High-resolution vacuum ultraviolet spectroscopy of 5d-4f transitions in Gd and Lu fluorides


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Observation, investigation, and characterization of vacuum ultraviolet (VUV) (~10 eV) luminescence due to interconfigurational 4f\textsuperscript{m}→4f\textsuperscript{m−1}5d transitions of trivalent rare earth (RE\textsuperscript{3+}) ions in a wide band-gap matrix requires a tuneable light source in the VUV, in particular for photon energies above 80 000 cm\textsuperscript{-1} extending into a wide sideband of 0.02–0.05 %.

The VUV spectroscopy was performed at the SUPR-LUMI station of HASYLAB at DESY. High-resolution VUV emission was recorded using an open position sensitive microchannel-plate (MCP) detector coated with CsI in combination with a 1 m VUV monochromator, at resolutions up to 0.5 Å in second order. The excitation spectra of VUV emission and decay curves were recorded using a Pouey type monochromator (Δλ=25 Å) equipped with a CsI sensitized microsphere plate detector. A SpectraPro 308i spectrograph with a R6358P (Hamamatsu) photomultiplier tube (PMT) was applied for measuring excitation spectra of UV/visible emission. Due to the extremely weak luminescence intensity, the VUV emission from LiLuF\textsubscript{4}:Ce\textsuperscript{3+} was investigated at the BW3 beamline of HASYLAB providing high-intensity excitation by XUV photons. In these measurements a high throughput 0.4 m VUV monochromator was used together with a MCP-PMT (Hamamatsu 1645 U-09) at a resolution of ~6 Å.

Single crystals of nominally pure LiGdF\textsubscript{4}, LiGdF\textsubscript{4} doped with 0.05 at. % Ce\textsuperscript{3+}, LiLuF\textsubscript{4}, and LuF\textsubscript{3}, both doped with 0.1 at. % Ce\textsuperscript{3+}, were grown by the Czochralski method. Powder samples of GdF\textsubscript{3} and LuF\textsubscript{3} were high-purity chemicals with a concentration of unwanted RE and other metals of 0.0005–0.001 %. The VUV emission from LiLuF\textsubscript{4}:Ce\textsuperscript{3+} has a well-resolved fine structure which shows at least seven lines spread over ~500 cm\textsuperscript{-1} extending into a wide sideband centered at ~78900 cm\textsuperscript{-1} [Fig. 1(b)]. A striking similarity was observed between the VUV emission spectrum from the LiGdF\textsubscript{4} crystal [which is essentially the same for the LiGdF\textsubscript{4}:Ce\textsuperscript{3+} crystal] in the range of 78 500–79 500 cm\textsuperscript{-1} and the excitation spectrum of the LiLuF\textsubscript{4}:Ce\textsuperscript{3+} crystal [Fig. 1(b)].
High-resolution excitation spectra (Δν = 0.8 Å) of (b) LiGdF₄ and (c) GdF₃ excited by 119 (84 033 cm⁻¹) and 117 nm (85 470 cm⁻¹) photons, respectively (lower energy scale). T = 10 K.

The methodology proposed in Ref. 18 allows the estimation of the energy for the lowest 4f⁶5d-4f⁷ Gd³⁺ ion doped into a particular host if the value of this energy is known for Ce³⁺. In LiGdF₄ weakly doped with Ce³⁺ the intensity of Ce³⁺ 5d-4f luminescence is practically negligible because of very efficient energy transfer from Ce³⁺ to Gd³⁺ resulting in the 311 nm emission from Gd³⁺. However, from the excitation spectrum of the 311 nm Gd³⁺ emission [Fig. 1(a)], the energy of the zero-phonon line for the lowest 4f-5d transition of Ce³⁺ in LiGdF₄ can be determined as 33 615 cm⁻¹. The estimated energy for the zero-phonon line of the lowest 4f⁶5d-4f⁷ transition in Gd³⁺ is 79 415 cm⁻¹, that is very close to the observed threshold in excitation for VUV emission from LiGdF₄ as well as to the energy of the shortest-wavelength emission line from this crystal (79 377 cm⁻¹).

The above consideration allows us to ascribe the observed VUV luminescence from LiGdF₄ (and from GdF₃) to interconfigurational radiative transitions in Gd³⁺ from the lowest 4f⁶5d level to the 4f⁷⁵g ground state of Gd³⁺. Excitation spectra of UV/visible luminescence from LiGdF₄ have a well-pronounced fine structure and their onsets lie at energies slightly below that of the VUV emission [see Figs. 2(b) and 2(c)]. The structureless excitation spectrum of VUV emission from GdF₃ has its threshold near 83 000 cm⁻¹ [Fig. 2(d)]. The decay times of VUV emission from both Gd compounds lie in the nanosecond range: 2.8 ns for LiGdF₄ and 0.97 ns for GdF₃ at 10 K. The complete thermal quenching of VUV emission observed from LiGdF₄ crystal as well as from GdF₃ takes place near 200 K.

FIG. 1. (a) High-resolution excitation spectrum of LiGdF₄:Ce³⁺(0.05%) monitoring 311 nm emission (upper energy scale). High-resolution emission spectra (Δν = 0.8 Å) of (b) LiGdF₄ and (c) GdF₃ excited by 119 (84 033 cm⁻¹) and 117 nm (85 470 cm⁻¹) photons, respectively (lower energy scale). T = 10 K.

FIG. 2. (a) High-resolution excitation spectrum of 4f⁶5d-4f⁷ Gd³⁺ emission at 127 nm from LiGdF₄ crystal together with high-resolution emission spectrum from LiGdF₄ crystal excited by 119 nm (84 033 cm⁻¹) photons. High-resolution excitation spectra (Δν = 0.8 Å) of 4f⁷⁵g Gd³⁺ emissions monitoring 312 nm (G⁶⁵g → S⁷/₂) and 593 nm (G⁶⁵g → P⁷/₂) emission. (d) Excitation spectrum (Δν = 2.9 Å) of 4f⁶5d-4f⁷ Gd³⁺ emission at 125 nm from GdF₃ together with high-resolution emission spectrum from GdF₃ excited by 117 nm (85 470 cm⁻¹) photons. T = 10 K.
that the respective non-radiative energy transfer is heavily spin forbidden, because the multiplicity of the lowest 4f⁷5d level of Gd³⁺ is eight, whereas the 4f⁷ levels of Gd³⁺ closest to this 4f⁷5d level are doublet or quartet.¹⁹

The crystal-field splitting of the ground state of Gd³⁺ is extremely small,²⁰ i.e., only a single zero-phonon line can be expected in the VUV emission spectrum of Gd³⁺. Thus, the fine structure of VUV emission from LiGdF₄ should be due to one zero-phonon line corresponding to the electronic origin of the 4f⁷5d-4f⁷3/2 transition plus vibronic lines. The shape of the spectra with a zero-phonon line, a few narrow vibronic lines corresponding to different modes of lattice vibrations, and a wide lower-energy vibronic side band is typical for the case of intermediate electron-lattice coupling which is confirmed by the estimation of the Huang-Rhys parameter S ~ 1 from the energy difference between the zero-phonon line and the maximum of the wide side band, taking into account the phonon spectrum of scheelite crystals.²¹

The Stokes shift of ~6000 cm⁻¹ observed for 4f⁷-4f⁷5d transitions in GdF₃ [Fig. 2(d)] is more than 10 times larger than the maximum phonon energy in RE trifluorides,²² i.e., the Huang-Rhys parameter S exceeds 5 for all phonon modes of lattice vibrations, which corresponds to the case of strong electron-lattice coupling. As a result the Gd³⁺ 4f⁷5d-4f⁷ emission and 4f⁷-4f⁷5d excitation spectra from GdF₃ have no vibronic fine structure. It should also be noted that the influence of oxygen contaminations in the powder sample on the spectrum of the VUV emission from GdF₃ cannot be significant because oxygen impurity luminescence in fluorides is known to be in the visible range.²³

The structure observed in the excitation spectra of the 592 and 311 nm emission from LiGdF₄, which spreads over about 6000 cm⁻¹, should correspond to features of 4f⁷-4f⁷5d transitions in Gd³⁺. The rectangular shape of the excitation spectrum for d→f emission [Fig. 2(a)] above the threshold confirms that the total absorption is observed for the stoichiometric LiGdF₄. Generally the penetration depth of exciting radiation is controlled by the absorption coefficient. Taking into account very different lifetimes of 5d and 4f excitations, the influence of well-known surface quenching is much stronger for the long-lived 4f excitations. So the dips in the excitation spectra [Figs. 2(b) and 2(c)] can be caused by absorption modulations.

Rather extensive studies have been performed earlier for 4f⁷-4f⁷5d transitions in Eu²⁺ (see Ref. 24, and references therein), which is isoelectronic to the Gd³⁺ ion. The structure observed for 4f⁷-4f⁷5d transitions in Eu²⁺ was well enough interpreted in first approximation as being due to the splitting of the 4f⁶ core in the 4f⁷5d state. We are not aware of any theoretical calculations describing 4f⁷-4f⁷5d transitions in Gd³⁺, and a detailed analysis of the structure of these transitions is beyond the scope of this communication. However, it should be noted that the energy range of this structure matches well the energy spread for the ground ⁷F⁵ multiplet of 4f⁶ configuration of Eu²⁺.

The VUV luminescence from the LiLuF₄:Ce³⁺ crystal possesses both fast (~82 600 cm⁻¹) and slow (~80 200 cm⁻¹) emission bands with nanosecond and considerably longer lifetimes, respectively [Fig. 3(a)]. The VUV emission from this crystal was rather weak and the spectrum with moderate resolution was only measurable under intense XUV excitation at BW3. Due to the same reason the excitation spectrum of VUV emission from this crystal near the f-d threshold was not recorded. The VUV emission from both the Ce³⁺ doped single crystal and pure powder of LuF₃ consists only of a single band (~80 500 cm⁻¹) with a slow decay (longer than detectable range) [Figs. 3(b) and 3(c)]. The high-resolution measurements of both VUV emission and excitation spectra of LuF₃ did not reveal any fine structure showing practically identical behavior for single crystal and powder samples. The VUV emission from LuF₃ is thermally quenched near 200 K.

Following the approach of Ref. 18 for the prediction of the energy for the lowest 4f³5d level of Lu³⁺ in a particular host, the energy of the Lu³⁺ low-spin (singlet) 4f³5d level in LiLuF₄ is expected at ~82 300 cm⁻¹, which is relatively good agreement with the energy of the high-energy band in the VUV emission spectrum of LiLuF₄. Considering the kinetic properties of VUV luminescence from LiLuF₄, the two bands observed in the VUV emission spectrum of the LiLuF₄ crystal can be ascribed to spin-allowed (high-energy band, fast decay) and spin-forbidden (low-energy band, slow decay) interconfigurational 4f³5d-4f³⁴ transitions from the lowest singlet and triplet levels of the 4f³5d configuration to the ⁵S₀ ground state of the 4f³⁴ configuration of Lu³⁺.

The VUV emission spectrum of LuF₃ consists only of a single wide band with a slow decay, which is ascribed to spin-forbidden 4f³5d-4f³⁴ transitions in Lu³⁺. This is not an unusual observation since in many hosts the VUV emission of the 4f²5d-4f⁴ transitions in RE³⁺ ions consists only of a spin-forbidden band because of the fast nonradiative relaxation from higher-lying low-spin states to the lower-lying high-spin state.⁶,⁷

The fine structure in the VUV emission spectrum of

FIG. 3. (a) Emission spectrum (Δλ=6 Å) from LiLuF₄:Ce crystal excited by 130 eV photons at BW3. Time-resolved spectrum (●) was recorded within the time window of 0.8 ns after the excitation pulse. Time-integrated spectrum (○) is also shown. High-resolution emission (Δλ=0.8 Å) spectrum (solid line) excited by 116 nm photons and high-resolution excitation spectrum (Δλ=1 Å) of 4f³5d-4f³⁴ Lu emission (△) recorded at 124.5 nm from LuF₃:Ce crystal (b) and LuF₃ powder (c). T=10 K.
LiLuF$_4$ was not resolved in our moderate-resolution measurements. However, in the excitation spectrum of the Ce$^{3+}$ emission in LiLuF$_4$:Ce$^{3+}$ from Ref. 14 both sharp zero-phonon lines and structureless side bands are observed in the energy range corresponding to Lu$^{3+}$ 4$f^{13}5d$-4$f^{14}$ transitions, indicating intermediate coupling for the LiLuF$_4$ crystal. The Stokes shift between emission and absorption for 4$f^{13}5d$-4$f^{14}$ transitions in Lu$^{3+}$ is larger in LuF$_3$ than in LiLuF$_4$, which results in the absence of vibronic fine structure in both emission and excitation spectra of VUV luminescence from LuF$_3$.

In conclusion, we observed VUV luminescence from LiGdF$_4$, GdF$_3$, LiLuF$_4$, and LuF$_3$ crystals which was ascribed to radiative interconfigurational 4$f^{6}5d$-4$f^{7}$ and 4$f^{13}5d$-4$f^{14}$ transitions in Gd$^{3+}$ and Lu$^{3+}$, respectively. Only fast nanosecond VUV luminescence is observed from Gd crystals, which is typical for spin-allowed 4$f^{m-1}5d$-4$f^{m}$ transitions in RE ions from the first half of lanthanide series. Both fast and slow emission was detected from LiLuF$_4$, corresponding to spin-allowed and spin-forbidden 4$f^{13}5d$-4$f^{14}$ transitions in Lu$^{3+}$. Fine structure due to zero-phonon lines and vibronic lines was well resolved in VUV emission and excitation spectra of LiGdF$_4$ whereas the spectra of GdF$_3$ and LuF$_3$ have a smooth shape because of stronger electron-lattice coupling between the 4$f^{m-1}5d$ electronic configuration of the Gd$^{3+}$ and Lu$^{3+}$ ions and the lattice vibrations.

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