

Figure S1a showed the wide survey photoemission spectrum of CaF_2 : 0.5 mol% Yb^{3+} , 1 mol% Gd^{3+} . The Ca 2s, 2p, 3s, 3p, and 3d core levels were observed at binding energies of 438, 347, 43, 25, and 5 eV, respectively. The F 1s, 2s, and 2p core levels were present at binding energies of 685, 29, and 9 eV, respectively. The doping concentration of Gd^{3+} was low (1 mol %), so the 4d spectrum of Gd was weak, as shown in figure S1c. Yb doping concentration was lower (0.5 mol %), so Yb 4d spectrum shown in figure S1d was barely distinguishable. The peaks at 185 eV, and 199 eV are attributed to the terms of Yb^{3+} . It is known that 4d spectrum of Yb^{2+} reveals a doublet (usually at 180.3 eV and 188.8 eV) with the intensity ratio of 3:2 and the energy separation of about 8.9 eV.¹ However, the characteristic peaks are not observed.

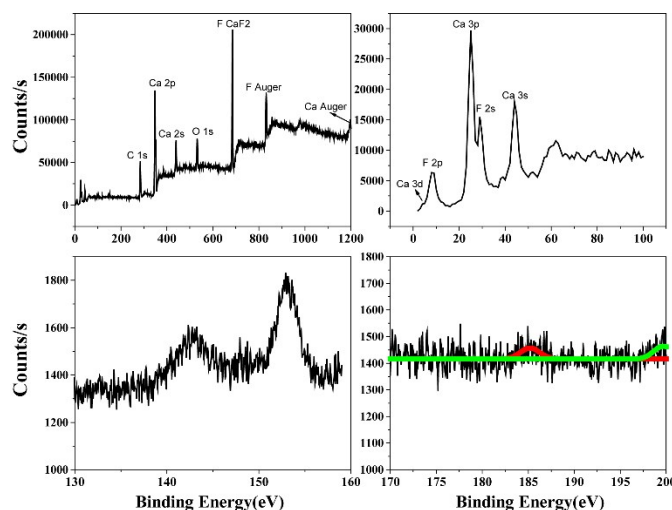


Figure S1. (a) Wide survey photoemission spectrum of CaF_2 : 0.5 mol% Yb^{3+} , 1 mol% Gd^{3+} , (b) the 0-100 eV region of photoemission spectrum of CaF_2 : 0.5 mol% Yb^{3+} , 1 mol% Gd^{3+} , (c) Gd 4d spectrum, (d) Yb 4d spectrum, red and green lines show trivalent component.

1. Y. Ohno, *Journal of Electron Spectroscopy and Related Phenomena*, 2008, **165**, 1-4.