

Vacuum ultraviolet and ultraviolet fluorescence and absorption studies of Er³⁺-doped LiLuF₄ single crystals

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The laser induced fluorescence spectrum of LiLuF₄:Er³⁺ single crystals, pumped by an F₂ pulsed discharge molecular laser at 157 nm, was obtained in the vacuum ultraviolet (VUV) and ultraviolet (UV) regions of the spectrum at room temperature. A number of new fluorescence peaks were observed for the first time. They were assigned to the dielectric dipole allowed transitions $4f^{10}5d \rightarrow 4f^{11}$ of the Er³⁺ ion. In addition, the absorption spectrum of the same crystal samples was recorded. The positions of the bands within the $4f^{10}5d$ configuration were located at 65 098, 69 198, 71 422, 74 343, and 76 916 cm⁻¹. The edge of the $4f^{10}5d$ bands was at 63 046 cm⁻¹.

The broad band emission features of the *d-f* interconfigurational transitions of the trivalent rare-earth (RE) activated ions in dielectric crystals offers the possibility for these materials to be used for generating coherent radiation in the vacuum ultraviolet (VUV) and ultraviolet (UV) regions of the spectrum.^{1,2} The most widely used ion for generating UV laser radiation is the Ce³⁺ ion, activated in various dielectric host materials. LiYF₄ was the first host material for Ce³⁺ in a solid state laser.³ Laser action was also obtained from other dielectric host materials such as LaF₃,⁴ LiLuF₄,⁵ and LiCaAlF₆.⁶ Waynant and Klein constructed the first solid state VUV laser, which operated at 172 nm.^{7,8} In this VUV laser, emission in a LaF₃:Nd³⁺ is stimulated by Kr₂* pump source. The realization of a new pumping scheme, using the pulsed discharge F₂ molecular laser at 157 nm,^{9,10} opens the way for the wide use of RE activated ions in dielectric crystals for generating coherent VUV radiation. Hence, the spectroscopic studies of the RE activated ions in wide-band-gap dielectric crystals is driven by the motivation for the development of new solid state tunable VUV and UV laser sources.

In this letter, we report on the interconfigurational $4f^{N-1}5d \rightarrow 4f^N$ VUV and UV fluorescence and absorption features of the Er³⁺ ion in the LiLuF₄ (LiLuF) dielectric host. The crystal samples were excited with the use of a pulsed discharge F₂ molecular laser at 157 nm. Interconfigurational electric dipole transitions ($4f^{10}5d \rightarrow 4f^{11}$) of the Er³⁺ ions were observed. To the best of our knowledge, this is the first time that these transitions are observed using this pumping arrangement. The absorption spectra of the LiLuF:Er crystals were studied as well in the same spectral region. The edge of the $4f^{10}5d$ configuration of the Er³⁺ ion was found to be at 63 046 cm⁻¹ relative to the ground state level of the trivalent ⁴I_{15/2} ion with the $4f^{11}$ configuration.

The LiLuF:Er crystals were grown from carbon cru-

cibles, using the Bridgman–Stockbarger method. The concentration of the ions in the samples was 1 at. %. The samples were optically polished disks, having a diameter of 5 mm and their thickness was varied between 0.5–2.0 mm. The experimental apparatus for obtaining the excitation spectrum is the same as in Ref. 11. It consists of the laser pumping source, the vacuum chamber where the samples were placed, the focusing optics, and the detection electronics.

The laser pumping source was a lab-built F₂ molecular laser.¹² It delivers 12 mJ per pulse with a pulse width of 12 ns at full width at half-maximum (FWHM). We have used only 1 mJ per pulse to irradiate the crystal samples. The detection system consisted of a 0.2 m VUV monochromator (Acton VM502), a solar blind photomultiplier (EMI 9412), or a secondary electron multiplier (SEM), and a box-car integrator interfaced to a computer. The fluorescence spectrum was detected with a resolution better than 0.5 nm. The optical paths of the pumping laser beam and the fluorescence light signal were kept within stainless steel vacuum lines at 10⁻⁵ mbar.

According to the calculations of Sugar and Reader,¹³ the onset of the $4f^{10}5d$ absorption band of the free ion is at 75 400 cm⁻¹ and that of the 6s band at 103 600 cm⁻¹.

The absorption spectrum of the rare-earth trivalent Er³⁺ ion has been studied previously in a number of crystal lattices.^{1,14–16} The edge of the $4f^{10}5d$ band of the Er³⁺ ion in KY₃F₁₀ host was found by Devyatkova *et al.*¹⁴ to be at 60 850 cm⁻¹. Five absorption bands of the $4f^{10}5d$ configuration have been observed in BaY₂F₈ hosts with the maximum of the absorption at 63 700, 67 900, 70 500, 73 400, and 74 600 cm⁻¹.¹⁵ The edge of the $4f^{10}5d$ band in this host material was at 61 900 cm⁻¹. With the LaF₃ crystal host, the $4f^{10}5d$ band was extended down to 58 000 cm⁻¹.¹⁶

The laser induced fluorescence spectrum of the LiLuF:Er crystal, after F₂ laser pumping in the spectral range from 150 to 300 nm is shown in Fig. 1. The fluorescence bands were assigned to transitions between the edge of the energy levels

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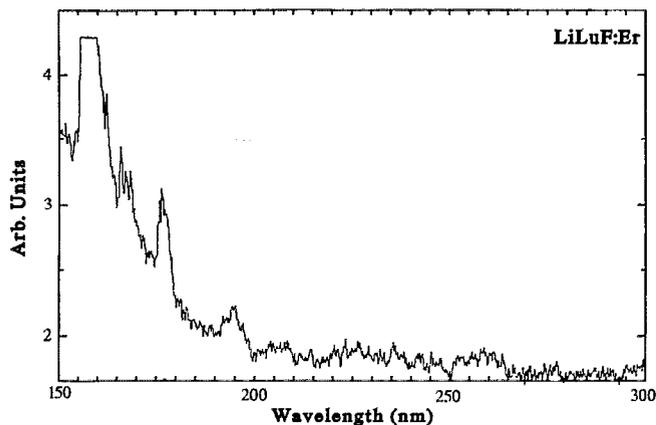


FIG. 1. Room-temperature laser induced fluorescence spectrum of LiLuF:Er crystal under the F_2 laser pumping in the spectral region 150–300 nm.

of the $4f^{10}5d$ configuration and the energy levels of $4f^{11}$ configuration of the Er^{3+} ion.

The absorption spectrum of Fig. 2 was taken using optically polished samples. Regarding the $4f^{11}$ states of the Er^{3+} ion, the crystal field splitting is of the order of few hundred cm^{-1} (Ref. 17). Because the $4f$ electrons do not interact strongly with the crystal lattice the spectral lines from the transitions within the $4f^{11}$ configuration are narrow. Concerning the $4f^{10}5d$ states of the Er^{3+} ion the crystal field splitting is of the order of few thousands cm^{-1} (Ref. 1) at room temperature. This is why the crystal field of the host lattice interacts strongly with the $5d$ electron due to the large radius of the corresponding orbital. The crystal field perturbation is much stronger than the spin-orbit interaction or the interconfigurational mixing and the strong crystal field interaction is responsible for the broad band character of the components of the $5d$ level. Similar splitting has been observed in other dielectric crystals doped with rare-earth ions such as LaF:Pr,² YLF:Nd,¹⁸ YLF:Ce,³ etc.

The presence of five distinct bands indicates the location of five components of the $4f^{10}5d$ configuration at 65 098, 69 198, 71 422, 74 343, and 76 916 cm^{-1} (maximum of ab-

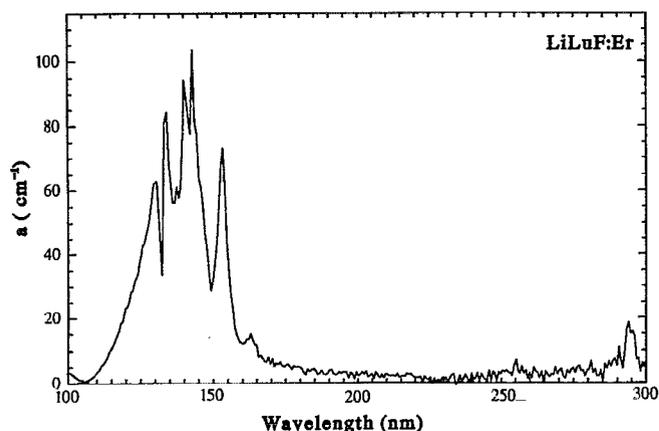


FIG. 2. Room-temperature absorption spectrum of the LiLuF:Er crystal in the spectral region 100–300 nm. The crystal sample was 0.05 cm thick and the concentration of Er^{3+} ions was 1 at. %.

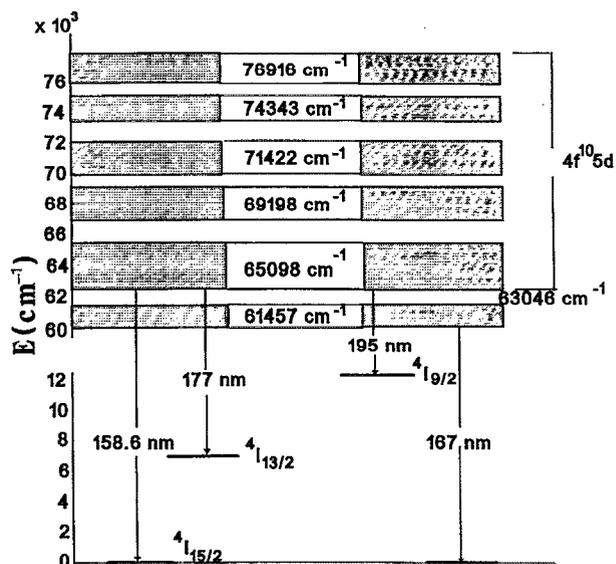


FIG. 3. Simplified energy diagram of the Er^{3+} ion, where the various transitions of the laser induced fluorescence spectra are shown.

sorption) from the ground state, $4I_{15/2}$, of the Er^{3+} ion. The edge of these bands was found to be around 63 046 cm^{-1} . The measured absorption coefficient, for all the crystal samples, is the contribution from both the volume and the surface reflection.

Regarding the excitation of the crystal samples using the F_2 laser at 157 nm (63 690 cm^{-1}), we expect to observe the transitions from the $4f^{10}5d$ band situated at 65 098 cm^{-1} to the lower energy levels of $4f^{11}$ single configuration, Fig. 3.

Hence, the emission bands, with maxima at 158.6, 177, and 195 nm, Fig. 1, are assigned to the transitions from the edge of the lower energy level of $4f^{10}5d$ mixed configuration to the energy levels of $4f^{11}$ single configuration of the Er^{3+} ion:

$$4f^{10}5d(63\,690\text{ cm}^{-1}) \rightarrow 4f^{11}(4I_{15/2})\,158.6\text{ nm},$$

$$4f^{10}5d(63\,690\text{ cm}^{-1}) \rightarrow 4f^{11}(4I_{13/2})\,177\text{ nm},$$

$$4f^{10}5d(63\,690\text{ cm}^{-1}) \rightarrow 4f^{11}(4I_{9/2})\,195\text{ nm}.$$

From the absorption spectrum of Fig. 2, the presence of an additional weak absorption band with maximum absorption at 163 nm is indicated. This band has been observed previously as well by Deviatkova *et al.*¹⁴ in KY_3F_{10} matrixes at 164.4 nm (60 850 cm^{-1}). Emission from this band at 169 nm has been observed when the excitation wavelength was at 158 nm. Therefore, the emission wavelength at 167 nm, Fig. 1, can be assigned to the transition from this band to the ground level $4I_{15/2}$ of $4f^{11}$ configuration.

In summary, the room-temperature laser induced fluorescence and the absorption spectra of LiLuF:Er single crystals have been studied in the VUV and UV regions of the spectrum. A number of new fluorescence peaks were observed for the first time and they were assigned to the electric dipole allowed transitions $4f^{10}5d \rightarrow 4f^{11}$ of the Er^{3+} ion. We have not observed any constant visible coloration of the crystal

samples under F_2 laser pumping, and this fact is encouraging for the potential use of these materials for generating coherent VUV and UV light.

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