

## Nanostructural Evolution and Property of Silicates Doped with Er<sup>+3</sup>

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The telecommunications industry has taken advantage of Er<sup>+3</sup>'s photoluminescence at 1.54 $\mu$ m to develop Er<sup>+3</sup> doped optical amplifiers for application in high bandwidth data transmission lines [1]. Development of next generation of optical amplifiers requires enhancement of the width and flatness of the 1.54 $\mu$ m emission peak. Co-doping with Al<sup>+3</sup> and Y<sup>+3</sup> has been shown to improve these optical properties while increasing Er<sup>+3</sup> solubility in a Si or silica host [2,3]. We have used HRTEM imaging, Nano-EDXs Analysis, as well as X-ray Diffraction to study the nanostructural evolution of Er<sup>+3</sup> doped silicates co-doped with either Al<sup>+3</sup> or Y<sup>+3</sup>.

Amorphous nanopowders (10-20 nm in diameter) with a composition of SiO<sub>2</sub>-18Al<sub>2</sub>O<sub>3</sub>-2Er<sub>2</sub>O<sub>3</sub> (SAE) were synthesized by combustion flame – chemical vapor condensation, while nanopowders of SiO<sub>2</sub>-8Y<sub>2</sub>O<sub>3</sub>-2Er<sub>2</sub>O<sub>3</sub> (SYE) were synthesized by sol gel synthesis [4]. The SAE and SYE samples were then heat treated at 600, 800, 1000, 1200, and 1400 $^{\circ}$ C. Upon annealing these far-from equilibrium nanopowders showed an increase in both peak width and intensity of photoluminescence at  $\sim$ 1.54 $\mu$ m (figure 1).

HRTEM analysis of the SAE nanopowders shows the amorphous nature of the nanopowders at 600 $^{\circ}$ C, and the formation of nanocrystals at 800 $^{\circ}$ C (figure 2a and 2b). With increasing temperature, agglomeration of these nanocrystals results in a crystalline matrix with amorphous nanoinclusions (figure 2c). These results are supported by selected-area electron diffraction patterns (figure 2a and 2b inserts) which show a broad amorphous diffraction rings at 600 $^{\circ}$ C, with the appearance of crystalline spots at 800 $^{\circ}$ C.

Nano-Energy Dispersive X-rays analysis of SAE and SYE samples after heat treatment reveal the existence of an amorphous cristobalite phase (SiO<sub>2</sub>) and a crystalline phase consisting of Si, O, Er, and the codopant. The composition and structure of this phase is determined by further XRD analysis. For the SYE samples, this crystalline phase has a pyrochlore structure with a composition of Er<sub>x</sub>Y<sub>2-x</sub>Si<sub>2</sub>O<sub>7</sub>. The formation of this solid solution is indicated by the similarity in patterns for Er<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>. In an analogous manner, the SAE system also develops a pyrochlore phase of Er<sub>x</sub>Al<sub>2-x</sub>Si<sub>2</sub>O<sub>7</sub>.

Diffusion of Er<sup>+3</sup> ions to take up specific lattice locations results in enhanced optical properties of these silicate materials. Noted phase separations are evaluated by comparison with Y<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> systems in which equilibrium phases of cristobalite and Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> are found. Identical valence and nearly matching ionic radii suggest the formation of a solid solution in which the Er<sup>+3</sup> replaces Y<sup>+3</sup> ions.

## References

- 1) Becker, P.C.; Olsson, N.A.; Simpson J.R. *Erbium-Doped Fiber Amplifiers Fundamentals and Technology*. Harcourt Brace & Company, London (1999).
- 2) Zhou, Y.; Lam, Y.L.; Wang, S.S.; Liu, H.L.; Kam, C.H.; Chan, Y.C. *Appl. Phys. Lett.* (1997), 71, 587.
- 3) Ting C.; Chen S.; Hsieh W.; Lee H. *J. Appl. Phys.* (2001), 90, 5564.
- 4) Haines, C.D.; Ranganathan, V.; Halpern, S.B.; Kear, B.H.; Klein, L.C.; Sigel, G.; Yao, N. *Broad, Flat Fluorescence Emissions from Nanostructured Rare-Earth Doped Silicates* (Submitted)

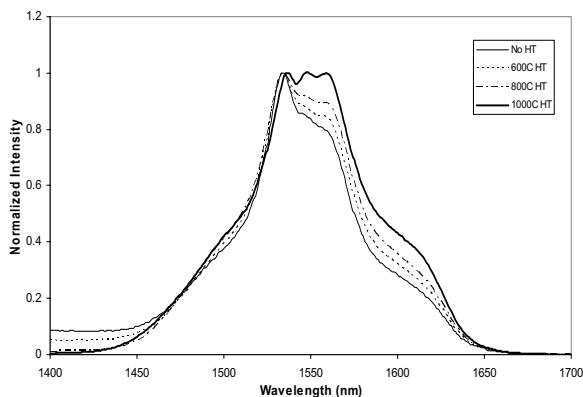


Figure 1a. Photoluminescence Spectra for SAE samples after heat treatment at 600, 800 and 1000 °C.

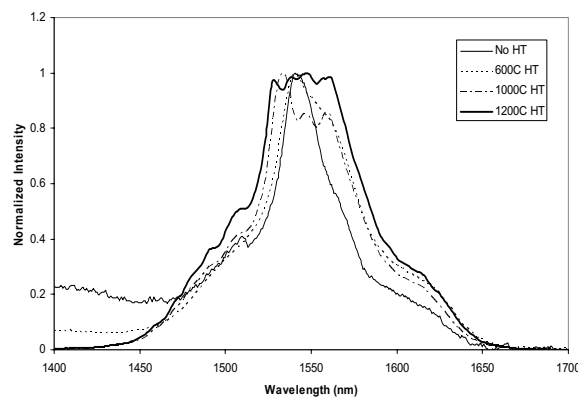


Figure 1b. Photoluminescence Spectra for SYE samples after heat treatment at 600, 1000 and 1200 °C.

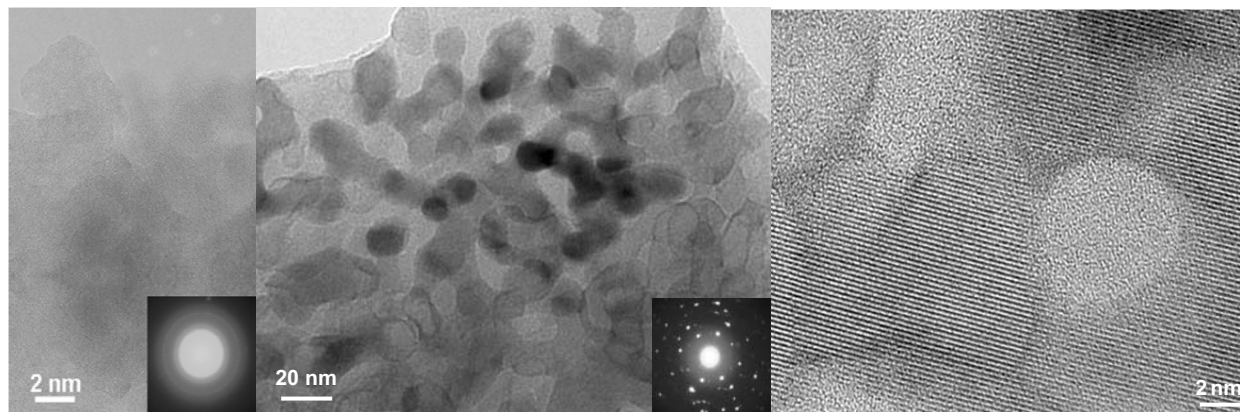


Figure 2a

Figure 2b

Figure 2c

Fig 2a. Amorphous SAE samples annealed at 800°C. Fig 2b. Growth of nanocrystalline phase in SAE samples after heat treatments of 1000°C. Fig 2c. Amorphous Silica Nanoinclusions in devitrified SAE samples after annealing at 1400°C.