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Luminescence excitation spectra of LiGdF$_4$ and LiLuF$_4$ in the region of interconfigurational $4f^n$–$4f^{n-1}5d$ transitions in the Gd^{3+} and Lu^{3+} ions

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Abstract

The shapes of luminescence excitation spectra for stoichiometric crystals LiGdF$_4$ and LiLuF$_4$ measured in the spectral region of $4f^n$–$4f^{n-1}5d$ transitions in Gd^{3+} and Lu^{3+} ions are analyzed on the basis of diffusion model for the energy migration to the surface quenching centers along Gd^{3+} and Lu^{3+} sublattices. The main features of the excitation spectra were well enough simulated with the use of simple diffusion approach. Estimation of the diffusion length L for the energy migration along Gd^{3+} sublattice in LiGdF$_4$ at 10 K gave reasonable values $L \sim 150$, 1200 and 2250 Å for the migration via $5d$, $^6G_{7/2}$ and $^6P_{7/2}$ levels, respectively.
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Up to recently the detailed spectroscopic studies of interconfigurational $4f^n$–$4f^{n-1}5d$ transitions have been performed for all trivalent rare earth (RE) ions except for Gd^{3+} and Lu^{3+} for which the onset of these transitions (in fluorides) lies at photon energies higher than 78 000 and 80 000 cm^{-1}, respectively (Loh, 1966). Experimental difficulties for the studies of these ions arise because the special window-free optics and detectors in combination with synchrotron radiation excitation should be applied for the measurements at such high photon energies. Recent experiments (Kirm et al., 2004, 2005; Makhov et al., 2006) using a state of the art high-resolution vacuum ultraviolet (VUV) spectroscopy technique with synchrotron radiation (Chen et al., 2003) have revealed that some Gd^{3+} and Lu^{3+} containing fluoride crystals emit at low temperature the VUV luminescence ($hv \sim 10$ eV) which is due to the interconfigurational $4f^65d$–$4f^7$ transitions in the Gd^{3+} ion and $4f^{13}5d$–$4f^{14}$ transitions in the Lu^{3+} ion, respectively.

The radiative $4f^65d$–$4f^7$ transitions in the Gd^{3+} ion are parity- and spin-allowed, i.e. VUV luminescence from the Gd^{3+} containing materials is fast with decay times in the nanosecond range (Kirm et al., 2004). Many other slow emissions are also observed from the Gd^{3+} compounds, in particular, under the excitation to the Gd^{3+} $4f^65d$ configuration, which are due to the parity-forbidden transitions within the Gd^{3+} $4f^7$ configuration. The VUV luminescence from the Lu^{3+} containing materials shows mainly a slow decay because of spin-forbidden character of the $4f^{13}5d$–$4f^{14}$ radiative transitions in the Lu^{3+} ion. The Lu^{3+} compounds possess only the VUV luminescence because of the absence of excited states within the completely filled $4f^{14}$ configuration of Lu^{3+}.

The excitation spectra of Gd^{3+} and Lu^{3+} emission show rather complicated shapes in the region of the $4f^n$–$4f^{n-1}5d$ transitions in these ions (Kirm et al., 2004, 2005). In particular, in the stoichiometric crystal LiGdF$_4$ the shapes of excitation spectra for various kinds of Gd^{3+} emission are strongly different (Fig. 1). Besides, the onsets of excitation spectra near the edge of $4f^n$–$4f^{n-1}5d$ transitions for different Gd^{3+} emissions are slightly shifted with respect to each other. In the present paper, the shapes of experimental excitation spectra for the
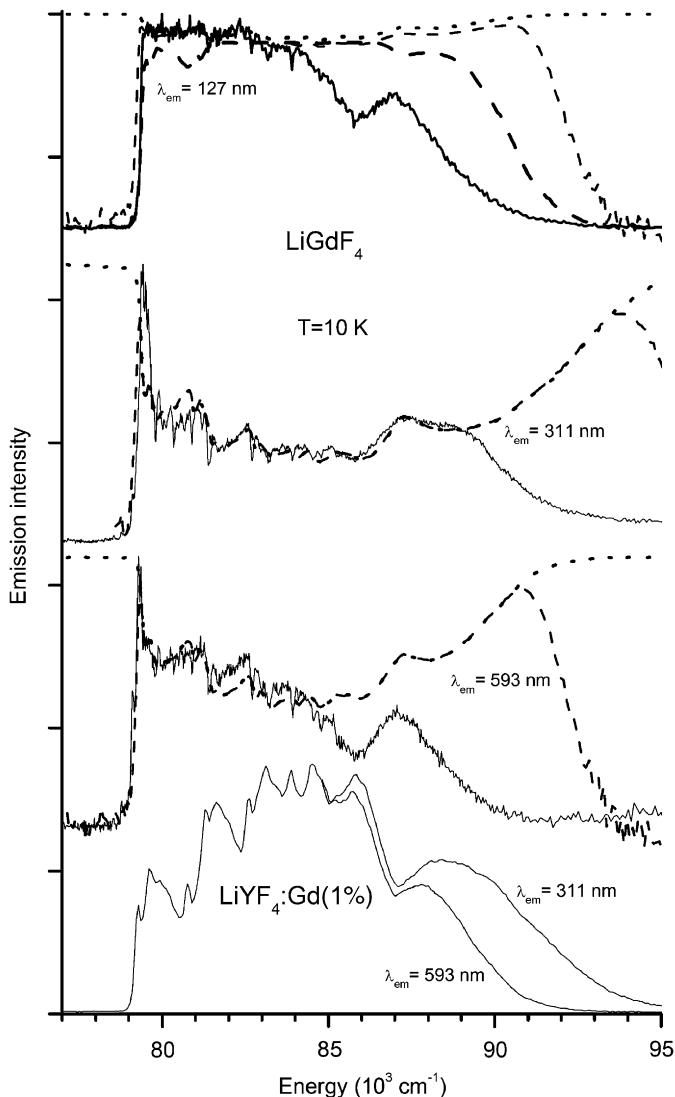
Fig. 1. High-resolution ($\Delta\lambda = 1\,\text{Å}$) experimental excitation spectra (solid curves) of $4f^65d$–$4f^7$ (127 nm), $4f^7$–$4f^7$ ($^6P_{7/2}$–$^8S_{7/2}$, 311 nm) and $4f^7$–$4f^7$ ($^6G_{7/2}$–$^6P_{7/2}$, 593 nm) emissions of Gd^{3+} from the LiGdF$_4$ crystal and of Gd^{3+} $4f^7$–$4f^7$ ($^6P_{7/2}$–$^8S_{7/2}$) and $4f^7$–$4f^7$ ($^6G_{7/2}$–$^6P_{7/2}$) emissions from the LiYF$_4$:Gd^{3+} (1%) powder sample. $T = 10\,\text{K}$. Simulated excitation spectra of Gd^{3+} emissions from the LiGdF$_4$ crystal (dashed and dotted curves) according to formula (1). The relative value of the parameter L for simulated spectra for the 127 nm emission (the same for all of them) is accepted as being equal to 1. For simulated spectra for the 593 and 311 nm emissions $L = 8$ and 15 relative units, respectively. The values of parameter d for simulated spectra for the 593 and 311 nm emissions $d = 300$ (dashed curves) and ∞ (dotted curves) relative units and for simulated spectra for the 127 nm emission $d = 30$, 300 and ∞.

stoichiometric LiGdF$_4$ and LiLuF$_4$ compounds are analyzed on the basis of diffusion model describing energy migration along Gd and Lu sublattices. High-resolution ($\leqslant 1\,\text{Å}$) excitation spectra have been recorded under excitation by synchrotron radiation using the SUPERLUMI setup operated at the DORIS storage ring of HASYLAB at DESY. Detailed experimental aspects of the measurements can be found elsewhere (Kirm et al., 2004, 2005).

The structure observed in the excitation spectra of different emissions from LiGdF$_4$, which spreads over about $6000\,\text{cm}^{-1}$, should correspond to features of the $4f^7$–$4f^65d$ transitions in Gd^{3+}. The rectangular shape indicates the saturation of the excitation spectrum for $4f^65d$–$4f^7$ emission from LiGdF$_4$ above the threshold confirming that the total absorption is observed for this stoichiometric compound. Nevertheless, the penetration depth of exciting radiation is modulated by the value of varying absorption coefficient. Taking into account drastically different lifetimes of the $5d$ and $4f$ excitations, the influence of well-known surface quenching (surface losses, see e.g. Lushchik et al., 2004) due to the energy migration along Gd sublattice to the surface quenching centers can be much stronger for the long-lived $4f$ excitations. In such model, the minimum intensity in the excitation spectra of the $4f^7$–$4f^7$ emissions from LiGdF$_4$ would correspond to the maximum of the absorption coefficient and vice versa. This is well illustrated by the comparison of excitation spectra for stoichiometric and diluted Gd samples (Fig. 1), which are anti-correlated. It is interesting to note that for LiYF$_4$ weakly doped with Gd^{3+} the excitation spectra of all kinds of emissions practically coincide in the region of the $4f^7$–$4f^65d$ transitions. This is an indication of the absence of surface quenching effects in crystals with low doping concentration because of the low absorption coefficient and inefficient energy migration along Gd sublattice.

The influence of surface losses on excitation spectra can be taken into consideration in a more quantitative way by using a simple diffusion model (Vasil'ev and Mikhailin, 1987; Ackermann et al., 1976; Elango et al., 1976). In accordance with this model the shape of luminescence excitation (quantum yield) spectrum $\eta(E)$ is modulated by

$$\eta(E) = \eta_v(1 - R(E))(1 - \exp(-\mu(E)d))/(1 + \mu(E)L), \quad (1)$$

where η_v is the volume quantum yield, R is the reflectance, μ is the absorption coefficient, L is the diffusion length, and d is the crystal thickness. The diffusion length parameter depends sensitively on the value of lifetime τ of electronic excitation responsible for the emission $L = (D\tau)^{1/2}$, where D is diffusion coefficient. Obviously, the reflectance is low in the energy region just above the edge of Gd^{3+} $4f^7$–$4f^65d$ transitions, and its influence can be neglected. Unfortunately, the absorption spectrum of LiGdF$_4$ is unknown and cannot be easily recorded in this spectral region. However, one can use the excitation spectrum of LiYF$_4$ weakly doped with Gd^{3+} as a rough approximation of the LiGdF$_4$ absorption spectrum (in relative units), since for small concentration of the doping ion the respective absorption coefficient is not very high. Hence, in accordance with formula (1) $\eta(E)$ is proportional to $\mu(E)$ for small $\mu(E)$ values. Certainly, it is also necessary to take into account a small blue shift of Gd^{3+} $4f^7$–$4f^65d$ transition energy for LiGdF$_4$ compared to LiYF$_4$:Gd^{3+}, which can be determined from the energy difference between zero-phonon lines (ZPLs) in VUV emission spectra of these compounds and is equal to $\sim 170\,\text{cm}^{-1}$ (Kirm et al., 2005). The fitting parameters d and L will be both in arbitrary units because the absolute value of absorption coefficient is not available.

The curves calculated by formula (1) with different values of fitting parameters L and d are shown in Fig. 1 as well. It is easily seen that the main features of LiGdF$_4$ excitation spectra in the region of the $4f^7$–$4f^65d$ transitions in Gd^{3+} can be well enough simulated with the use of such a simple approach. Since the absorption coefficient on the Gd^{3+} $4f^7$–$4f^65d$ transitions is very large for the stoichiometric compound, the parameter d—crystal thickness—can be considered as infinity in comparison with very small penetration depth. However, near the onsets (and also in the higher energy region of interest) where the absorption coefficient is considerably smaller, this assumption is not anymore valid. Therefore, it is not possible to simulate excitation spectra of LiGdF$_4$ at such conditions by using the excitation spectrum of LiYF$_4$:Gd (1%) as approximation for absorption spectrum, because for good simulation it is necessary to have absorption spectrum with large dynamical range for changing the absorption coefficient near the onset. On the other hand, the shapes of simulated curves do not depend on the value of parameter d almost in the whole region of the Gd^{3+} $4f^7$–$4f^65d$ transitions. Accordingly, the diffusion length parameter L can be treated quantitatively separately from the d value. Our approach fails to simulate the shapes of the spectra near the onsets and, in particular, the shift of the excitation spectrum onset only by changing the value of the diffusion length L. However, this difficulty can be overcome (including the shift of the onset) by decreasing the parameter d (this can be considered as equivalent to decreasing the absorption coefficient near the edge of absorption), as was carried out for some of the simulated curves in Fig. 1. From the physical point of view the shift of the onset observed can indicate the presence of some kind of near-defect absorption at the long-wavelength tail of the Gd^{3+} $4f^7$–$4f^65d$ transitions in LiGdF$_4$.

The rough estimation of absolute values of absorption coefficient for LiGdF$_4$ can be obtained by using data on absorption in CaF$_2$:Gd^{3+} (0.1%) presented by Schlesinger et al. (1978). If one relies on the value of $\sim 10^2$ cm^{-1} from that paper for the maximal absorption coefficient of the material with 0.1% concentration of Gd^{3+} (at $hv \sim 80\,000$ cm^{-1} for CaF$_2$:Gd^{3+} (0.1%)), the diffusion lengths for the energy migration in LiGdF$_4$ at 10 K along Gd sublattice via $5d$, $^6G_{7/2}$ and $^6P_{7/2}$ levels can be estimated as being equal to ~ 150, 1200 and 2250 Å, respectively. The latter value is consistent with the value $L = 656$ Å obtained by De Vries et al. (1988) for the energy migration in LiGdF$_4$ via the Gd^{3+} $^6P_{7/2}$ level at 298 K from the analysis of emission decay curves. Much lower value of the diffusion length for energy migration via the $5d$ level than via the $4f$ ($^6G_{7/2}$ and $^6P_{7/2}$) levels of Gd^{3+} could be expected because of much smaller lifetime for $5d$ state (2.8 ns, Kirm et al., 2004) compared to that for $4f$ levels (~ 10 ms at 4.2 K for the $^6P_{7/2}$ level, De Vries et al., 1988). However, difference in the lifetimes is too large ($\sim 3.5 \times 10^6$) for the obtained ratio (~ 15) of the diffusion lengths for energy migration via the $^6P_{7/2}$ and $5d$ levels. Another factor, which controls the diffusion length, is the diffusion coefficient D, which should be obviously larger for the $5d$ level than for the $4f$ ones. Although the spectral overlap of the absorption and
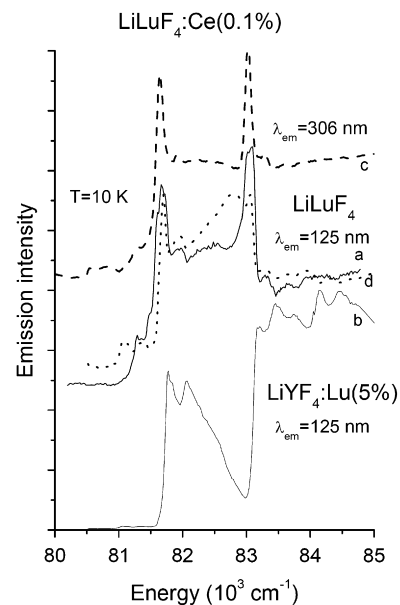
emission bands for the $4f$–$4f$ transitions is higher ($\sim 100\%$ for nearly resonant energy transfer) than that for $5d$–$4f$ transitions (the latter can be estimated as being $< 5\%$ from the intensity of ZPL compared to that of the whole emission spectrum of LiGdF$_4$, see Kirm et al., 2004), more important is much better overlapping of wavefunctions for extended $5d$ states compared to that for highly localized and shielded by outer shells $4f$ states (in the case of energy transfer via exchange interaction) or higher rates of radiative transitions for parity allowed $5d$–$4f$ transitions (in the case of energy transfer via dipole–dipole interaction). The estimates give the values of $D = 8 \times 10^{-4}$ and 5×10^{-8} cm^2/s for the migration via the $5d$ and $^6P_{7/2}$ levels, respectively. The value of D for the $5d$ level is of the same order of magnitude as for migration of valence holes in alkali-halide crystals.

Decrease in the emission intensity in all experimental excitation spectra towards higher energies in the region of $88\,000$–$90\,000$ cm^{-1} may be ascribed to the onset of absorption by the host. It seems to be a general rule that the RE^{3+} $4f^{n-1}5d$–$4f^n$ luminescence is hardly excited under band-to-band excitation. Due to the strong host absorption the emission intensity in the simulated excitation spectrum becomes much higher than that in the experimentally recorded spectrum at these photon energies. An additional difference can arise because of the sharp increase in the reflectivity near the fundamental absorption edge of the host, which was not taken into account in the simulated spectra.

The shapes of excitation spectra for the VUV luminescence from the Lu^{3+} doped LiYF$_4$ crystal and from the stoichiometric compound LiLuF$_4$ are strongly different in the region of $4f^{14}$–$4f^{13}5d$ transitions in Lu^{3+}, as can be seen from Fig. 2.

Fig. 2. High-resolution ($\Delta\lambda = 1$ Å) experimental excitation spectra of Lu^{3+} $4f^{13}5d$–$4f^{14}$ emission from (a) LiLuF$_4$ and (b) LiYF$_4$:Lu^{3+} (5.0%) crystals recorded at 125 nm and of Ce^{3+} $5d$–$4f$ emission from the LiYF$_4$:Ce^{3+} (0.1%) crystal (c) recorded at 306 nm (dashed curve). $T = 10$ K. Simulated excitation spectrum (dotted curve) of Lu^{3+} $4f^{13}5d$–$4f^{14}$ emission from the LiLuF$_4$ crystal with the ratio of parameters $L/d = 1 : 5$ (d).

Similar to the case of LiGdF$_4$ crystal, it is reasonable to suggest that the structures observed in excitation spectrum of LiLuF$_4$ in this region are determined by near-surface losses. The excitation spectrum can be simulated with formula (1) where again the excitation spectrum of LiYF$_4$ weakly doped with Lu^{3+} was used as a rough approximation of LiLuF$_4$ absorption spectrum (in relative units) in the region of $4f^{14}$–$4f^{13}5d$ transitions of the Lu^{3+} ion. The result of simulation is shown in Fig. 2 with the ratio of parameters L/d being equal to 1:5. The small red shift of Lu^{3+} $4f^{14}$–$4f^{13}5d$ transition energy $\sim 100\,\text{cm}^{-1}$ for LiLuF$_4$ compared to LiYF$_4$:Lu^{3+} was taken into account. It was chosen here as the best fit between the simulated and experimental spectra of LiLuF$_4$. From Fig. 2 it is obvious that the main features of LiLuF$_4$ excitation spectrum in the region of Lu^{3+} $4f^{14}$–$4f^{13}5d$ transitions can be well enough simulated with the use of the diffusion approach.

In this figure the excitation spectrum of the Ce^{3+} $5d$–$4f$ luminescence from LiLuF$_4$:Ce^{3+} (0.1%) is also shown in the region of the Lu^{3+} $4f^{14}$–$4f^{13}5d$ transitions. The structure of this spectrum is almost identical to that of excitation spectrum of VUV luminescence from LiLuF$_4$. This observation certainly indicates that the narrow lines in the excitation spectrum of LiLuF$_4$:Ce^{3+} (0.1%) do not exactly correspond to ZPLs of Lu^{3+} $4f^{14}$–$4f^{13}5d$ transitions in LiLuF$_4$, as was suggested by Kirikova et al. (2004). However, these features, which appear at edges of the strong absorption on Lu^{3+} $4f^{14}$–$4f^{13}5d$ transitions, with high probability are manifestations of the near-surface effects modulating the spectra.

In conclusion, the main features of luminescence excitation spectra for stoichiometric crystals LiGdF$_4$ and LiLuF$_4$ measured in the spectral region of the $4f^n$–$4f^{n-1}5d$ transitions in Gd^{3+} and Lu^{3+} ions can be well enough explained by using simple diffusion model for the energy migration to the surface quenching centers along Gd^{3+} and Lu^{3+} sublattices. In particular, the sharp structures at the edges of strong absorption on the Gd^{3+} and Lu^{3+} $4f^n$–$4f^{n-1}5d$ transitions can be well simulated by the near-surface quenching effect. Despite the limitations of the method, as discussed above, estimation of the diffusion lengths for the energy migration at 10 K along Gd^{3+}

sublattice in LiGdF$_4$ via $5d$, $^6G_{7/2}$ and $^6P_{7/2}$ levels gave the reasonable values $\sim$ 150, 1200 and 2250 Å, respectively.

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