One way to enhance the luminescence efficiency of phosphors is through energy transfer between donor and acceptor centres. For example, although Tb$^{3+}$ ions are a popular choice for the emitting centres when green light is required, they may be difficult to excite efficiently. The forbidden f-f transitions in the easily accessible near-ultraviolet region are weak, while the allowed f-d transitions which are strong occur at very short wavelengths (in LaF$_3$ below 200 nm in the vacuum-ultraviolet region [1]) and are therefore not easily accessible. The f-d transition energy of Ce$^{3+}$ ions is known to always be less than for Tb$^{3+}$ ions [1], so Ce$^{3+}$ ions can be excited at longer, more accessible wavelengths. Since energy transfer from Ce$^{3+}$ (donor) to Tb$^{3+}$ (acceptor) ions is known to occur in LaF$_3$ [2], this makes it possible to obtain intense emission from Tb$^{3+}$ ions by exciting them indirectly via the Ce$^{3+}$ ions in co-doped samples. Although this idea has been used in the past, there has been little investigation of the dependence of the energy transfer on the Ce and Tb concentrations [2] and the mechanism for the energy transfer has not been reported. Lifetime measurements of the emission from Ce$^{3+}$ ions in Ce,Tb co-doped LaF$_3$ samples obtained using the SUPERLUMI station at DESY were used to investigate the energy transfer mechanism.

![Figure 1](image1.png)

**Figure 1:** (a) Emission and (b) excitation spectra Ce doped LaF$_3$ (1 mol% Ce).

![Figure 2](image2.png)

**Figure 2:** (a) Emission and (b) excitation spectra Ce,Tb co-doped LaF$_3$ (1 mol% Ce, 20 mol% Tb).
Fig. 1(a) shows emission spectrum of Ce-doped LaF$_3$ (1 mol% Ce) excited with synchrotron radiation of wavelength 247 nm at SUPERLUMI. The two emission peaks at 285 and 303 nm correspond to transitions from the d-level to the $^2F_{5/2}$ and $^2F_{7/2}$ f-levels respectively. Fig. 1(b) shows that the excitation spectrum for the 285 nm emission consists of five peaks, corresponding to the different d-levels, as well as an increase below 120 nm associated with the bandgap of LaF$_3$.

Fig. 2(a) shows the emission spectrum of Ce,Tb co-doped LaF$_3$ (1 mol% Ce, 20 mol% Tb) obtained under the same conditions as for Fig. 1(a). It is dominated by several Tb emission peaks from the $^5D_4$ to the $^7F_J$ levels, with only a small amount of Ce emission. The excitation spectrum for the Tb emission at 542 nm ($^5D_4$–$^7F_5$ transition) is shown in Fig. 2(b). The Tb f-d excitation bands below 200 nm occur together with the Ce f-d excitation bands at 246, 234 and 218 nm, showing that energy transfer takes place from Ce to Tb. Non-radiative energy transfer from a donor to an acceptor is characterized by a decrease in the donor luminescence intensity and lifetime as the concentration of acceptor is increased. These changes have been quantitatively modelled [3] and comparing measurements to the theory can be used to identify the mechanism for energy transfer.

Decay curves of the Ce emission were recorded for co-doped Ce,Tb LaF$_3$ with a fixed concentration of Ce donor and varying concentrations of Tb acceptor. These were fitted to multi-exponential functions convoluted with the instrument response function obtained from the stray light signal, and the mean lifetimes were calculated from the fit parameters. Fig. 3(a) shows the results for selected samples and there is a clear decrease in the Ce lifetime with increasing Tb concentration as a result of energy transfer. To obtain the energy transfer mechanism, the relative change in the mean lifetime of the Ce with increasing Tb concentration is compared to the relative change in the Ce luminescence intensity (measured using a Cary Eclipse fluorescence spectrometer) in Fig. 3(b). The experimental data points correspond well to the theoretical curves of energy transfer for the quadrupole-quadrupole interaction as well as for the exchange interaction with the parameter $\gamma = 11.6$, but do not fit the dipole-dipole or dipole-quadrupole interaction models. This result is unexpected since dipole-dipole or dipole-quadrupole interactions were reported to be responsible for energy transfer between Ce and Tb in CaAl$_2$SiO$_6$ [4], although lifetime measurements were not used in that study. Despite the widespread use of Ce as a co-dopant with Tb, little information exists on the interaction mechanisms in different hosts and further work is required to understand this interesting combination of dopants better.

Figure 3: (a) Decay curves of Ce in co-doped LaF$_3$. (b) Change in Ce luminescence due to addition of Tb.

References