Low Temperature Synthesis of Lanthanide Doped $NaYF_4$ Crystals and temperature effect on NIR-to-Vis Upconversion

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Motivations

- NIR-to-Vis upconversion photoluminescence (UCPL) refers to a visible light emission under a near-infrared excitation (anti-Stokes).
- Upconversion materials have broad applications in biological labeling, imaging and therapy, photovoltaics, temperature sensing, and anti-counterfeiting.
- Most well-known material, lanthanide-doped $NaYF_4$, are synthesized by using hydrothermal and thermal decomposition methods at high temperature (>300 °C) in an inert atmosphere. Herein highly crystallized cubic $NaYF_4$: Yb^{3+}, Er^{3+} are synthesized at low temperatures (≤ 80 °C) and in air.

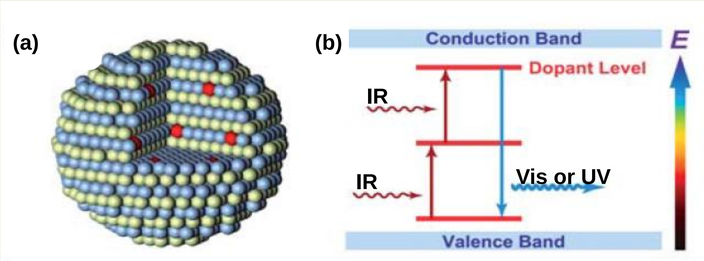

Figure 1. (a) Schematic structure of UC crystals composed of a crystalline host ($NaYF_4$) and lanthanide dopant(s), and (b) energy level diagram of the upconverting phenomenon.[1]

Material Synthesis and Characterizations

- $NaYF_4$: Yb^{3+}, Er^{3+} crystals are synthesized in an aqueous solution by using $ReCl_3 \cdot 6H_2O$, NH_4F, NaCl as precursors (Re = Y, Yb, Er).
- As-synthesized crystals are further annealed at 400, 500, 600 °C (in air) for different durations.
- High temperature (up to 500 °C) UCPL is investigated by performing a spectroscopy at an elevated temperature.

Results and Discussion

- Role of solvent: crystal structure of host material ($NaYF_4$) can be varied by a rational selection of solvents. Reaction in water favors a cubic crystal growth and hexagonal $NaYF_4$ can be prepared by adding ethanol.

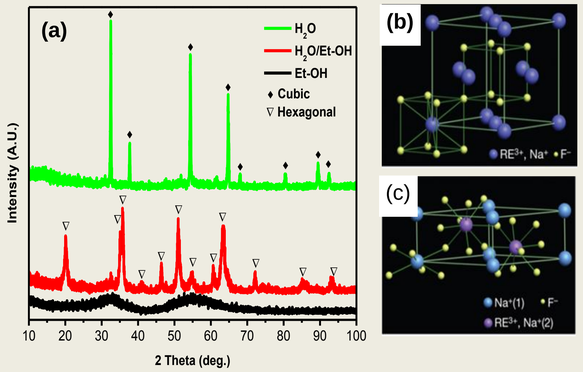

Figure 2. (a) XRD patterns of as-synthesized samples within different solvents (water, ethanol and mixture of water/ethanol, 4/1 v/v) at 75-80 °C in air, (b) cubic and (c) hexagonal crystal structure[2] of lanthanide doped $NaYF_4$.

- Thermal annealing dramatically enhances UC emission, especially for red light. Structurally, this process increases crystallinity by reducing defect density and relieving internal stresses. The as-synthesized crystals has a tendency to "shrink" after annealing (right shift of peaks in XRD), where particle size also increases as in SEM images.
- Thermal quenching on UCPL is also observed. Thermally created traps can disturb the light emitting by reducing population of photons.
- In comparison to room temperature UCPL, high temperature spectra suggest red emission is more sensitive to thermal treatment, indicating the $^4F_{9/2}$ level is prone to this process.

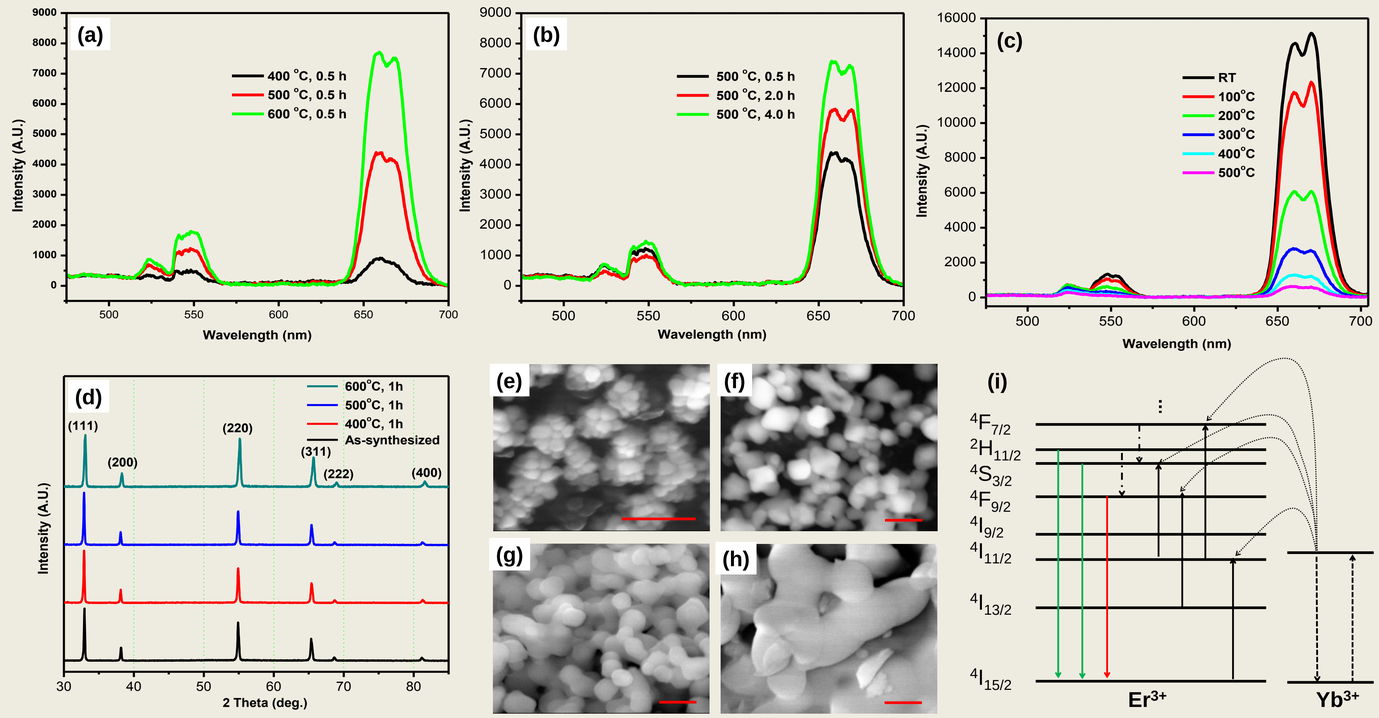

Figure 3. (a, b) Room temperature UCPL spectra of annealed samples, (c) in-situ UCPL spectra at different temperatures, (d) XRD of as-synthesized and annealed samples, (e)-(h) SEM images of as-synthesized, 400, 500, and 600 °C annealed samples (scale bar, 500 nm), and (i) energy level diagram[3] for UCPL of $NaYF_4$: Yb $^{3+}$, Er^{3+}.

Conclusions and Acknowledgement

- **Lanthanide doped $NaYF_4$ crystals can be synthesized readily by using co-precipitation within an aqueous solution at low temperatures and in air.**
- **Thermal annealing induces high efficient NIR-to-Vis upconversion.**
- **Thermal quenching effect on upconversion of cubic $NaYF_4$: Yb $^{3+}$, Er^{3+} is observe by in-situ high temperature PL spectroscopy.**
- **Multiple emissions (red and green) of UCL shows red PL is more sensitive to temperatures.**
- **We acknowledge financial support from NCESR, NSF, and MDA.**

References

[1] Wang F., Banerjee D., Liu Y., Chen X., Liu X., Analyst, 2010, 135, 1839-1854
[2] Wang F., Han Y., Lim C. S., Lu Y., Wang J., *et al.*, Nature, 2009, 463, 1061-1065
[3] Ye X., Collins J.E., Kang Y, Chen J., Chen D., *et al.*, PNAS. 2010, 52, 22430-22435