Supporting Information

A Mechanistic Understanding of Non-Classical Crystal Growth in Hydrothermally Synthesized Sodium Yttrium Fluoride Nanowires

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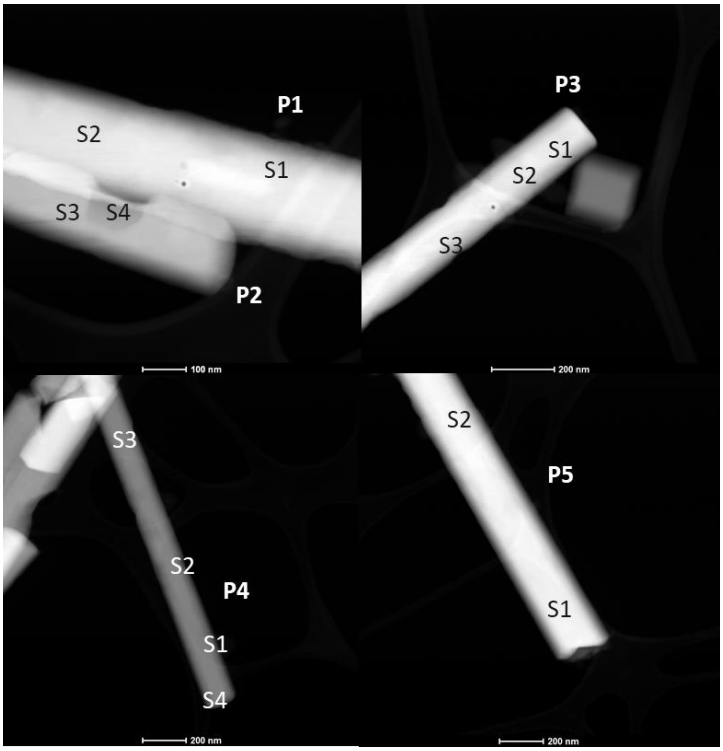
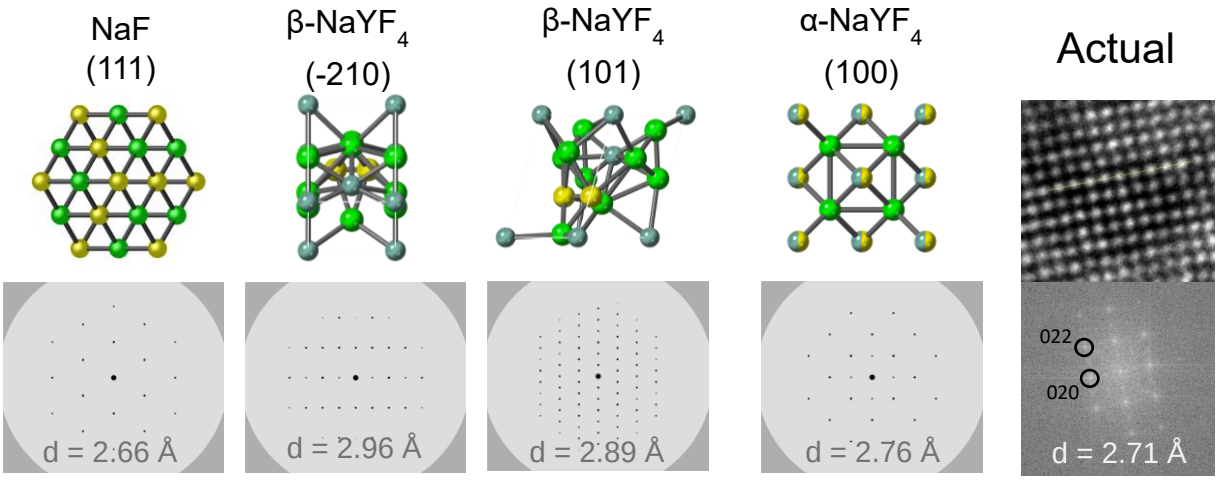
Figure S1: STEM-EDS analysis of mixed-α nucleated β particles (percentages in atomic percent with respect to total rare earth concentration)



Particle	Spot	Y%	Yb%	Er%
P1	S1	93.3	6.16	0.5
	S2	94.4	4.88	0.8
P2	S1	98.4	1.32	0.3
	S2	97.1	2.73	0.2
P3	S1	98.8	0.26	1
	S2	98.7	0.47	0.9
	S3	90.6	7.8	1.6
P4	S1	94.7	5.26	0
	S2	91.6	5.32	3.1
	S3	94.7	4.72	0.6
	S4	90.3	8.15	1.6
P5	S1	89.5	8.8	1.7
	S2	90.1	8.16	1.7

Figure S2: Simulations of SAED patterns of various orientations of potential particles in the synthesis vessel with similar d spacings compared to experimental data



022: Theoretical = 0.514 $Å^{-1}$, Experimental = 0.515 $Å^{-1}$
020: Theoretical = 0.351 $Å^{-1}$, Experimental = 0.359 $Å^{-1}$

Figure S3: Mass Spectrum via Atom Probe Tomography of the β-$NaYF_4$ end cap

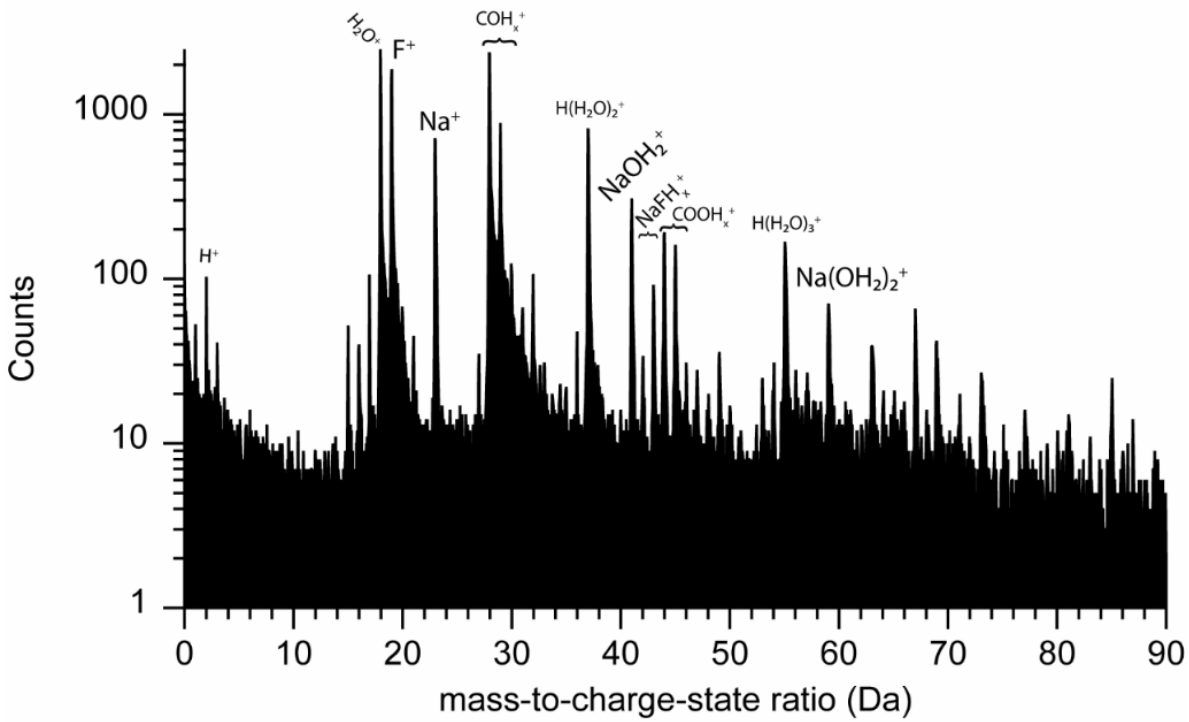


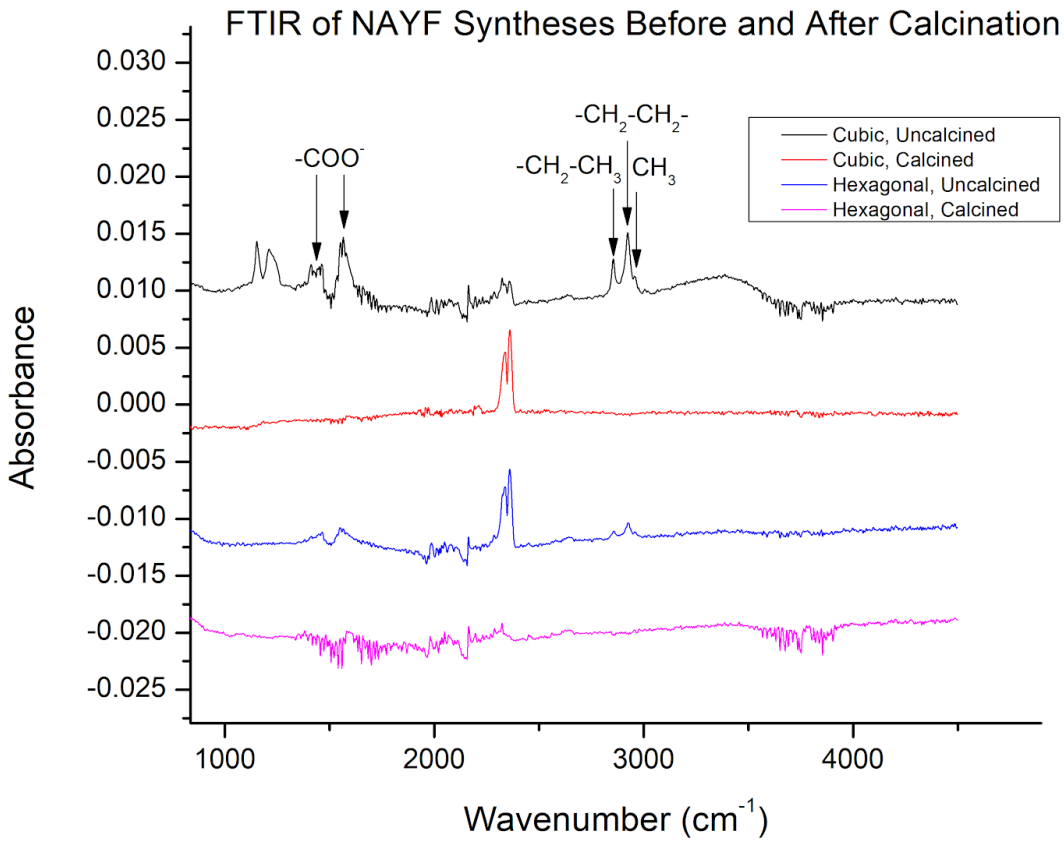
Table S4: DLS characterization of $NaYF_4$ particles

	Average hydrodynamic radius (nm)	Average Zeta Potential (mV)
α (cubic)	326.9	-71.0
β (hexagonal)	750.8	+18.7

Figure S4: Sample DLS data

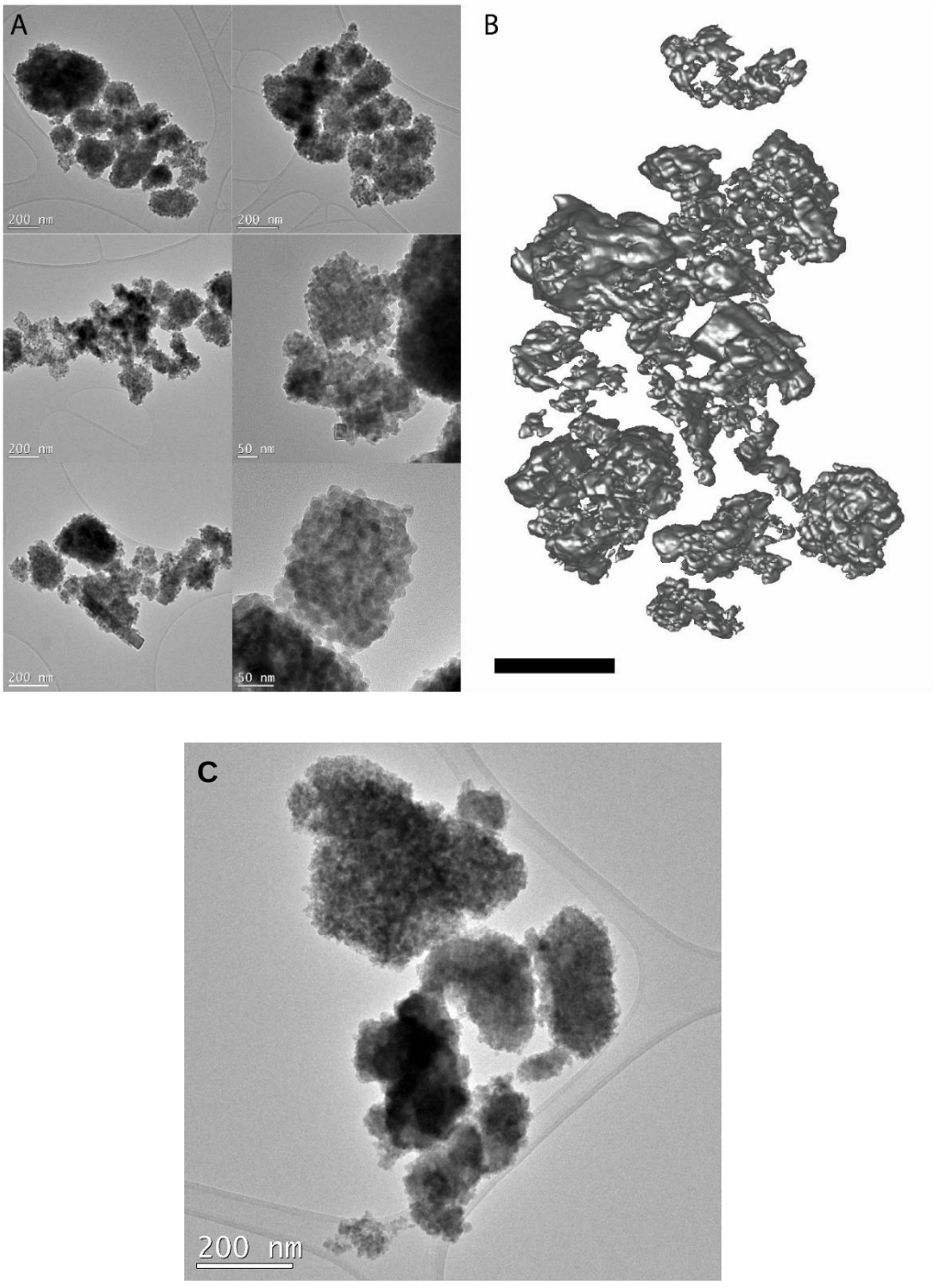
Representative DLS data. Many scans were averaged in Table S4, so numbers vary slightly.

Figure S5: FTIR of $NaYF_4$ particles before and after calcination



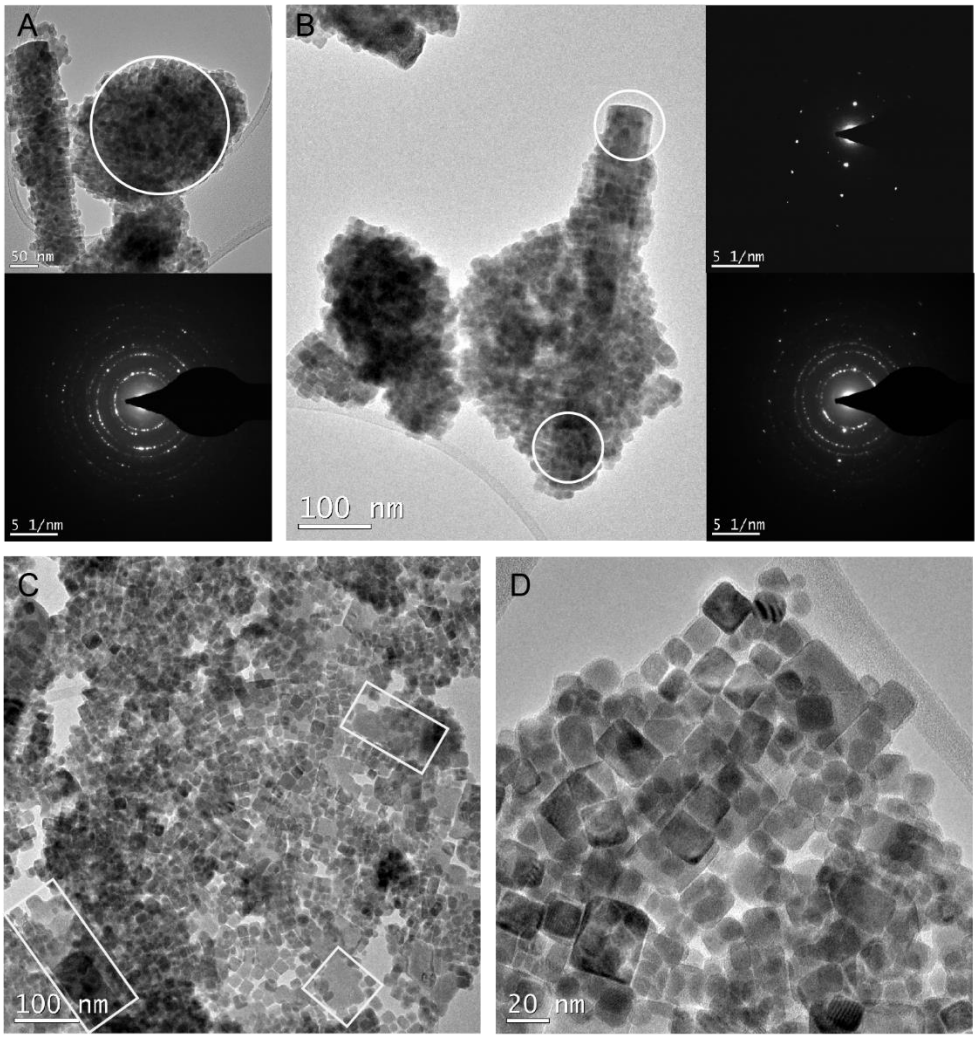
Experimental: Fourier-Transform Infrared (FTIR) spectra were taken on a Bruker VERTEX 70v FTIR Spectrometer in attenuated total reflectance (ATR) mode. Powdered $NaYF_4$ samples were placed on the diamond ATR crystal and 16 scans were averaged. The spectral resolution of the instrument is 2 cm^{-1}.

Figure S6: TEM of faceted α-$NaYF_4$ clusters



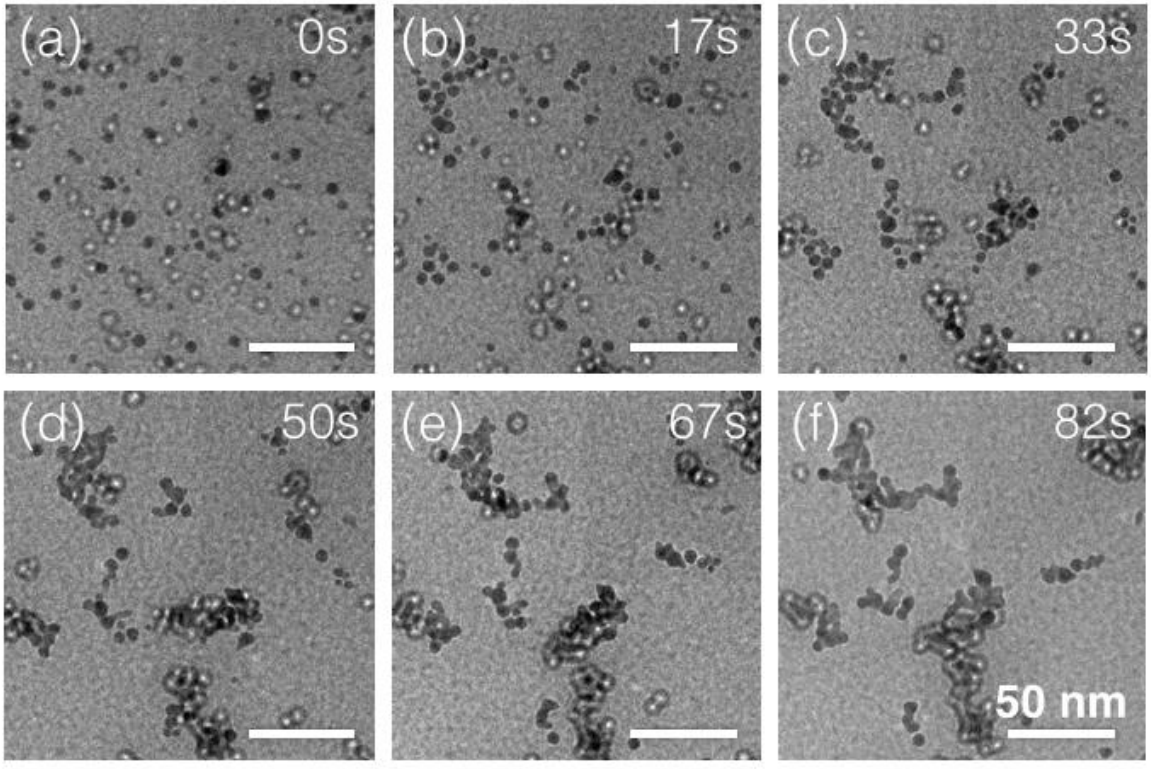
(A) Multiple clusters of α-$NaYF_4$ showing clear mesoscale faceting.at the three hour time point (B) Tomographic reconstruction of several α-$NaYF_4$ clusters. Scale = 200 nm. (C) Cluster of α-$NaYF_4$ showing mesoscale faceting at 100 minute time point

Figure S7: TEM of α-$NaYF_4$ Mesocrystals



(A) TEM and SAED of an α-$NaYF_4$ cluster from the three hour synthesis showing orientation along multiple axes. Also note the single β-$NaYF_4$ nanowire growing inside a cluster of small α-$NaYF_4$. Circled region is approximate area of SAED. (B) β-$NaYF_4$ nanowire growing from a clearly faceted α-$NaYF_4$ cluster with SAED. Note crystallographic orientation of both species in bottom SAED. (C) Two dimensional layer of α-$NaYF_4$ from the same synthesis showing clear mesoscopic order. Highlighted particles appear to have undergone oriented attachment. (D) Zoom on mesoscopically ordered α-$NaYF_4$.

Figure S8: Liquid cell TEM of cubic $NaYF_4$ particles suspended in water aggregating due to the electron beam.



EXAFS Structural Analysis: Further details

I. Data reduction to $k^3\chi(k)$

The transmission edge jumps were about 0.025 and 0.05 optical density units. Fluorescence count rates were 70 kHz and 100 kHz near the edge. The tall white-line peak at the edge is sensitive to overabsorption, so it was possible to use the transmission data (assumed free of this effect) as a template with which to apply a simple correction to the fluorescence data. The resulting EXAFS data was good to about 14$Å^{-1}$.

2. Model for P$\bar{6}$ crystal structure

We assume that the Yb is in a Y site. To resolve the mixed occupancy of the Y2/Na1 site, we first transformed the structure into a P1 basis using WebATOMS,[1] doubled the c-axis lattice parameter, and halved the *z* position parameter of each atom, thus leaving the Cartesian-coordinate positions of all the atoms unaffected, but making an empty space in the doubled

structure. We then filled that space with a copy of the existing atoms, shifted by $\vec{c}/2$, resulting in a structure which was identical to the original but described using twice as many atoms in twice as big a cell. We then removed the Y2 site in the original half and the Na1 site in the copied half. The resulting crystal-structure description, with Yb in the Y1 site is as follows:

```
## This P1 file was generated by Demeter 0.9.26
## Demeter written by and copyright (c) Bruce Ravel, 2006-2018
#
# File modified to double c and remove Y2 in the lower copy and Na1 in
the upper.
#Note that Na2 is half-occupied, so path strengths need to
# be adjusted
space = P 1
a     =   5.91480    b     =   5.91480    c     =   6.99200
alpha =  90.00000    beta  =  90.00000    gamma = 120.00000
rmax  =   5.24400    core  = Y1
polarization = 0  0  0
shift =   0  0  0
atoms
# el.     x           y           z        tag
  Yb      0.00000     0.00000     0.00000   Yb1
  Na     0.66670     0.33333     0.25000   Na1
  Na     0.33333     0.66670     0.34450   Na2
  Na     0.33333     0.66670     0.15550   Na2
  F      0.64600     0.12560     0.00000   F1
  F      0.87440     0.52040     0.00000   F1
  F      0.47960     0.35400     0.00000   F1
  F      0.69700     0.72200     0.250000   F2
  F      0.27800     0.97500     0.250000   F2
  F      0.02500     0.30300     0.250000   F2
  Yb      0.00000     0.00000     0.50000   Yb1a
  Yb      0.66670     0.33333     0.75000   Yb2a
  Na     0.33333     0.66670     0.84450   Na2a
  Na     0.33333     0.66670     0.65550   Na2a
  F      0.64600     0.12560     0.50000   F1a
  F      0.87440     0.52040     0.50000   F1a
  F      0.47960     0.35400     0.50000   F1a
  F      0.69700     0.72200     0.750000   F2a
  F      0.27800     0.97500     0.750000   F2a
  F      0.02500     0.30300     0.750000   F2a
```

This table became the input for WebATOMS to make the feff.inp file. To address the vacancies on the Na2 sites, we manually halved all the path amplitudes involving this site.

3. Fitting

We tried fitting with Yb in Y1 and Y2 sites, but found that fitting Yb only in the Y1 position produced the lowest reduced chi-squared value. We ended up with 8 paths, ranging in distance from the nearest-neighbor fluorines at 2.45 Å (undistorted structure) to a Na2 shell at 4.18 Å.

The free parameters used were overall E_0, overall S_0^2, distance shifts for the two 1NN fluorine shells, the $\Delta\sigma^2$ for these shells (equal for the two), the $\Delta\sigma^2$for the higher shells, a distance shift relative to the reference structure for the F and Y atoms, and an independent one for the Na1 atom at 3.83 Å. We also tried freeing the occupancy for the Na2 sites, the distance of the Na2 shell at 3.58 Å and the $\Delta\sigma^2$for the Na2 site at 4.18 Å but none of these helped the fit.

4. Results

We find that the EXAFS fits with our substituted $P\bar{6}$ model, but with most distances shorter than in the pure $Na_{1.5}Y_{1.5}F_6$ model, which makes sense as Yb^{3+} is a smaller ion than Y^{3+}. The Yb-F distances were 2.25,2.40 Å (error bar 0.02 Å, reference structure 2.454,2.458 Å). The Na1 at a nominal distance of 3.84 Å is instead at 3.78$\pm$ 0.03 Å, and the one at 4.12 Å in the reference structure is found at 4.12$\pm$0.03 Å. The other distances are 0.05$\pm$0.02 Å greater than in the reference structure.

SI References

(1) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12* (4), 537–541. https://doi.org/10.1107/S0909049505012719.