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Author(s)	Epicier, T.; Konno, J. T.; Sato, K. et al.
Citation	
Version Type	VoR
URL	https://hdl.handle.net/11094/89459
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Quantitative analysis of an Yb^{3+}-doped YAG optical ceramic at the atomic level by STEM-HAADF

T Epicier[1], TJ Konno[2], K Sato[2], G Boulon[3]

1 University of Lyon, INSA of Lyon, MATEIS UMR CNRS 5510, Bât. B. Pascal, 69621 Villeurbanne, France
2 Materials Processing and Characterization Division, Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Sendai 983-0836, Japan
3 University of Lyon, Claude Bernard/Lyon1 University, Physical Chemistry of Luminescent Materials Lab., UMR CNRS 5620, Bât Kastler, 69622 Villeurbanne, France.

Thierry.epicier@insa-lyon.fr
Keywords: YAG optical ceramic, rare earth dopant, atomic STEM

The research activity on advanced optical materials for various applications, such as lasers, scintillators, phosphors with LEDs, is greatly increasing with the availability of sintered transparent polycrystalline ceramics, which present some advantages compared to single crystals (sizes, mechanical strength, overall production cost). Understanding their optical properties requires a detailed investigation of their microstructure, especially regarding the exact location of the required dopants (e.g. rare earth elements such as Ce^{3+}, Nd^{3+} or Yb^{3+}). For example, it was recently shown by careful Transmission Electron Microscopy (TEM) observations that Ce^{3+} strongly segregates at grain-boundaries within YAG (Yttrium Aluminium Garnet $Y_3Al_5O_{12}$) [1].

Identifying dopants at the atomic level by Electron Microscopy techniques is now possible according to the technological progress, especially in the so-called STEM-HAADF mode [2].

In STEM-HAADF imaging (Scanning TEM in High Angle Annular Dark Field), the incoherent signal scattered at large angles (between 75 and 210 mrad in the present study) is collected on an annular detector. The intensity for one atom is roughly proportional to Z^2, where Z is the atomic number of the probed specie. Then, heavy atoms (such as rare-earth elements) give rise to a brighter contrast that lighter species (such as O, Al and even Y in the YAG structure). Atomic resolution is achieved if the probe size is smaller than the interatomic distance within the material of interest under adequate viewing directions. Crystallographic details concerning the YAG phase are shown in figure 1.

We have performed both High Resolution (HR) and HAADF imaging in the [001] orientation of undoped YAG and 1.4 at.% Yb^{3+}-doped YAG polycrystal using a TITAN FEI electron microscope, operating at 300 kV. Whereas C_s-corrected HREM imaging failed in resolving unambiguously dopants even in very thin crystalline region (down to 5 nm, as confirmed by a careful calibration using low-loss EELS), uncorrected HAADF imaging, with an electron probe below 0.2 nm in size, has allowed Yb-containing atomic columns to be revealed, owing to the contrast enhancement caused by the presence of heavy Yb atoms which substitute to Y atoms in both types of columns '1' and '2' depicted in figure 1 d) (Z_{Yb} = 70, to be compared to Z_Y = 39).

A statistical analysis of the histograms of integrated intensities of atomic columns within both pure and doped YAG crystals will be presented, which is statistically fully consistent with the hypothesis of a random distribution of Yb^{3+} within the YAG lattice [4].

References

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[4] The authors gratefully acknowledge funding from an ICC-IMR program in the frame of the French-Japanese ELyT international laboratory (www.elyt.com). L. Esposito (ISTEC-CNR, Faenza, Italy) is gratefully acknowledged for providing the Yb^{3+}-doped YAG sample.

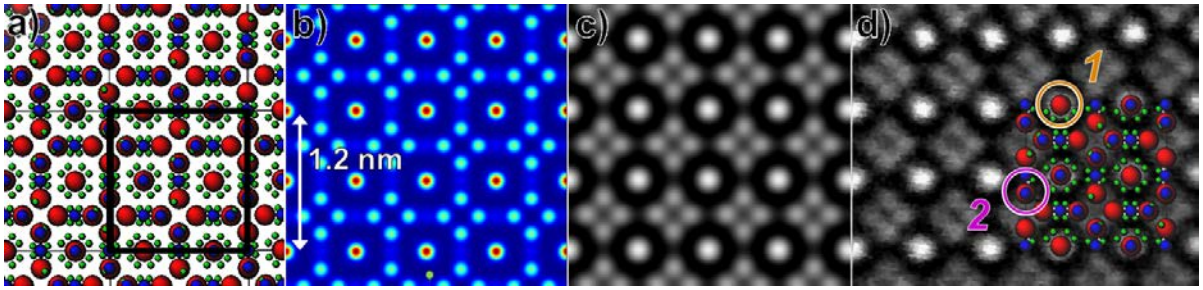

Figure 1. *YAG crystalline structure ((Yttrium-Aluminium-Garnet $Y_3Al_5O_{12}$, cubic structure with a = 1.20062 nm, space group: Ia-3d). a): atomic projection along [001]; Y, Al an O atoms are respectively displayed in red, blue and green. b): Z^2 map showing the more pronounced intensity of 'type 1' atomic columns with respect to 'type 2' columns (labeled in d)), which indeed contain twice less atoms per unit length (2 pairs (Y + Al) and 1 such pair per cell respectively). c): indicative STEM simulation of an ideally one-cell thick crystal according to the experimental conditions used in this work, with a probe size of 0.15 nm. d): typical experimental image from a pure YAG crystal; Y-containing columns '1' and '2' are labeled, both being possible hosts for Yb^{3+}. Figures b) and c) were generated with the QSTEM program [3].*

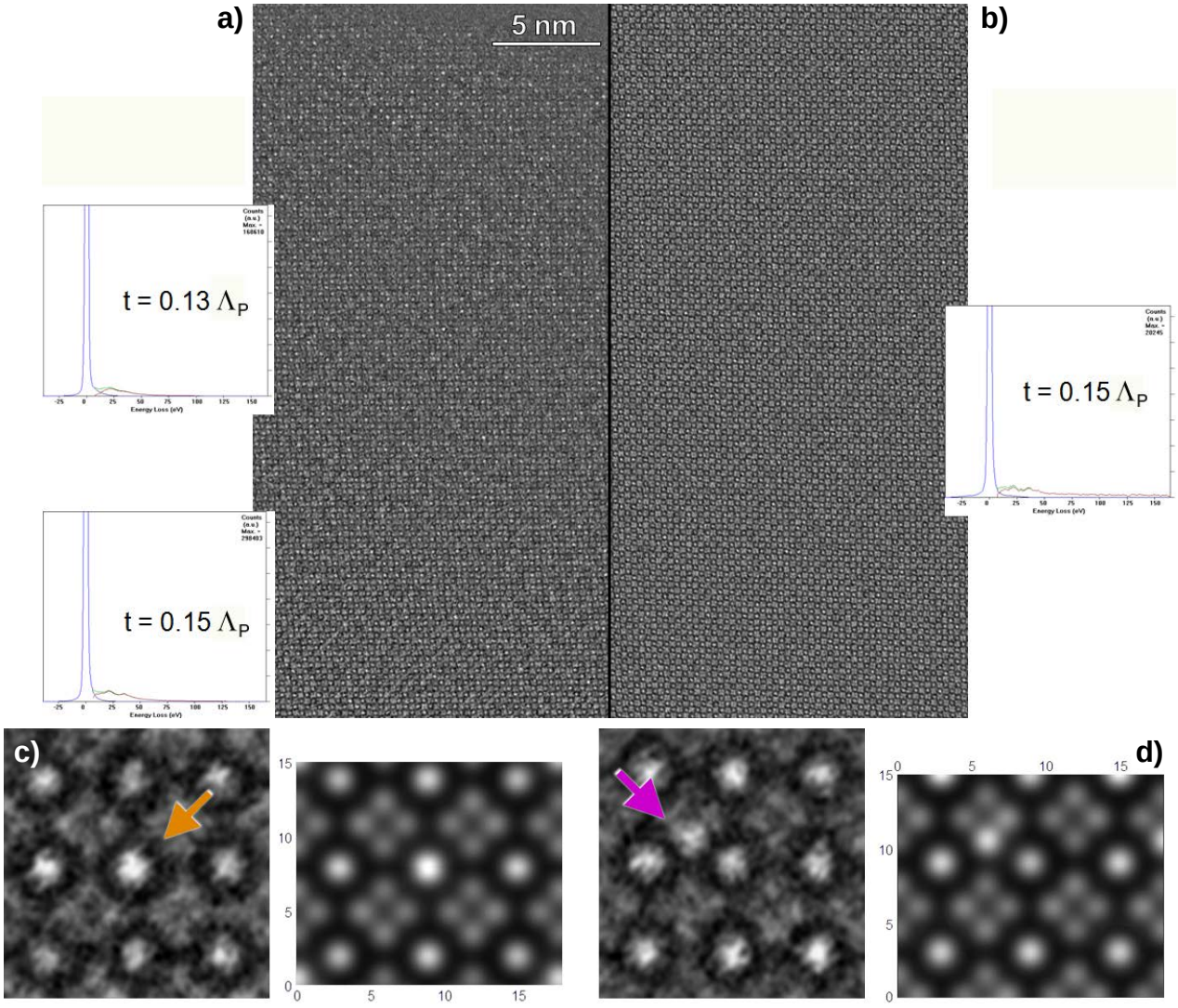

Figure 2. *a-b): Low-mag STEM-ADF images of the 1.4 at.% Yb^{3+}-doped (a) and the pure YAG (b) samples. EELS low-loss spectra are reported to ascertain their thicknesses t are comparable. c-d) : enlarged details showing Yb^{3+}-containing columns of type 1 (c) and 2 (d), and corresponding QSTEM simulations for one Yb^{3+} dopant in the doped column (thickness equal to 5 nm according to fig. 2a).*