Supplementary Information for “Crystallographic and Spectroscopic Evidence for the Intrinsic Distortion in Disordered Crystal: $\beta$-NaGdF$_4$”

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Crystal Structure

Figure S1. Crystal average structure of $\beta$-NaREF$_4$ (SG: $P-6$). The (1a) site is occupied by RE$^{3+}$ ions, the (lf) 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 $\beta$-NaGdF$_4$, $\beta$-NaGdF$_4$:0.5%Eu, $\beta$-NaGdF$_4$:1%Eu, $\beta$-NaGdF$_4$:10%Eu, and $\beta$-NaEuF$_4$ samples.
First-principles simulations

All calculations were performed using the DMol³ 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 $3\times3\times2$ $k$-point. The energy tolerance accuracy, maximum force, and displacement were set as $10^{-5}$ Ha, $2\times10^{-3}$ Ha/Å, and $5\times10^{-3}$ Å, respectively.

**Figure S3.** 3 type different arrangement of Gd$^{3+}$ and Na$^+$ ions at 1f site in $\beta$-NaGdF$_4$ along c axis super cell model.

**Comments for Figure S3:** In order to research the arrangement of Gd$^{3+}$ and Na$^+$ ions at 1f site in $\beta$-NaGdF$_4$ along c axis, the binding energy of 3 kinds (shown in Figure S3) of $\beta$-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 $I\bar{f}$ 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-NaGdF₄:Eu³⁺

Figure S4. Emission spectra of β-NaGd₁₋ₓF₄ₓ:xEu (x=0.005, 0.01, 0.1) samples under direct and indirect excitation at the wavelength λₑₓ=393.8 nm(a) and 271.4 nm(b).
EXAFSs

EXAFS fitting report of $\beta$-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 $\beta$-NaEuF$_4$

Figure S5. Fit of the theoretical (a) $\chi(R)$ and (b) $\chi(k)$ (points) in R and K space$^{[6]}$, respectively, to the Eu L$_{III}$ edge data of $\beta$-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\textsubscript{III} and Gd L\textsubscript{III} edge in pure β-NaEuF\textsubscript{4} and β-NaGdF\textsubscript{4}.

<table>
<thead>
<tr>
<th>Cation Site</th>
<th>Bond</th>
<th>Experimental radial distance of β-NaEuF\textsubscript{4} (Å)</th>
<th>Experimental radial distance of β-NaGdF\textsubscript{4} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1f</td>
<td>RE\textsubscript{1f}F\textsubscript{2}</td>
<td>2.3236</td>
<td>2.3277</td>
</tr>
<tr>
<td></td>
<td>RE\textsubscript{1f}F\textsubscript{1}</td>
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<td>2.4138</td>
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<tr>
<td></td>
<td>RE\textsubscript{1f}Na\textsubscript{1f}</td>
<td>3.6107</td>
<td>3.7845</td>
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<tr>
<td></td>
<td>RE\textsubscript{1f}Gd\textsubscript{1a}</td>
<td>3.9242</td>
<td>3.8614</td>
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<tr>
<td>1a</td>
<td>RE\textsubscript{1a}F\textsubscript{1}</td>
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<tr>
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<td>RE\textsubscript{1a}Gd\textsubscript{1a}</td>
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<td>RE\textsubscript{1a}Gd\textsubscript{1f}</td>
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<td>RE\textsubscript{1a}Na\textsubscript{1f}</td>
<td>3.9399</td>
<td>3.9672</td>
</tr>
</tbody>
</table>

Comments for Figure S6 and Table S1: The EXAFSs testing and fitting on β-NaEuF\textsubscript{4} sample, which belongs to the same family of compounds as β-NaGdF\textsubscript{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\textsubscript{4} was used. And according to the result listed in Table S1, the trend of bond length is similar to ones in β-NaGdF\textsubscript{4} crystal. This can illustrate that β-NaEuF\textsubscript{4} and β-NaGdF\textsubscript{4} have the same crystal structure.
EXAFS fitting report of β-NaEuF₄

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
tenot_f and alpha_2 --> 0.2613
All other correlations are below 0.25
Reference


