Spectroscopy in STEM/TEM

IM.4.P091
Detection and quantitative measurement of the number of Yb-dopants in a YAG crystal at the atomic level by high resolution STEM-EELS

T. Epicier[1], M. Bugnet[2], G. Botton[2]

[1]INSA-CNRS, MATEIS, umr CNRS 5510, Vulleurbanne, France
[2]McMaster University, CCEM & Department of Materials Science and Engineering, Hamilton, Canada

thierry.epicier@insa-lyon.fr
Keywords: YAG, Yb dopant, optical ceramic, HAADF, atomic STEM-EELS

Studying quantitatively the bulk distribution of dopants within materials by means of atomically-resolved STEM-HAADF imaging has become possible and efficient using modern microscopes. Because the STEM detector collects incoherent electrons scattered at large angles, the ADF intensity varies as $Z^{\square}$ [1], where Z is the atomic number of the probed atom and $\square \approx 1.6$-2. ADF-STEM is then in its principle, and since its origin, suitable to the detection of heavy atoms on a substrate [2], or later on, of dopants embedded in a matrix (for example Sb atoms in silicon [3]). More recently, aberration corrected microscopes were used to identify single dopants and/or impurities in various materials (oxide materials, semi-conductors, ceramic interfaces or catalysts), where the added specie generally substitutes to one specific site, leading, in projection, to one specific type of atomic columns concerned by the doping (see for instance references cited in [4]). However, adding direct chemical information obtained with a spectroscopic method, such as EELS (Electron Energy-Loss Spectroscopy) may bring an unambiguous confirmation that HAADF intensity variations attributed to dopants are not artefact, or produced by any other unexpected impurity. A combined STEM-EELS study of dopants is then possible, as was demonstrated in the case of oxide materials |5].

Good candidates for such studies are luminescent garnet-based structures, such as RE-doped YAG, where RE designates a rare earth element, and YAG, the Yttrium-Aluminium-Garnet $Y_3Al_5O_{12}$, a cubic phase with space group Ia-3d [6] and a = 1.20062 nm. In these compounds, two different sites and types of atomic columns in the <100> projection are concerned by RE^{3+} dopants, see figure 1. We focus here on Yb^{3+}-doped YAG polycrystalline ceramics. This system has great potentialities for replacing single crystals for optical applications, such as in lasers and scintillators. It is then important to check that the dopant distribution is homogeneous, since any kind of heterogeneity (second phases, grain-boundary segregation, clustering) drastically affects the optical properties (e.g. see [7]). Previous HAADF obtained with an uncorrected FEI-TITAN, 300 kV microscope images of Yb^{3+} doped YAG crystals were already reported [8]. We present here the STEM-EELS study of a 1.4 Yb^{3+} at. % doped YAG sample (substitution ratio [Yb]/[Y] = 10 %; details on the elaboration, optical and microstructural characterization can be found in [7]). Results were produced at 200 kV on a double-corrected FEI TITAN-cubed equipped with a Gatan 866 spectrometer. Figure 1 shows that the distribution of Yb^{3+} ions can be revealed in STEM-HAADF micrographs, owing to the contrast enhancement caused by the difference in atomic weights (Z_{Yb} = 70 and Z_Y = 39).STEM-EELS analysis was performed on slightly thicker areas compared to figure 1, because of very rapid irradiation effects in thin regions. Results (such as shown in figure 2) will be discussed quantitatively in terms of statistics (including prediction from the binomial law and thickness estimation), EELS quantification and measurement of the HAADF intensity of atomic columns [9].

1. E.J. Kirkland, R.F. Loane, J. Silcox, *Ultramicroscopy*, 23, (1987), 77.
2. A.V. Crewe, J. Wall, J. Langmore, *Science*, 168,(1970), 1338.
3. P.M. Voyles, D.A. Muller, J.L. Grazul, P.H. Citrin, H.J.L. Gossman, *Nature London* 416, (2002), 826.
4. A. Mittal and K.A. Mkhoyan, *Ultramicroscopy*, 111, 8, (2011), 1101.
5. M. Varela, S.D. Findlay, A.R. Lupini, H.M. Christen, A.Y. Borisevich, N. Dellby, O.L. Krivanek, P.D. Nellist, M.P. Oxley, L.J. Allen, S.J. Pennycook, *Phys. Rev. Letters*, 92, 9, (2004), 095502.
6. A. Nakatsuka, A. Yoshiasa, and T. Yamanaka, *Acta Cryst. B*, 55, (1999), 266.
7. L. Esposito, T. Epicier, M. Serantoni, A. Piancastelli, D. Alderighi, A. Pirri, G. Toci, M. Vannini, S. Anghel, G. Boulon, *J. Eur. Cer. Soc.,* 32 (2012), 2273.
8. T. Epicier, T.J. Konno, K. Sato, G. Boulon, p.127 in Proceed. EMC2012 (15th Electron Microscopy Congress), vol.1, ed. D.J. Stokes, M. Rainforth, RMS, (2012).
9. We thank N. Gauquelin (CCEM, McMaster Univ., Hamilton - Canada), K. Sato and T.J. Konno (IMR, Tohoku Univ., Sendai - Japan) and G. Boulon (ILM, University Lyon I – France) for fruitful discussions.

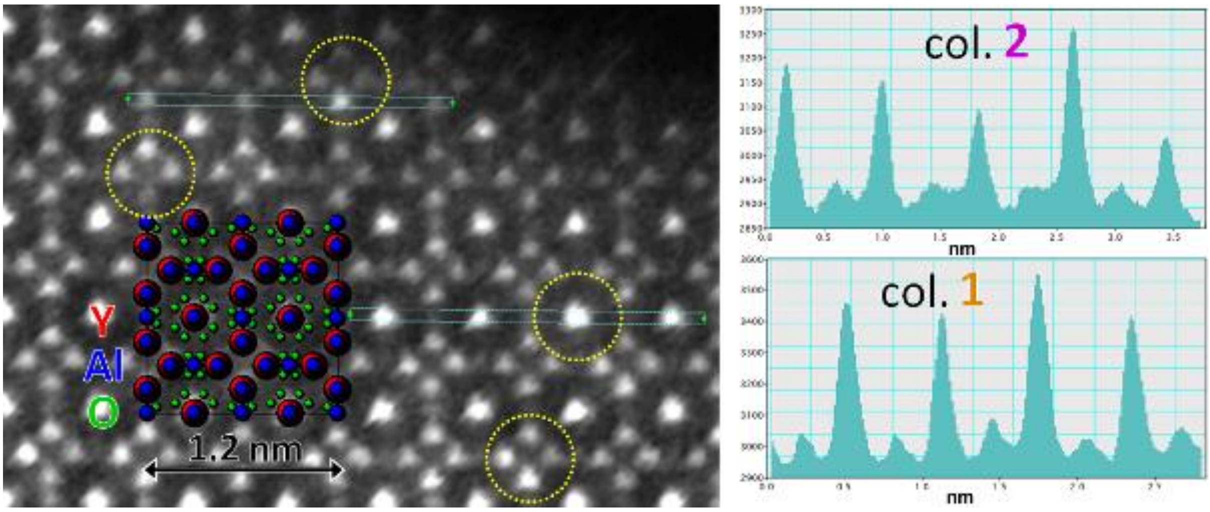

Figure 1. [001] HAADF image of a Yb-doped YAG crystal: note intensity reinforcements (circles) at two types of atomic positions (labelled 'col. 1' and 'col. 2' respectively – col. 1 has twice the atomic density of col. 2, and thus leads to brigther dots –) where Yb is known to substitute to Y. The projection of the cubic cell is shown (Al atoms in blue, Y in red, O in green).

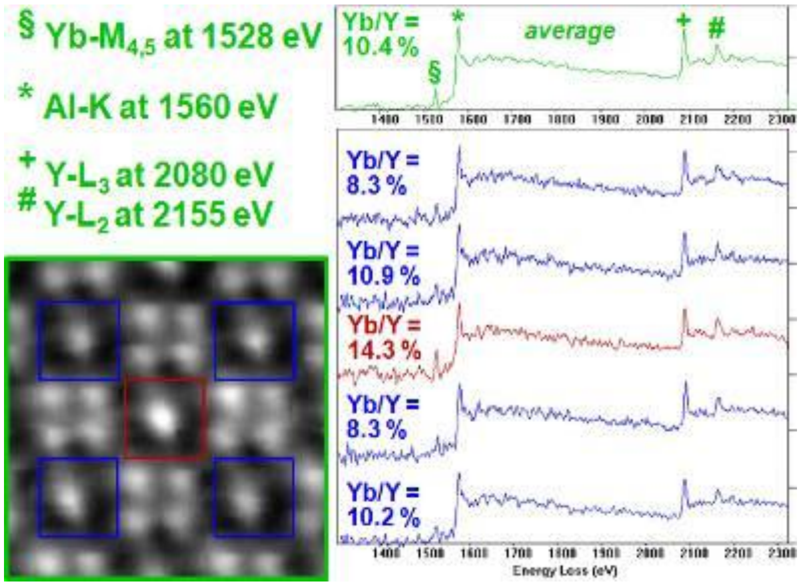

Figure 2. 2x2 nm STEM image during SI acquisition (16x16 pixels with 0.2 s/pixel) and corresponding EELS spectra showing an evident correlation between the 'column 1' HAADF intensity and the Yb content, maximal at the central column (red frame).