Supporting Information

**SI-Figure 1.** Room temperature excitation spectra ($\lambda_{em} = 590$ nm) of BaF$_2$: M$^+$, Gd$^{3+}$, Eu$^{3+}$ particles.

**SI-Figure 2.** Powder X-ray diffraction patterns of BaF$_2$: Na$^+$ 15% and CaF$_2$: Na$^+$ 15% particles. The reflection marked with an asterisk originates from the instrumental setup.
**SI-Figure 3.** Powder X-ray diffraction patterns of BaF$_2$: Na$^+$, La$^{3+}$ and CaF$_2$: Na$^+$, La$^{3+}$ particles with various dopant concentrations. The reflection marked with an asterisk originates from the instrumental setup.

**SI-Figure 5.** $^{19}$F-MAS-NMR-spectra of the crystalline reference compounds BaF$_2$, CaF$_2$, NaF and LaF$_3$.

**SI-Figure 6.** Comparison of the $^{139}$La-NMR-spectra recorded under static and MAS conditions, respectively for the CaF$_2$: La 15%, Na 15% sample.
**SI-Figure 7.** $^{19}$F-MAS-NMR-spectra recorded in dependence of the degree of codoping and their respective deconvolution.

**SI-Figure 8.** Comparison of the $^{23}$Na spin echo decays for the sodium rich singly and co-doped samples.