VUV 5d – 4f luminescence of Gd$^{3+}$ doped into CaF$_2$

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High-resolution (~1 Å) emission and excitation spectra as well as luminescence decay kinetics have been studied for CaF$_2$ doped with Gd$^{3+}$ (0.1%) and Ce$^{3+}$(0.05%) under excitation by synchrotron radiation near and above the edge of interconfigurational 4f$^6$–4f$^5$d transitions in Gd$^{3+}$ and 4f$^5$–5d transitions in Ce$^{3+}$. The fast (τ~8.5 ns) VUV luminescence has been detected from the crystal the spectrum of which shows zero-phonon line at 77660 cm$^{-1}$ and dominating vibronic line at energy interval ~370 cm$^{-1}$. The vibronic structure in VUV emission spectrum well correlates with that observed at the onset of the Gd$^{3+}$ 4f$^6$–4f$^5$d emission spectrum. The obtained results confirm that the VUV luminescence observed in CaF$_2$:Gd$^{3+}$,Ce$^{3+}$ originates from 4f$^5$5d–4f$^4$ radiative transitions in Gd$^{3+}$. The vibronic structure in emission and excitation spectra of Gd$^{3+}$ d–f luminescence from the CaF$_2$:Gd$^{3+}$,Ce$^{3+}$ crystal differs from that observed for other trivalent rare earth ions doped into CaF$_2$: indicating that Gd$^{3+}$ ions reside in sites of different type in CaF$_2$ than that of tetragonal (C$_{4v}$) symmetry.

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1 Introduction It is well known [1] that some trivalent rare earth (RE) ions doped into wide band-gap matrices possess luminescence in the vacuum ultraviolet (VUV) spectral range. This luminescence originates from parity-allowed interconfigurational 4f$^{n+1}$5d – 4f$^n$ transitions in the RE ions. Up to recently, RE$^{3+}$ luminescence in VUV has been detected only from three heavier RE ions, namely from Nd$^{3+}$, Er$^{3+}$, and Tm$^{3+}$. However, recent studies [2, 3] have revealed that Gd$^{3+}$ containing wide band-gap fluoride crystals with scheelite and YF$_3$ structure emit VUV luminescence (hν ~ 10 eV), which is due to the interconfigurational 4f$^6$5d–4f$^5$ transitions in the Gd$^{3+}$ ion. The observation of 4f$^6$5d–4f$^5$ emission from the Gd$^{3+}$ ion is a rather unexpected result because of the considerable number of closely spaced 4f$^5$ levels in the same energy region as the 4f$^6$5d states, that can open an efficient non-radiative relaxation channel from the lowest Gd$^{3+}$ 4f$^6$5d level. The possible reason for the observation of efficient radiative decay from the Gd$^{3+}$ 4f$^6$5d level is that the competing non-radiative transitions are heavily spin-forbidden because the multiplicity of the lowest 4f$^6$5d level of Gd$^{3+}$ is eight, whereas the 4f$^5$ levels of Gd$^{3+}$ closest to this 4f$^6$5d level are doublet or quartet [4]. In the present work the spectral and temporal characteristics of VUV, UV and visible luminescence from CaF$_2$ doped with Gd$^{3+}$(0.1%) and Ce$^{3+}$(0.05%) have been studied under excitation by synchrotron radiation near and above the edge of interconfigurational 4f$^5$–4f$^6$5d transitions in Gd$^{3+}$ and 4f$^5$–5d transitions in Ce$^{3+}$.

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2 Experimental High-resolution (~1 Å) VUV emission and excitation spectra as well as decay kinetics of VUV luminescence have been measured using the SUPERLUMI set-up operated at the DORIS storage ring of HASYLAB at DESY [5]. High-resolution VUV emission spectra were recorded using an open position sensitive microchannel-plate detector coated with CsI in combination with a 1-meter VUV monochromator, at resolutions up to 0.5 Å in second order [6]. The excitation spectra of VUV emission and decay curves were recorded using a Pouey type monochromator (typical spectral resolution $\Delta \lambda = 20$ Å) equipped with a CsI sensitized microsphere plate detector. The time resolution of the detection system with this detector was better than 0.2 ns. An 0.3 m Czerny-Turner-type monochromator-spectrograph SpectraPro-308i (Acton Research Inc.) with a R6358P (Hamamatsu) photomultiplier tube was applied for measuring excitation spectra of UV/visible luminescence. Emission spectra in the UV/visible spectral range were recorded at the same spectrograph SpectraPro-308i with a liquid nitrogen cooled CCD detector (Princeton Instruments Inc.). The spectral resolution of ~ 0.25 nm was achieved with the 1200 grooves/mm grating using 0.05 mm slit width. The excitation spectra were recorded with an instrumental resolution of primary monochromator as high as 0.7 Å. High-resolution VUV emission spectra were calibrated very carefully by using reference (scattered) lines from primary monochromator. However, since the wavelength calibration accuracy of the primary monochromator is about 0.5 Å in the region around 130 nm, the wavelength positions of all features in VUV emission and excitation spectra were determined with accuracy of ~0.5 Å. Single crystals of CaF$_2$ doped with 0.1 mol. % Gd$^{3+}$ and 0.05 mol. % Ce$^{3+}$ were grown by the vertical Bridgman method in the fluorine atmosphere. The samples were cleaved prior to the installation into a flow-type liquid helium cryostat.

3 Results and discussion The Ce$^{3+} 5d - 4f$ emission and $4f - 5d$ excitation spectra (Fig. 1) recorded from the CaF$_2$:Gd$^{3+},$Ce$^{3+}$ crystal as well as from CaF$_2$ singly doped with 0.05 mol. % Ce$^{3+}$ well correspond to the spectra of Ce$^{3+}$ center in CaF$_2$ in a site of tetragonal (C$_{4v}$) symmetry where charge compensation of Ce$^{3+}$ is achieved by an interstitial fluorine ion located at the nearest-neighbor position along [100] direction from the Ce$^{3+}$ ion [7, 8]. The vibronic structure in these spectra is dominated by the line at the energy interval ~ 480 cm$^{-1}$ from the zero-phonon lines, which well corresponds to the longitudinal optical phonon energy in CaF$_2$ [9], but has been usually interpreted as the local breathing mode oscillations of the eight fluorine ions surrounding the Ce$^{3+}$ ion [10].

![Fig. 1](image_url)

At low temperature the VUV ($\lambda \sim$129.5 nm) luminescence has been detected from the CaF$_2$:Gd$^{3+},$Ce$^{3+}$ crystal under the excitation in the spectral region of $4f - 5d$ transitions in Gd$^{3+}$ (Fig. 2). The VUV emission spectrum of CaF$_2$:Gd$^{3+},$Ce$^{3+}$ shows a narrow zero-phonon line at 77660 cm$^{-1}$ followed by a broad side band centered near 77100 cm$^{-1}$, which is superimposed by the phonon fine structure with dominating vibronic line separated by ~370 cm$^{-1}$ from the zero-phonon line. The decay time of the VUV
luminescence is 8.5 ± 0.1 ns at 10 K. The excitation spectrum of VUV luminescence agrees well with the Gd$^{3+}$ 4f$^7$ − 4f$^6$5d absorption spectrum in CaF$_2$:Gd$^{3+}$ obtained in [10]. The zero-phonon line and other features in the VUV emission spectrum well correlate with the structure observed at the onset of the Gd$^{3+}$ 4f$^7$ − 4f$^5$5d excitation spectrum. The obtained results clearly show that the VUV luminescence observed from the CaF$_2$:Gd$^{3+}$,Ce$^{3+}$ crystal is due to 4f$^5$5d − 4f$^7$ radiative transitions in Gd$^{3+}$.

![Excitation spectrum of CaF$_2$:Gd$^{3+}$,Ce$^{3+}$](image)

**Fig. 2** Spectra of CaF$_2$:Gd$^{3+}$,Ce$^{3+}$ in the region of Gd$^{3+}$ 4f$^7$ − 4f$^6$5d transitions. High-resolution (Δλ ~ 1 Å) VUV emission spectrum under 124.7 nm excitation (solid line). Moderate-resolution (Δλ ~ 3 Å) excitation spectrum of Gd$^{3+}$ 4f$^6$5d − 4f$^7$ emission (dashed line). Excitation spectrum of self-trapped exciton emission (dotted line). The spectral lines tentatively ascribed to zero-phonon lines are marked by symbol “∗”, and to dominating vibronic lines by symbol “|”.

The methodology proposed in Ref. [11] allows the estimation of the energy for the lowest 4f$^6$ − 4f$^6$15d transition in the RE$^{3+}$ ion doped into a particular host if the value of this energy is known for Ce$^{3+}$. From the excitation and emission spectra of Ce$^{3+}$ 5d − 4f luminescence, the energy of the zero-phonon line for the lowest 4f − 5d transition of Ce$^{3+}$ in CaF$_2$ is 31930 cm$^{-1}$. Accordingly the estimated energy for the zero-phonon line of the lowest 4f$^7$ − 4f$^6$5d transition in Gd$^{3+}$ is 77730 cm$^{-1}$, that is very close to the observed lowest-energy narrow line in the excitation spectrum (which coincides with the highest-energy narrow line in the emission spectrum). This estimation is an additional confirmation that the VUV luminescence observed in CaF$_2$:Gd$^{3+}$,Ce$^{3+}$ originates from 4f$^5$5d − 4f$^7$ transitions in Gd$^{3+}$.

The orange (590-640 nm) luminescence, which is due to 4f$^6$ 6$^6$G$^{7/2}$ − 6$^4$P$^4$ transitions in Gd$^{3+}$ [12], is also observed from CaF$_2$:Gd,Ce under the excitation to 4f$^5$5d configuration of Gd$^{3+}$. Obviously there exists some probability for non-radiative relaxation from the lowest 4f$^5$5d level of Gd$^{3+}$ to closely spaced energy levels of Gd$^{3+}$ 4f$^7$ configuration that will result in the population of the emitting 4f$^7$ 6$^{6}$G$^{7/2}$ level. The excitation spectrum of VUV luminescence completely coincides with the excitation spectrum of this orange luminescence, as expected (see Fig. 2).

The Gd$^{3+}$ 4f$^7$ − 4f$^5$5d excitation spectrum shows considerably more structures compared to the Gd$^{3+}$ 4f$^7$ − 4f$^6$5d absorption spectrum obtained for CaF$_2$:Gd$^{3+}$ in Ref. [10]. Several features in the spectrum can be tentatively ascribed to zero-phonon lines accompanied by vibronic structure, the dominating vibronic lines being separated by ~ 370 cm$^{-1}$ from zero-phonon lines, similar to the Gd$^{3+}$ 4f$^5$5d − 4f$^7$ emission spectrum. We are not aware of any theoretical calculations of 4f$^7$ − 4f$^5$5d transitions in Gd$^{3+}$ and hence, the detailed analysis of the structure of excitation spectrum cannot be performed. However, the energy range and many features of this structure correspond well to the energy level system of the ground 7F$_J$ multiplet of the 4f$^6$ core in Gd$^{3+}$ 4f$^5$5d configuration as can be seen in Fig. 2 where the energy level structure of the 4f$^6$ 7F$_J$ multiplet of Eu$^{3+}$ (in LaF$_3$ [13]) is superimposed on the Gd$^{3+}$ excitation spectrum with the ground level coinciding with the lowest-energy zero-phonon line. The decrease of VUV emission intensity towards higher energies is obviously due to the edge of intrinsic absorption of the host crystal the energy of which can be estimated from the excitation spectrum of self-trapped exciton emission from CaF$_2$ (see Fig. 2).
Well resolved fine structure due to zero-phonon lines and vibronic lines along with broad side-bands observed in VUV emission and excitation spectra of CaF$_2$:Gd$^{3+}$,Ce$^{3+}$ indicate intermediate electron-lattice coupling between the 4f$^5$5d electronic configuration of the Gd$^{3+}$ ion and the lattice vibrations in CaF$_2$:Gd$^{3+}$,Ce$^{3+}$ system. The estimation of the Huang-Rhys parameter $S \sim 1.2 \pm 1.5$ from the energy difference between the zero-phonon line and the maximum of the wide side band, taking into account the phonon spectrum of CaF$_2$ [9] or the energy of the dominating vibronic line in the obtained spectra, confirms this conclusion.

It is usually accepted that at doping concentration below 0.1 % the RE$^{3+}$ ions of any kind reside in CaF$_2$ predominantly in the tetragonal $C_{4v}$ sites for which the vibronic structure in the spectra is dominated by the line at the energy interval ~ 480 cm$^{-1}$ from-zero-phonon lines. However, the RE$^{3+}$ centers of different symmetry were also detected for many RE$^{3+}$ ions [7, 8, 14]. In particular, the trigonal centers ($C_{3v}$) of two types are often observed, in which charge compensation is achieved either by the fluorine ion in the next-nearest neighbor position along [111] direction from the RE$^{3+}$ ion (if the crystals were grown under reducing conditions) or by the oxygen ion O$^{2-}$ which replaces fluorine ion in the cube surrounding the RE$^{3+}$ ion (if the crystals were grown in the presence of oxygen). The cubic (O$_h$) centers with remote charge compensation of RE$^{3+}$ ion were also identified [15].

The vibronic structure in emission and excitation spectra of Gd$^{3+}$ $d-f$ luminescence from the CaF$_2$:Gd$^{3+}$,Ce$^{3+}$ crystal differs from that observed for other trivalent RE ions doped into CaF$_2$ and is dominated by the line at ~370 cm$^{-1}$ which does not correspond to any well-defined peak in phonon spectrum of CaF$_2$. This difference was already observed in Ref. [10] in the Gd$^{3+}$ 4f$^5$5d $- 4f^4$ absorption spectrum of CaF$_2$:Gd$^{3+}$. This can indicate that Gd$^{3+}$ ions reside in CaF$_2$ predominantly in sites of different type than of tetragonal ($C_{4v}$) symmetry, and some pseudo-local mode (where the atomic amplitudes near the mass defect are changed) with the energy ~370 cm$^{-1}$ is involved in electron-lattice coupling between the 4f$^5$5d electronic configuration of the Gd$^{3+}$ ion and the lattice vibrations in CaF$_2$.

4 Conclusions The obtained results clearly evidence that the VUV luminescence observed in CaF$_2$:Gd$^{3+}$,Ce$^{3+}$ originates from 4f$^5$5d $- 4f^4$ radiative transitions in Gd$^{3+}$. The vibronic structure in emission and excitation spectra of Gd$^{3+}$ $d-f$ luminescence from the CaF$_2$:Gd$^{3+}$,Ce$^{3+}$ crystal differs from that observed for other trivalent RE ions doped into CaF$_2$ the reason of which needs further experimental and theoretical studies.

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