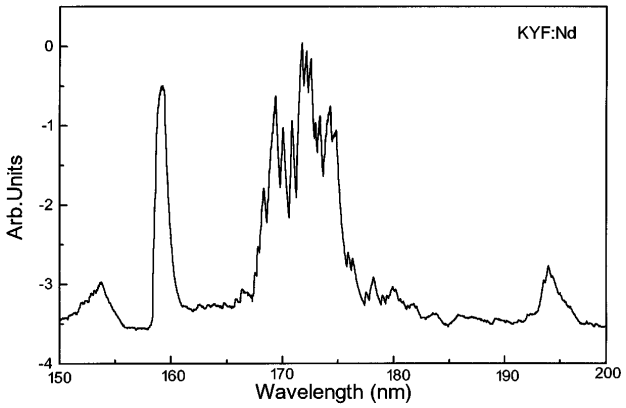

Fig. 3. Laser-induced fluorescence spectrum of the KYF:Nd crystal sample under F_2 laser pumping in the spectral region from 150 to 200 nm.

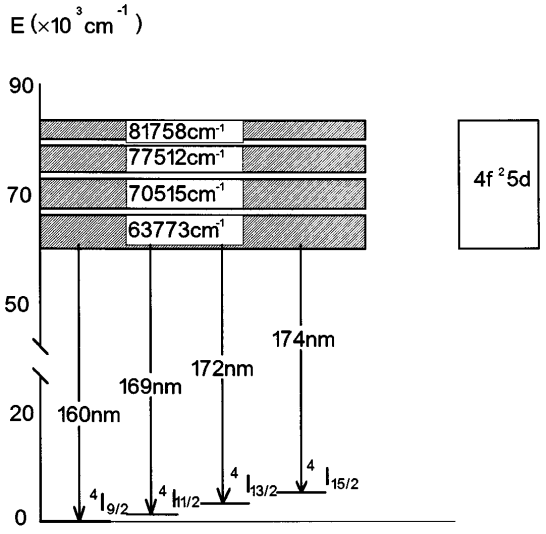

Fig. 4. Simplified energy diagram of KYF:Nd; the absorption bands of the $4f^25d$ configuration and the various transitions are shown. The numbers inside the bands indicate the position at which the maximum of the absorption takes place. E is the energy of the levels of the Nd^{3+} ion from the $^4I_{9/2}$ ground state.

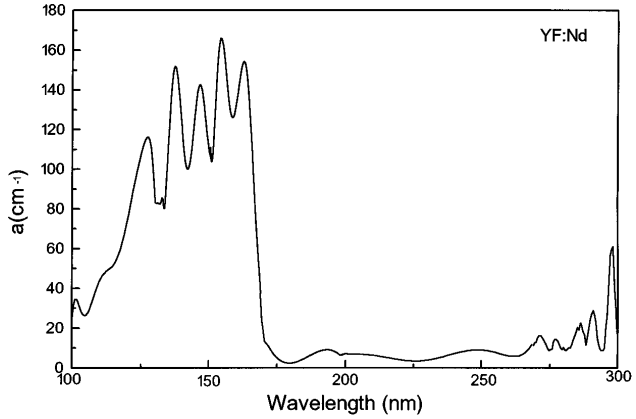

Fig. 5. Absorption spectrum of the YF:Nd crystal in the spectral region from 100 to 300 nm; a is the absorption coefficient of the crystal.

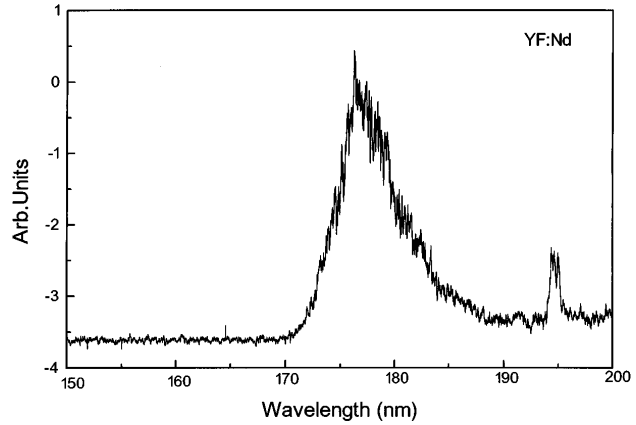

Fig. 6. Laser-induced fluorescence spectrum of the YF:Nd crystal sample under F_2 laser pumping in the spectral region from 150 to 200 nm.

that the excitation mechanism involves a two-photon absorption process. One photon is absorbed from the $^4I_{9/2}$ ground state of the Nd^{3+} ion to the $4f^25d$ manifold of the state:

$$4f^3(^4I_{9/2}) + h\nu(157\text{ nm}) \rightarrow 4f^25d\ (63\,769\text{ cm}^{-1})$$

[where $h\nu$(157 nm) indicates the absorption of one photon at 157 nm], and from there with the absorption of an additional photon the system occupies the highly excited states of the Nd^{3+} ion.

From there, through internal relaxation and emission of a photon at 153.7 nm, the system relaxes again to the levels of the $4f^3$ configuration.

B. YF:Nd

The absorption spectra of the YF:Nd crystal in the spectral range from 99 996 cm^{-1} (100 nm) to 33 332 cm^{-1} (300 nm) is shown in Fig. 5. We attribute the spectrum in the range from 59 557 cm^{-1} (167.9 nm) to 85 052 cm^{-1} (117.5 nm) to the absorption of light from the ground state of the Nd^{3+} ion to the levels of $4f^25d$ configuration (Fig. 5). It seems that the crystal field splits this band into five components, with the maximum of absorption being at 61 802 cm^{-1} (161.8 nm), 64 722 cm^{-1} (154.5 nm), 68 210 cm^{-1} (146.6 nm), 72 671 cm^{-1} (137.6 nm), and 78 428 cm^{-1} (127.5 nm). The edge of the band was found to be near 59 557 cm^{-1} (167.9 nm).

The fluorescence spectrum of the YF:Nd crystal, as in the case of the other dielectric hosts, depends strongly on the excitation wavelength.[7] On excitation of the crystal sample with the pulsed F_2 laser at 157 nm, the emission spectrum reveals the presence of a main broadband with a maximum at 56 687 cm^{-1} (see Fig. 6). We assigned this broad emission band to the transitions from the levels of the $4f^25d$ configuration to the $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$ levels of the $4f^3$ configuration (see Fig. 7).

C. YLF:Nd

The absorption spectrum of YLF:Nd crystals was studied previously by Devyatkova *et al.*[7] Because of the S_4 symmetry of this crystal, the $4f^25d$ band is expected to split into five Stark components; however, from the absorption spectrum shown in Fig. 8 we can see that seven peaks appear, with the maximum of absorption at 57 239 cm^{-1}

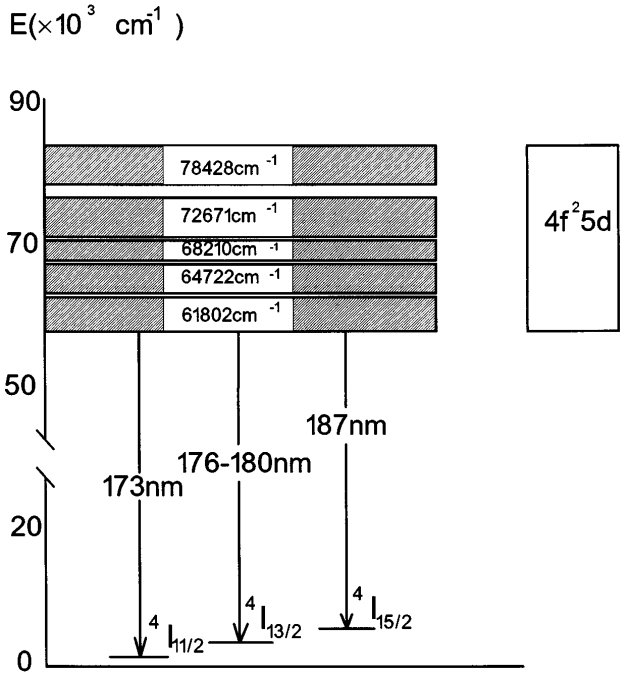

Fig. 7. Simplified energy diagram of YF:Nd; the absorption bands of the $4f^25d$ configuration and the various transitions are shown. The numbers inside the bands indicate the position at which the maximum of the absorption takes place.

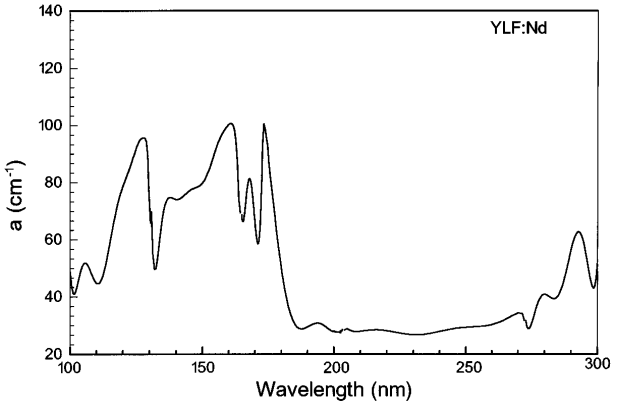

Fig. 8. Absorption spectrum of the YLF:Nd crystal in the spectral region from 100 to 300 nm.

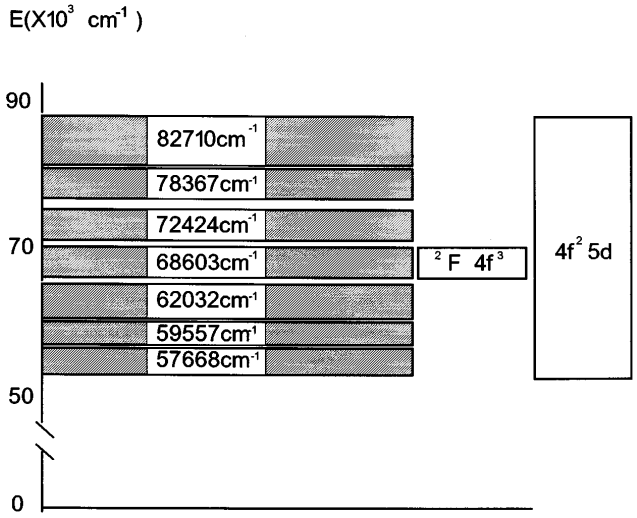

Fig. 9. Simplified energy diagram of YLF:Nd; the absorption between the $^4I_{9/2}$ ground state of the Nd^{3+} ion and the bands of the $4f^2 5d$ configuration is shown. The numbers inside the bands indicate the position at which the maximum of the absorption takes place.

(174.7 nm), 59 577 cm^{-1} (167.9 nm), 62 032 cm^{-1} (161.2 nm), 68 603 cm^{-1} (145.8 nm), 72 424.5 cm^{-1} (138.1 nm), 78 367 cm^{-1} (127.6 nm), and 82 710 cm^{-1} (120.9 nm). The position of six of these components is in agreement with the position found by Devyatkova *et al.*[7] within 100–400 cm^{-1}. The edge of the $4f^2 5d$ band was found to be at 53 845 cm^{-1} (185.7 nm), and this result is in agreement with previous measurements performed with different crystal samples.[8,9]

The additional absorption peak near 68 603 cm^{-1} (145.8 nm; Fig. 8) is probably due to the absorption from the high-lying energy levels of the Nd^{3+} ion of the $4f^3$ configuration, and this argument is reinforced by the fact that the $4f^3(^2F)$ band of the Nd^{3+} free ion is situated near 68 000 cm^{-1} (Ref. 6; see Fig. 9).

4. CONCLUSIONS

The laser-induced fluorescence spectra in the VUV region of KYF:Nd and YF:Nd single crystals pumped by a pulsed-discharge molecular F_2 laser at 157 nm were obtained. The absorption spectrum of the same crystal samples and of YLF:Nd were obtained in the VUV spectral region. The electric crystal field is responsible for the Stark effect and splits all the levels of single and mixed configurations. The number and the spacing of the components depend on the symmetry and on the intensity of the crystal field.

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