Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for "Crystallographic and Spectroscopic Evidence for the Intrinsic Distortion in Disordered Crystal: β-$NaGdF_4$"

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Crystal Structure

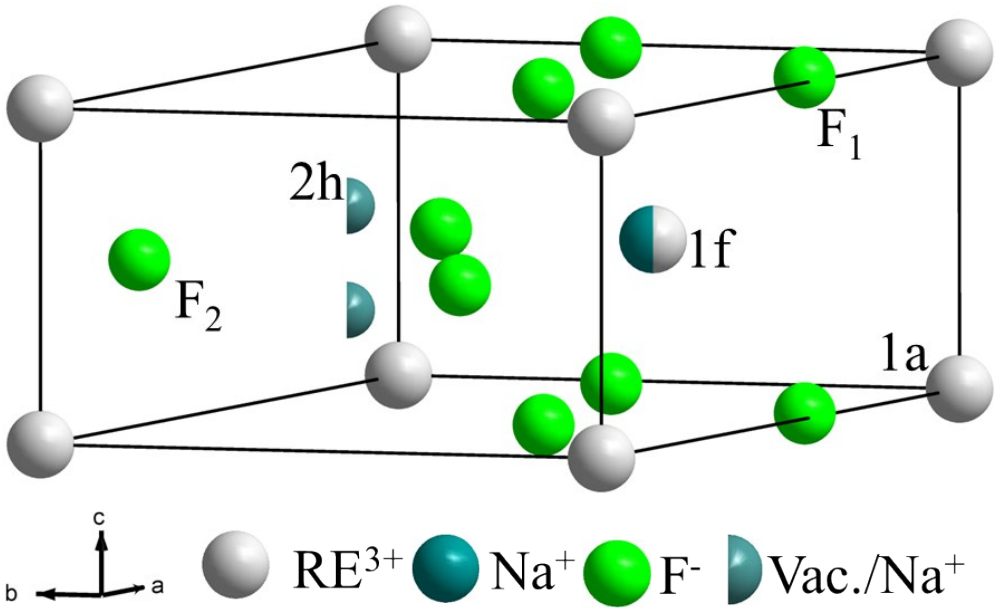

Figure S1. Crystal average structure of *β*-$NaREF_4$ (SG: *P*-6). The (*1a*) site is occupied by RE^{3+} ions, the (*1f*) site is half occupied by RE^{3+} ions and half by Na^+ ions, whereas the (*3j*) and (*3k*) sites are occupied by two types of fluorine ions denoted F_1 and F_2, respectively[1].

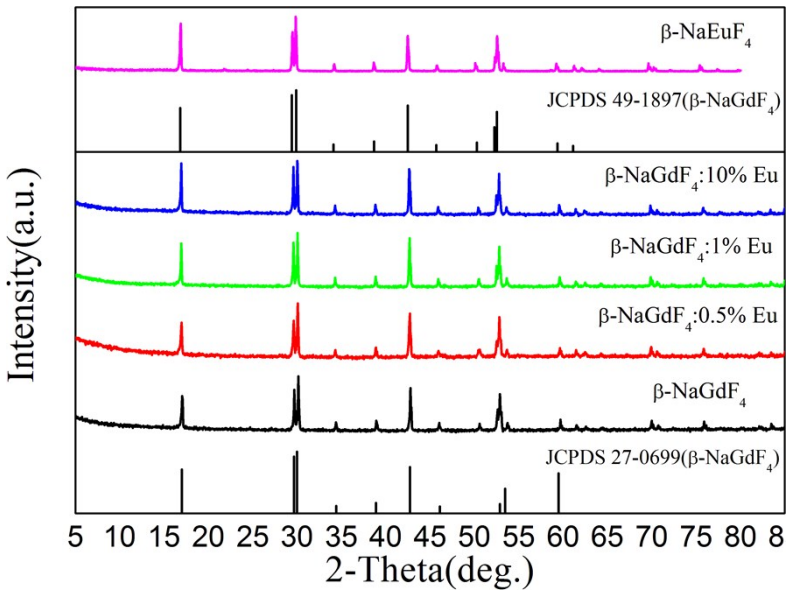

Figure S2. XRD patterns of *β*-$NaGdF_4$, *β*-$NaGdF_4$:0.5%Eu, *β*-$NaGdF_4$:1%Eu, *β*-$NaGdF_4$:10%Eu, and *β*-$NaEuF_4$ samples.

First-principles simulations

All calculations were performed using the DMol^3 package of Materials Studio 7.0[2], which is based on the density functional theory (DFT) methods. The Local Density Approximation (LDA) with the Perdew and Wang (PWC) exchange-correlation function in DFT[3,4], and the basis set using double numerical plus d-functions (DND) atomic orbitals version 3.5 were employed[5]. The real-space global orbital cutoff radius was chosen to be 5.8 Å. The Brillouin-zone was sampled into 3×3×2 *k*-point. The energy tolerance accuracy, maximum force, and displacement were set as 10^{-5} Ha, 2×10^{-3} Ha/Å, and 5×10^{-3} Å, respectively.

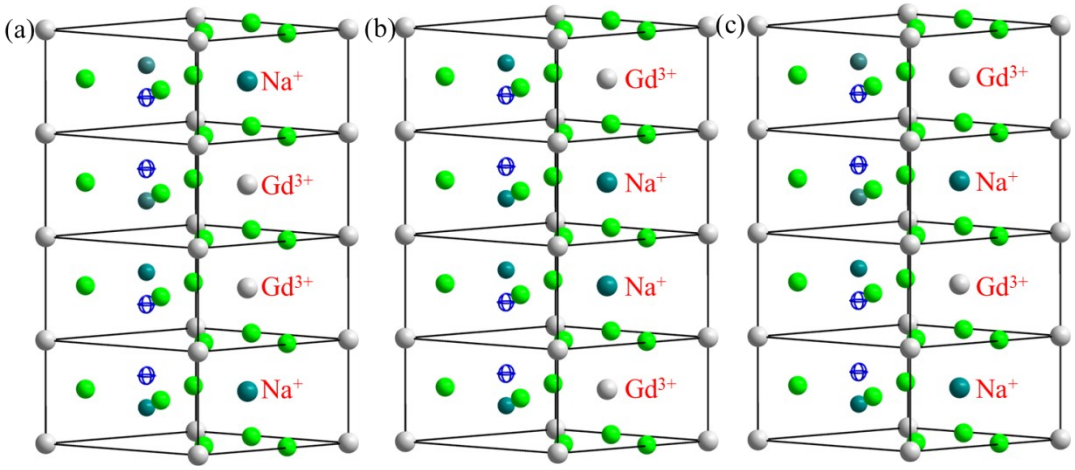

Figure S3. 3 type different arrangement of Gd^{3+} and Na^+ ions at 1f site in *β*-$NaGdF_4$ along c axis super cell model.

***Comments for Figure S3*:** In ordered to research the arrangement of Gd^{3+} and Na^+ ions at *1f* site in *β*-$NaGdF_4$ along c axis, the binding energy of 3 kinds (shown in Figure S3) of *β*-$NaGdF_4$ super cell model were calculated. The binding energy is -3257.90243 eV, -3257.34877 eV and -

3259.09539 eV, respectively, for 3 different kinds of structure model. Comparing the results of binding energy, the super cell model, in which Gd^{3+} and Na^{+} ions arrangement at *1f* site alternate with a translation distance c' = 2c, has the lowest binding energy. The result illustrate that the situation of (c) is most likely to be in the real case.

Photoluminescence (PL) spectra of β-$NaGdF_4:Eu^{3+}$

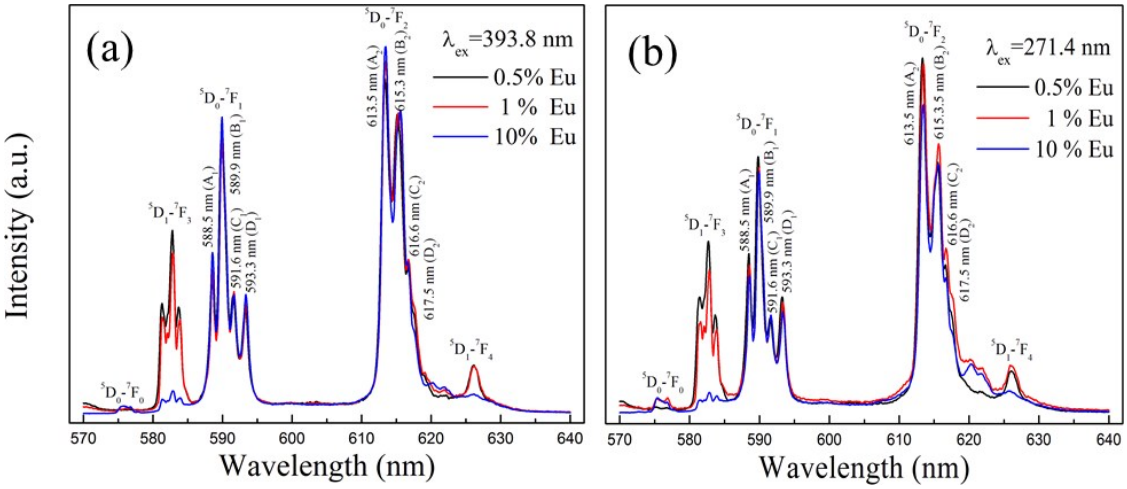

Figure S4. Emission spectra of β-$NaGd_{1-x}F_4$:xEu (x=0.005, 0.01, 0.1) samples under direct and indirect excitation at the wavelength λ_{ex}=393.8 nm(a) and 271.4 nm(b).

EXAFSs

EXAFS fitting report of *β*-$NaGdF_4$

Reduced Chi-square = 422

R-factor = 0.0025

Guess parameters +/- uncertainties (initial guess):

amp = 0.99 +/- 0.098 (1.0000)

enot_f = 4.80 +/- 0.87 (0.0000)

ss_1 = 0.0069 +/- 0.0015 (0.0030)

ss_3 = 0.0056 +/- 0.0040 (0.0030)

enot_g = -6.23 +/- 6.09 (0.0000)

enot_n = 16.00 +/- 0.18 (0.0000)

ss_4 = 0.00091 +/- 0.0059 (0.0030)

alph_1 = 0.00092 +/- 0.0041 (0.0100)

alph_2 = -0.014 +/- 0.013 (0.0100)

alph_3 = -0.014 +/- 0.0088 (0.0100)

alph_4 = 0.051 +/- 0.10 (0.0100)

Def parameters (using "FEFF0: Path 1: [F1_1]"):

ss_2 = 0.0069

Correlations between variables:

ss_4 and alph_4 --> 0.8802

amp and ss_1 --> 0.8325

enot_g and alph_3 --> 0.8149

enot_f and alph_1 --> 0.6758

ss_3 and ss_4 --> -0.5811

ss_3 and alph_4 --> -0.5127

enot_f and alph_2 --> 0.4960

enot_g and ss_4 --> 0.4330

ss_3 and alph_3 --> 0.4003

enot_f and enot_n --> 0.3488

enot_g and alph_4 --> 0.3187

All other correlations are below 0.25

EXAFS fitting result and report of β-$NaEuF_4$

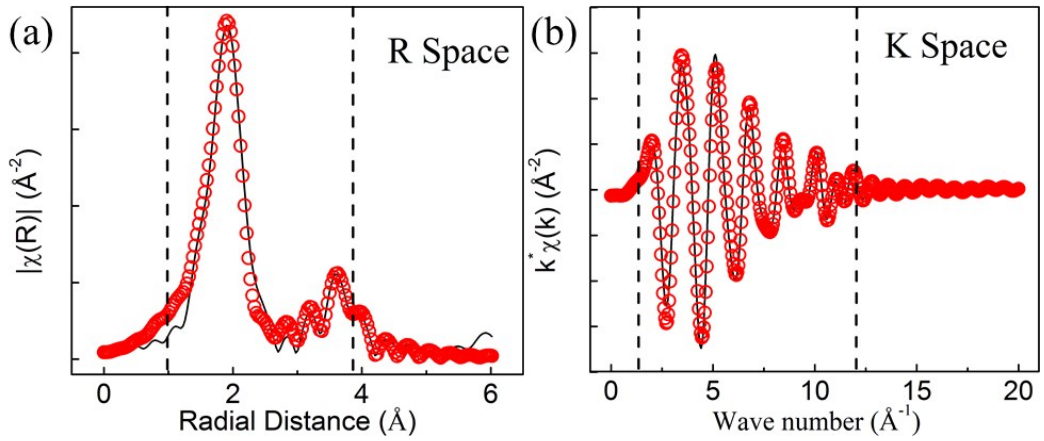

Figure S5. Fit of the theoretical (a) χ(R) and (b) χ(k) (points) in R and K space[6], respectively, to the Eu L_{III} edge data of β-$NaEuF_4$ (solid line) at 300 K. The range over which the fit has been made is shown by the dash line.

Table S1. The bond length (Å) of simulation value of Eu L_{III} and Gd L_{III} edge in pure β-$NaEuF_4$ and β-$NaGdF_4$.

Cation Site	Bond	Experimental radial distance of β-$NaEuF_4$ (Å)	Experimental radial distance of β-$NaGdF_4$ (Å)
1f	RE_{1f}-F_2	2.3236	2.3277
	RE_{1f}-F_1	2.4098	2.4138
	RE_{1f}-Na_{1f}	3.6107	3.7845
	RE_{1f}-Gd_{1a}	3.9242	3.8614
1a	RE_{1a}-F_1	2.3359	2.3322
	RE_{1a}-F_2	2.3734	2.3694
	RE_{1a}-Gd_{1a}	3.6107	3.6043
	RE_{1a}-Gd_{1f}	3.9242	3.8614
	RE_{1a}-Na_{1f}	3.9399	3.9672

Comments for Figure S6 and Table S1: The EXAFSs testing and fitting on β-$NaEuF_4$ sample, which belongs to the same family of compounds as β-$NaGdF_4$, also was carried out. The experiment and fitting result of shown in Figure S6 and Table S1. In the fitting process the same structural model as β-$NaGdF_4$ was used. And according to the result listed in Table S1, the trend of bond length is similar to ones in β-$NaGdF_4$ crystal. This can illustrate that β-$NaEuF_4$ and β-$NaGdF_4$ have the same crystal structure.

EXAFS fitting report of β-$NaEuF_4$

Reduced Chi-square = 3900

R-factor = 0.000250

Guess parameters +/- uncertainties (initial guess):

amp = 1.00 +/- 0.100 (1.0000)

enot_e = 1.12 +/- 4.51 (0.0000)

ss_1 = 0.0075 +/- 0.0011 (0.0030)

enot_n = 14.49 +/- 0.40 (0.0000)

enot_f = 5.02 +/- 0.99 (0.0000)

ss_3 = 0.0071 +/- 0.0034 (0.0030)

ss_4 = 0.0011 +/- 0.0026 (0.0030)

alpha_1 = -0.0039 +/- 0.0039 (0.0100)

alpha_2 = -0.022 +/- 0.011 (0.0100)

alpha_3 = -0.0040 +/- 0.0075 (0.0100)

Def parameters (using "FEFF0: Path 1: [F1_1]"):

ss_2 = 0.0075

Correlations between variables:

enot_e and alpha_3 --> 0.9337

amp and ss_1 --> 0.7683

ss_3 and ss_4 --> -0.7549

enot_f and alpha_1 --> 0.7374

alpha_2 and alpha_3 --> 0.4638

amp and enot_f --> -0.3479

enot_e and alpha_2 --> 0.3261

ss_1 and enot_f --> -0.3077

alpha_1 and alpha_3 --> -0.2716

amp and ss_4 --> 0.2672

ss_4 and alpha_1 --> -0.2641

enot_f and alpha_2 --> 0.2613

All other correlations are below 0.25

Reference

[1] Burns, J. H. Crystal Structure of Hexagonal Sodium Neodymium Fluoride and Related Compounds. Inorg. Chem. **1965**, 4(6), 881-886.

[2] Delley, B. From Molecules to Solids with the DMol^3 Approach [J]. J. Chem. Phys. **2000**, 113(18), 7756-7764.

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[4] Perdew, J. P., Wang Y. Accurate and Simple Analytic Representation of the Electron-gas Correlation Energy [J]. Phys. Rev. B: Condens. Matter **1992**, 45(23), 13244-13249.

[5] Inada, Y.; Orita H. Efficiency of Numerical Basis Sets for Predicting the Binding Energies of Hydrogen Bonded Complexes: Evidence of Small Basis Set Superposition Error Compared to Gaussian Basis Sets [J]. J. Comput. Chem. **2008**, 29, 225-232.

[6] Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-ray Absorption Spectroscopy Using IFEFFIT [J]. J. Synchrotron Radiat. **2005**, 12, 537-541.