In-situ TEM study of the phase transformation in a single lanthanide co-doped NaYF4 unconverting nanoparticle

KIM, Y.H.[1], Pin, M.W.[1], Park, E.J.[2], Kim, Y.I.[1], Jeon, C.H.[2], Kwon, J.H.[1] and Ha, T.H.[2]

[1] Korea Research Institute of Standards and Science, Republic of Korea, [2] Korea Research Institute of Bioscience and Biotechnology, Republic of Korea

Upconverting nanoparticles (UCNPs) have attracted much attention as potential materials for biomedical applications such as bioimaging and near-infrared (NIR)-initiated drug delivery systems, due to a unique luminescence mechanism: UCNPs convert long-wavelength light to short-wavelength light through the excitation processes with multiple photons[1-3]. They can be also used for various optical devices such applications as solid-state lasers, solar cells, displays, and low-intensity IR imaging devices due to specific optical properties, low background light, and low toxicity[4-6]. The Yb^{3+}-sensitized Er^{3+} system in $NaYF_4$ nanocrystalline matrices ($NaYF_4$:Yb,Er) is considered to be the most efficient UCNP. It is well known that the upconversion efficiency of $NaYF_4$:Yb,Er nanoparticles depends on the phase of nanoparticles, cubic alpha-phase and/or hexagonal beta-phase. Although the phase transformation phenomena, alpha-phase to beta-phase and/or beta-phase to alpha-phase in $NaYF_4$:Yb,Er UCNP, have been studied for a long time, the atomistic evolution during the phase transformations on the nanometer-sized scale has not been detailedly explored to date[7-9]. The study on the phase transformation was mainly carried out via ex-situ experiments, heating with a furnace and structural analysis with X-ray diffraction. There still remains a lack of understanding in the alpha- to beta-phase and/or beta- to alpha- phase transformations of $NaYF_4$:Yb,Er UCNPs.

In situ heating experiments of $NaYF_4$:Yb,Er UCNPs were conducted in a transmission electron microscope (TEM) to investigate the morphological and microstructural evolutions during heating. The atomic behavior on a single $NaYF_4$:Yb,Er UCNP is observed in real time based on the analysis of high-resolution TEM images. We found two different routes to reach the stable alpha-phase from the metastable cubic structure on a single $NaYF_4$:Yb,Er UCNP during the heating. The first route is related to the formation of the beta-phase as an intermediated structure, and the other is the direct change from the metastable structure to the stable Φ#177;-phase with an assist from a liquid-like phase. The stable beta-phase of $NaYF_4$:Yb, Er partially emerged at 420 °C, and it was again transformed to the stable alpha-phase over 620 °C. The remaining metastable cubic phase in the single nanoparticle was directly transformed to the stable alpha-phase.

Reference

[1] Lee, J. *et al. Nat. Mater.* **13**, 524-529 (2014).
[2] Lai, J. *et al. ACS Nano* **9,** 5234-5245 (2015).
[3] Zhang, P. *et al. J. Am. Chem. Soc.* **129,** 4526-4527 (2007).
[4] Nam, S. H. *et al. Angew. Chemie-Int. Ed.* **50,** 6093-6097 (2011).
[5] Malinowski, M. *et al. J. Lumin.* **60-61,** 179-182 (1994).
[6] Zhou, Y. *et al. J. Solid State Chem.* **171,** 391-395 (2003).
[7] Thoma, R. E. *et al. Inorg. Chem.* **2**, 1005-1012 (1963.)
[8] Klier, D. T. *et al. J. Mater. Chem.* **3**, 11228-11238 (2015).
[9] Laihinen, T. *et al. J. Therm. Anal. Calorim.* **121**, 37-43 (2015).