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Observation of Void Formation in Cubic $NaYF_4$ Nanocrystals Using *In Situ* Heating Transmission Electron Microscopy

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Lanthanide-doped sodium yttrium fluoride ($NaYF_4$) nanocrystals have been heavily studied for their upconverting properties [1–3] and specifically their potential for laser cooling [4,5]. $NaYF_4$ is also notable for its two crystallographic polymorphs, cubic (α) and hexagonal (β). While there has been much research into synthetic methods of making one or the other [6–8], the actual, heat-driven phase conversion mechanism between the two remains poorly understood [9]. In 2010, Shan and colleagues reported their observation that α-$NaYF_4$ nanoparticles form hollow structures upon heating in a process analogous to the Kirkendall effect, which they propose is a step in the phase transformation [10]. Here we report an observation of that void formation using *in situ* heating transmission electron microscopy (TEM).

Cubic $NaYF_4$ was synthesized using hydrothermal methods [11] to form ~30 nm particles with a pseudo-cubic morphology, and washed and centrifuged with both ethanol and water. A dilute sample was dropcast from ethanol onto a Hummingbird Scientific MEMS heating chip. The chip was allowed to dry and placed in a Hummingbird Scientific 1550 series heating holder. The sample was inserted into a JEOL 2100 TEM equipped with a Direct Electron DE12 camera, and the sample was resistively heated to >300^{o}C in vacuum.

Our studies show a clear depletion of material from the center of the particles as heat is applied, allowing us to observe this Kirkendall-type void formation as it occurred (Figure 1). This provides insight into the exact mechanism of this process as a function of temperature. Additionally, we have shown that the crystal lattice is preserved on a particle after the void formation (Figure 2), which suggests that the particle has not yet undergone a total phase transformation. This suggests that there are more steps in this phase transformation that have yet to be elucidated.

These data show us that *in situ* TEM is an extremely useful technique to study these types of phase transformations, and we are optimistic that it can be employed to help us fully understand the phase transformation in the $NaYF_4$ system. This study may be aided by liquid cell and environmental TEM techniques, allowing us to watch the phase conversion in a more representative environment. Furthermore, we hope to study this system by coupling a light source to the *in situ* holder, allowing us to spectroscopically probe the phase transformation at the same time that we watch it happen [12].

References:

[1] P Ghosh, A Patra, J. Phys. Chem. C **112** (2008) p.19283–19292.
[2] M Huang, F Meng, Luminescence **20** (2005) p.276–278.
[3] F Wang et al., Nature **463** (2010) p.1061–1065.
[4] MP Hehlen, in: Proc. SPIE, 2010, pp. 1–12.
[5] X Zhou et al., Adv. Mater. **28** (2016) p.8658–8662.
[6] X Liang et al., Adv. Funct. Mater. **17** (2007) p.2757–2765.
[7] Y Sun et al., Nanotechnology **18** (2007) p.275609.
[8] G Yi et al., Nano Lett. **4** (2004) p.2191–2196.
[9] Y Sui et al., J. Phys. Chem. C **116** (2012) p.1732–1739.
[10] J Shan et al., J. Nanoparticle Res. **12** (2010) p.1429–1438.
[11] X Wang et al., Inorg. Chem. **45** (2006) p.6661–6665.
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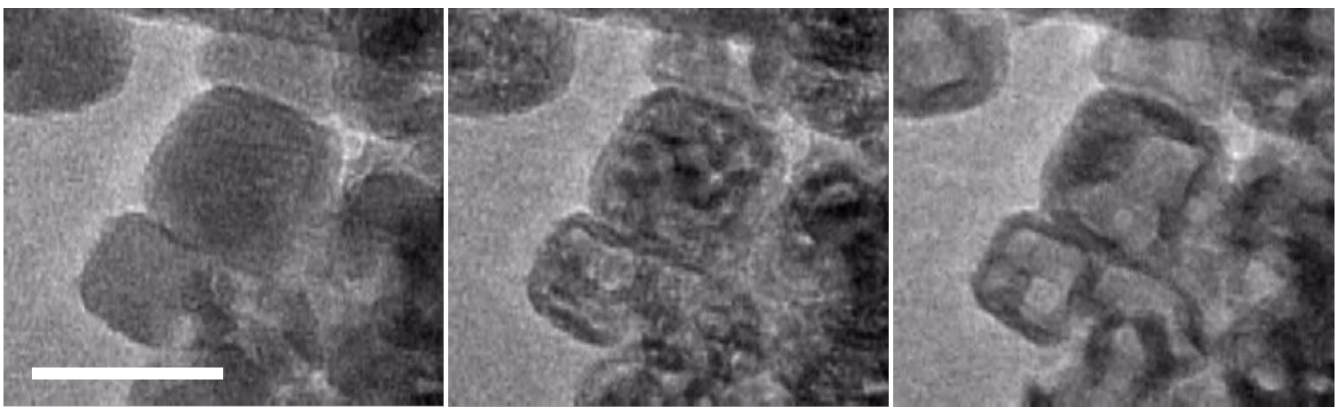

Figure 1. Progression (from left to right) of Kirkendall voids in *in situ* heated (~300^{o}C) α-$NaYF_4$, scale bar = 40 nm

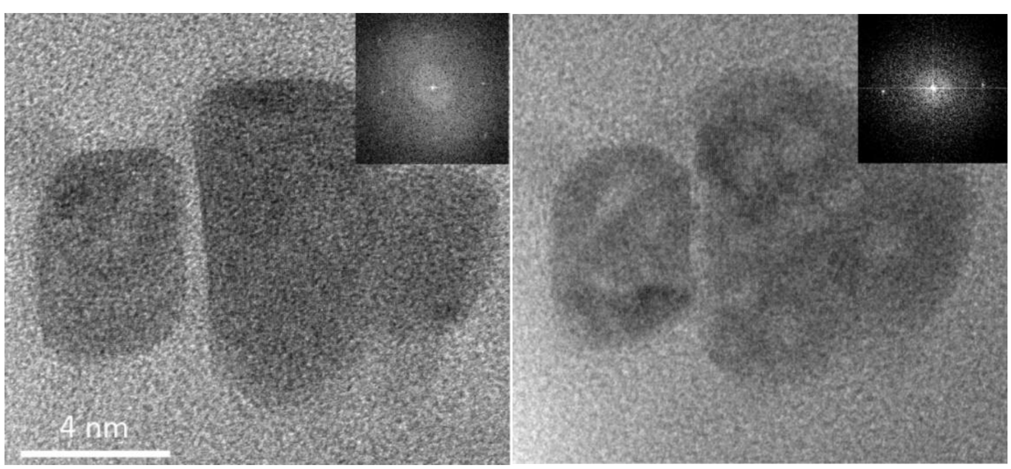

Figure 2. HRTEM and FFT of $NaYF_4$ particles before (left) and after (right) heating to ~300^{o}C, showing that the particles retain at least part of their crystallinity after the voids form

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