

## **Supporting Information**

**SI-Figure 1.** Room temperature excitation spectra ( $\lambda_{em}$ = 590 nm) of BaF<sub>2</sub>: M<sup>+</sup>, Gd<sup>3+</sup>, Eu<sup>3+</sup> particles.



**SI-Figure 2.** Powder X-ray diffraction patterns of  $BaF_2$ : Na<sup>+</sup> 15 % and CaF<sub>2</sub>: Na<sup>+</sup> 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<sup>+</sup>, La<sup>3+</sup> and CaF<sub>2</sub>: Na<sup>+</sup>, La<sup>3+</sup> particles with various dopant concentrations. The reflection marked with an asterisk originates from the instrumental setup.



SI-Figure 5. <sup>19</sup>F-MAS-NMR-spectra of the crystalline reference compounds BaF<sub>2</sub>, CaF<sub>2</sub>, NaF and LaF<sub>3</sub>.



SI-Figure 6. Comparison of the  $^{139}$ La-NMR-spectra recorded under static and MAS conditions, respectively for the CaF<sub>2</sub>: La 15%, Na 15% sample



SI-Figure 7. <sup>19</sup>F-MAS-NMR-spectra recorded in dependence of the degree of codoping and their respective deconvolution.



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