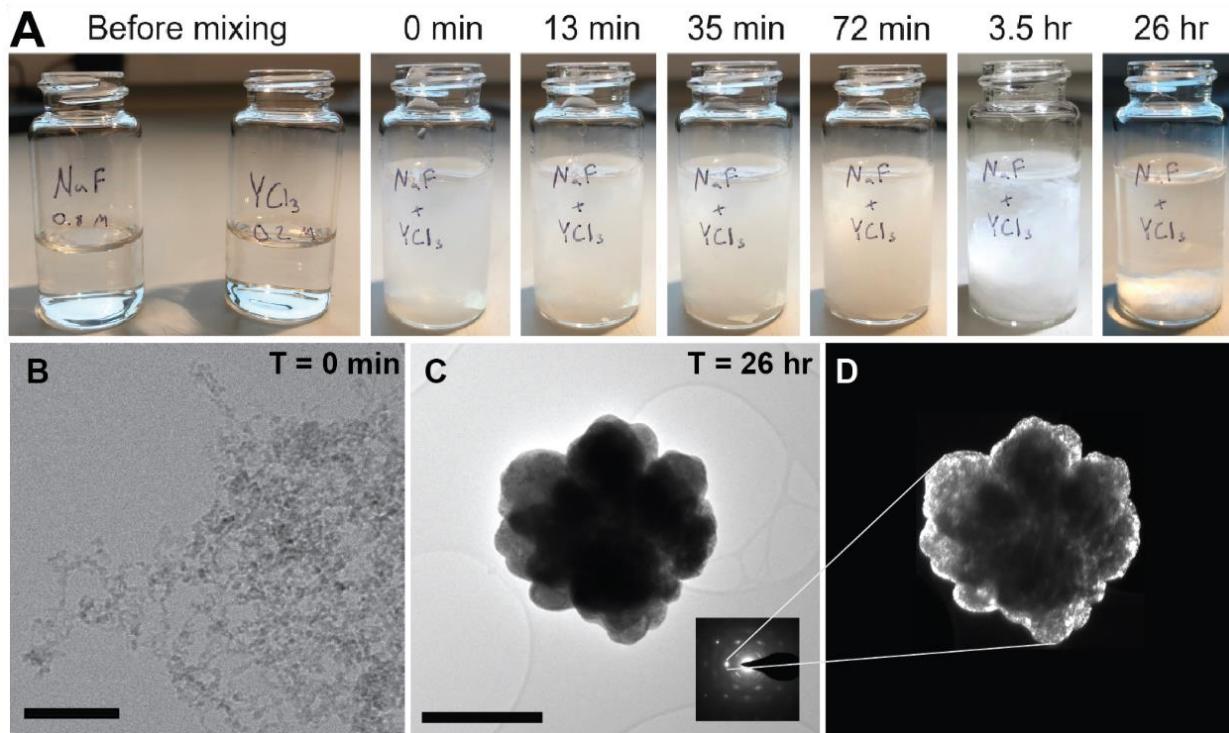


Multi-Step Crystallization and Chemical Evolution of Sodium Yttrium Fluoride

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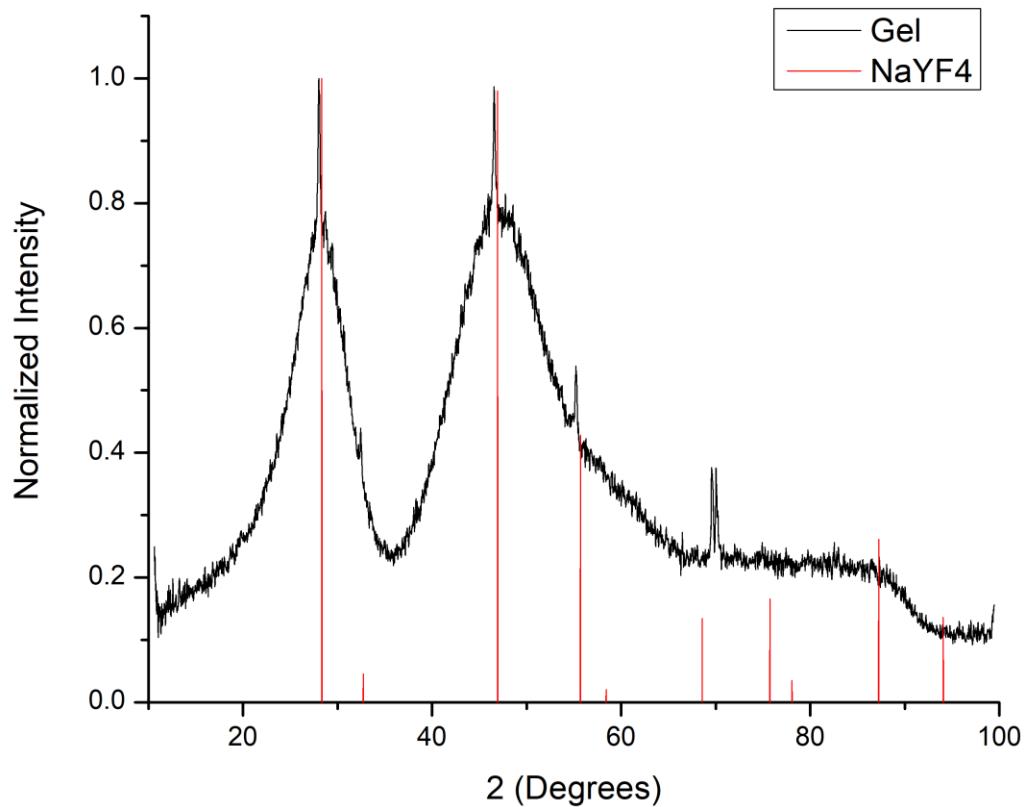
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Figure S1: Collapse of gel over time



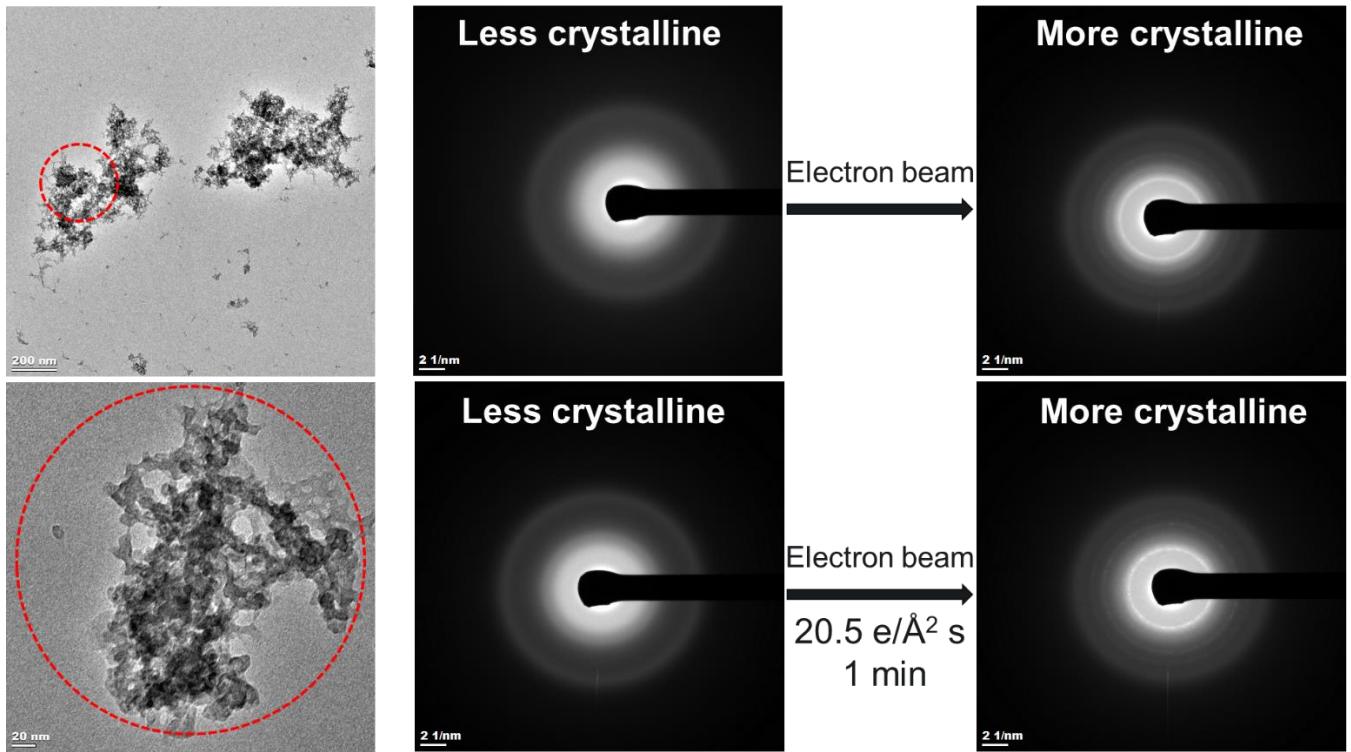
(A) Initial formation of the gel and its collapse over the course of hours. Apparent color variations are solely the result of variations in lighting from a nearby window. (B) Cryo-TEM of the product immediately after formation (scale bar = 50 nm) (C) TEM of the 26-hour product and diffraction (scale bar = 400 nm) and (D) dark field image showing its single crystalline nature (see Fig. 3A)

Figure S2: Powder X-ray Diffraction of the gel



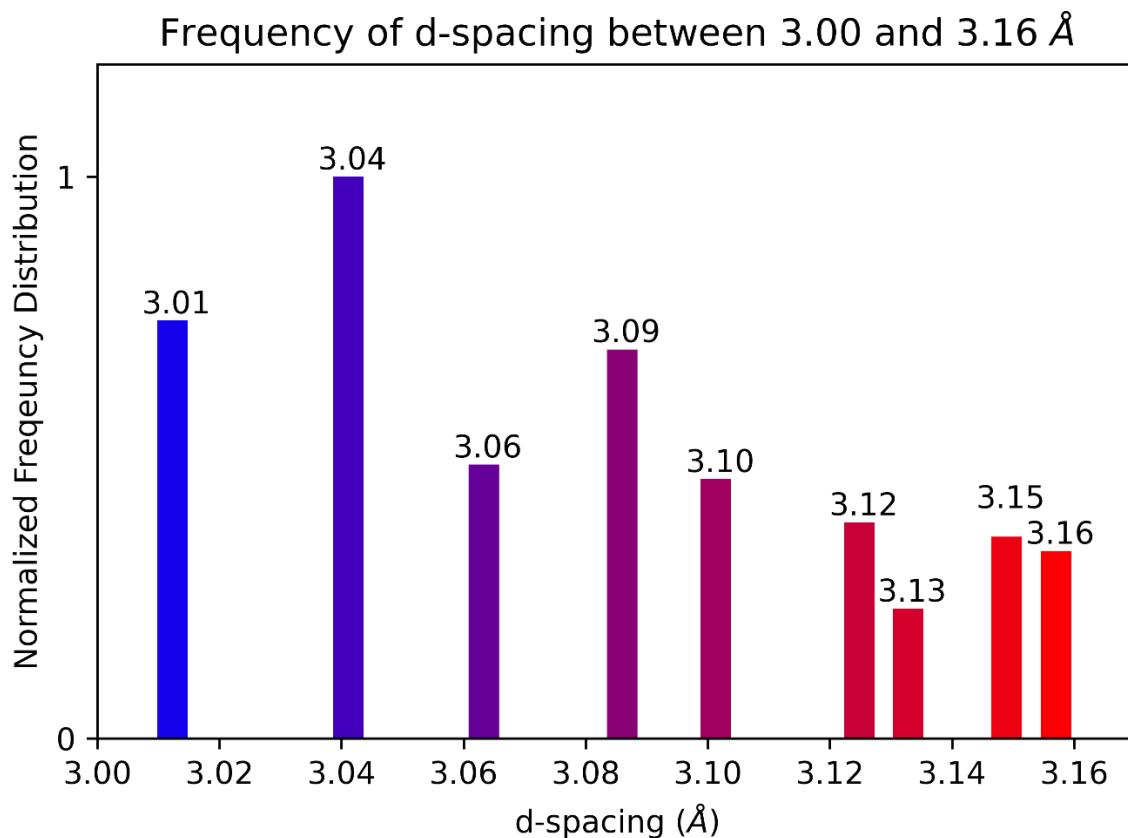
Powder X-ray diffraction measurements of the gel show very broad peaks with spacings consistent with cubic NaYF or YF₃. The sharp peaks correspond to large crystals of α -NaYF that have formed from the gel, as discussed in Fig. S1.

Figure S3: Beam-induced crystallization of the gel



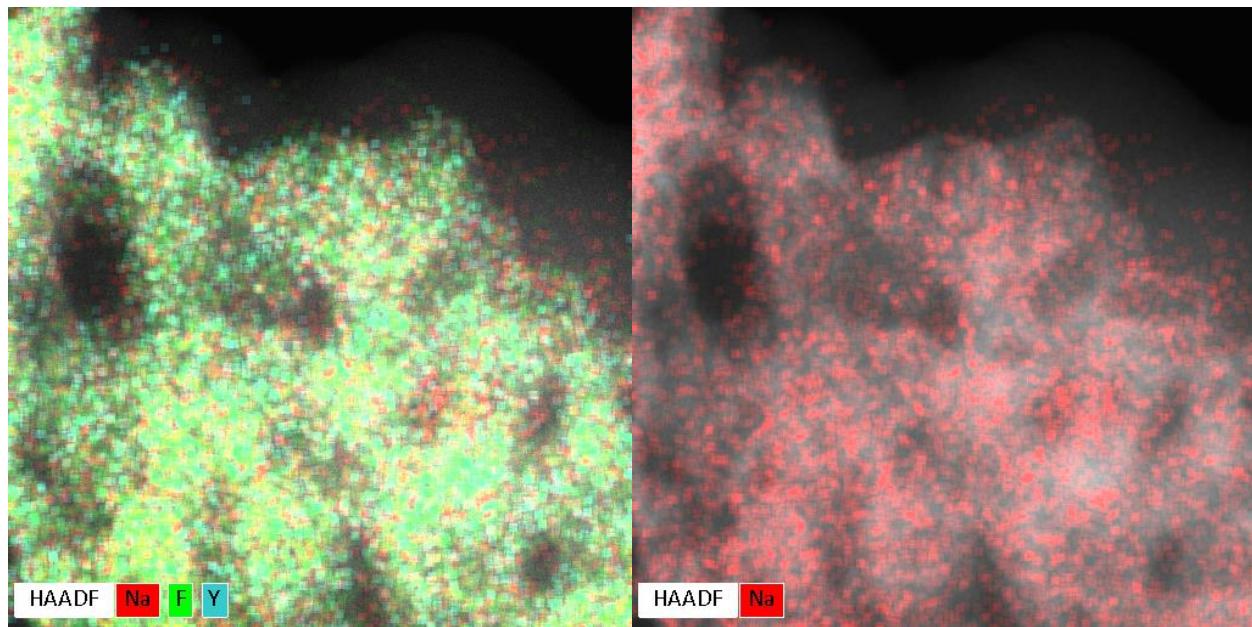
Standard TEM/SAED experiments on the gel in vacuum induced significant crystallization in the gel, as shown by the sharper rings in the SAED patterns. There is no significant change to the morphology of the particles during that time.

Figure S4: FFT analysis of TEM images



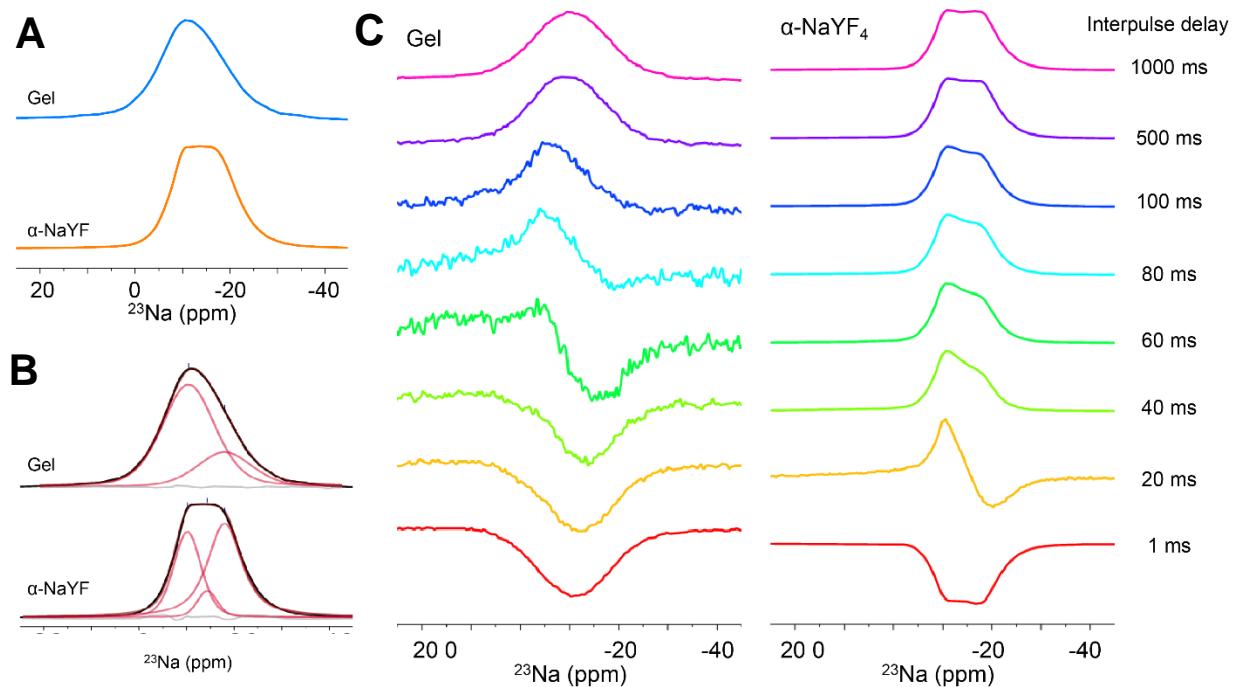
Histogram of all measured d-spacings in Fig. 2E in the 111 range. The full data set is also included in the supporting information files.

Figure S5: STEM-EDS maps



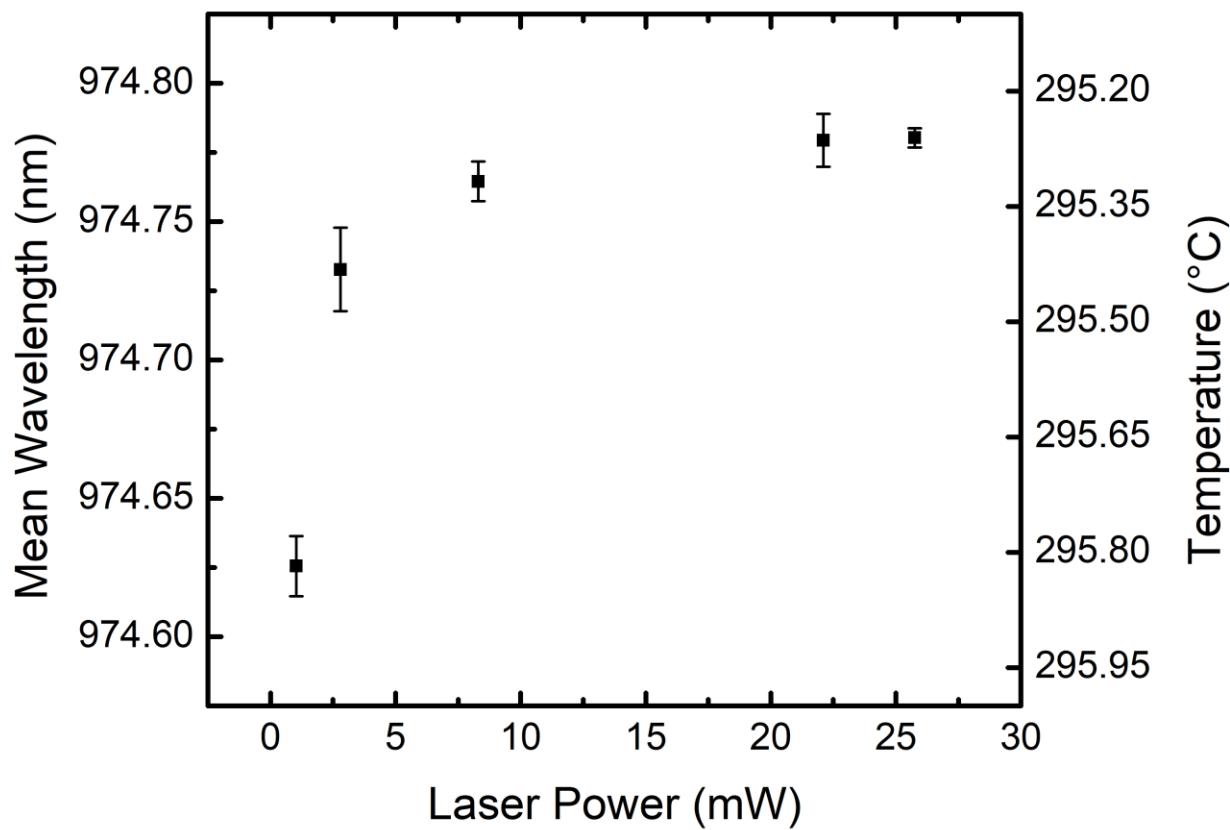
STEM-EDS maps of the gel showing the distribution of Na, Y, and F in the left image and Na only in the right image. This clearly shows that sodium is present within the gel, however other data are necessary to confirm fluctuations of the sodium content.

Figure S6: ^{23}Na NMR



(A) Single-pulse ^{23}Na NMR of the gel and the $\alpha\text{-NaYF}$. Excitation by a hard pulse at 86 kHz or a soft pulse at 17 kHz produce nearly identical results. (B) Deconvolution of (A) showing two major resonances centered at -18 ppm and -9.5 ppm, which are assigned to Na sites in the bulk and at the surface or near defects, respectively. (C) ^{23}Na inverse recovery spectra of the gel and the $\alpha\text{-NaYF}$ after varying Interpulse delay times.

Figure S7: Laser refrigeration of NaYF gel



Laser refrigeration data for 10% Yb³⁺ doped NaYF gel, showing a decrease in temperature of up to 0.55°C as the 1020 nm laser power is increased to 25 mW.

Laser refrigeration measurements were performed by attaching the gel sample to an optical fiber mounted inside an optical cryostat (Janis ST500). The Yb³⁺ cations were excited with a 1020 nm diode laser (QPhotonics QFBGLD-1020-400) to induce luminescent upconversion, cooling the gel. The upconverted photoluminescence of the NaYF gel was collected at several different laser irradiances. The mean fluorescent wavelength for each spectrum was compared against calibrations at known temperatures to determine cooling efficiency.