Atomic-scale imaging of dopant atoms and clusters in Yb-doped optical fibers

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ABSTRACT

Fabrication of Ytterbium-doped active fibers with different designs, compositions and high Yb concentration has attracted an intense interest. For making highly Yb-doped fibers, co-dopants like phosphorous (P) and aluminum (Al) are also employed in order to modify refractive index and increase Yb solubility, avoiding clusters and phase segregations. Indeed, Yb-clustering results in quenching effects and increased propagation losses due to energy transfer between clustered ions. Therefore, the chemical composition and phase homogeneity of the fiber core have key influences on the performance of an active fiber. However, conventional fabrication techniques such as MCVD (modified chemical vapor deposition) and OVD (outside vapor deposition) are approaching the limit.

In this contribution, we have developed an approach for fabrication of such active fibres based on granulated silica derived from the sol-gel process. The advantage of this method is the fabrication of active fibers with high dopant contents and homogeneity. Here, using high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in atomic scale, we report the direct, nano-scale and atomic-resolution observation of individual Yb dopant and co-dopant (i.e. Al, P) atoms for different fabricated fibers. The chemical mapping from STEM-EDX shows an extremely homogeneous distribution of the dopants and co-dopants in nano-scale for our fabrication protocol. However in atomic resolution, we also identified the possible Yb clusters in the range of 10 atoms within the core structure. The size, structure, and distribution of these clusters are determined with an Yb-atom detection efficiency of almost 100% by STEM.

Keywords: Ytterbium, granulated silica, Sol-gel, chemical mapping, HAADF-STEM

1. INTRODUCTION

Ytterbium-doped active fibers are considered as optical amplifiers so that a doped fiber is implemented as a gain medium to amplify an optical signal. The simple level structure of Yb considerably minimizes some undesirable effects such as excited state absorption and concentration quenching, which are usually observed in fibers doped with other rare elements (REs) and reduce the efficiency of the gain medium [1].

Concentration quenching is an energy transfer up-conversion (ETU) phenomena that arises due to the clustering of ions within the fiber core, which is typically observed in Er-doped fibers [2]. Since the two-manifold structure inhibits the ETU effect, the state absorption and concentration quenching are minimum in Yb-doped fibers. Additionally, the glass composition has a key influence on the properties of the Yb^{3+} ions, i.e absorption and emission spectra [3,4]. Co-dopants in the core of Yb-doped fibers, such as Phosphorus (P) and Aluminum (Al), can also change the optical properties of the fibers by modifying the refractive index and Yb solubility and thus a high doping density in the core is possible [5,6]. High doping level of Yb results in large unsaturated gains in short fiber length, which is extremely desirable.

In this regard, we have developed a protocol for fabrication of Ytterbium-doped fibres based on granulated silica derived from the sol-gel process. A remarkable feature of our protocol is the fact that the process starts from the liquid phase, which allows high concentration of dopants is homogeneously dissolved into the precursors [7]. In order to validate the homogeneity of dopants and screen the possible clustering of ions, here we implemented high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in nano and atomic scales. The high-angle

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electron-scattering cross section scales roughly to the atomic number $Z^{1.7}$ that is close to the limit of Rutherford scattering, Z^2 [8]. As a result, this image mode provides the maximum chemical contrast. It means the heavier an atom is, the more electrons can be collected on the HAADF and creating a brighter point on the image [8,9].
In practice, the HAADF STEM technique also confirmed to be the most efficient method to study single atoms on the surface and in the bulk [10-12]. Recently, K.V. Benthem *et al.* implemented an atomic resolution STEM to obtain detailed information about the nano-scale Pd catalyst particles and single Pd atoms in activated carbon fibers [12].
Therefore, the main purpose of this study is to investigate the homogeneity and clustering of dopants and co-dopants in fibre core in nano-scale or even atomic resolution. It allows to better understand and optimize the protocol of materials development and fiber drawing parameters.

2. EXPERIMENTAL DETAILS

As above-mentioned, the granulated silica derived from the sol-gel process was implemented for fabrication of Ytterbium-doped active fibres with a core diameter of 150 µm (Fig. 1). Co-dopants like phosphorous (P) and aluminum (Al) are also employed in order to modify refractive index and increase Yb solubility, avoiding clusters and phase segregations. The structure and chemical mapping of the fiber cores were observed by means of scanning electron microscopy and scanning/transmission electron microscope (S/TEM), using a FEI Titan Themis S/TEM (80-300 kV). The different feature of STEM compared to conventional TEM, is that it can focus the electron beam into a narrow spot, which is scanned over the sample and diffracted electrons can be detected by different detectors (Fig. 2). Various types of contrast in the image and different observation modes including bright field, high angle annular dark-field (HAADF), diffraction pattern, EDX, and high-resolution contrast have been employed. Indeed, scanning transmission electron microscopy (STEM-EDX) provides information in nano-scale chemistry and homogeneity while selected area electron diffraction mode gives information about material amorphization during the process. To prepare TEM samples the fibers were first mounted between two silicon wafers in order to make a sandwich. The sandwich was then cut by a diamond wire saw to obtain slices with thickness of 600µm. The slices were subsequently thinned by angular mechanical polishing on a tripod-polishing machine and diamond pads up to ≅ 15µm, followed by ion milling in a Gatan PIPS at 5-6° incident angle with Ar ions at 2.5-4 kV for final thinning up to transparency to the electron beam (less than 100 nm). Indeed, ion milling is a sputtering process and can remove very fine quantities of material. An inert gas, such as argon, is utilized to generate an ion beam and then bombard the surface of the sample. Compared to focus ion beam (FIB) method, the tripod polishing technique inhibits the concern that the high-energy ion beam utilized in the

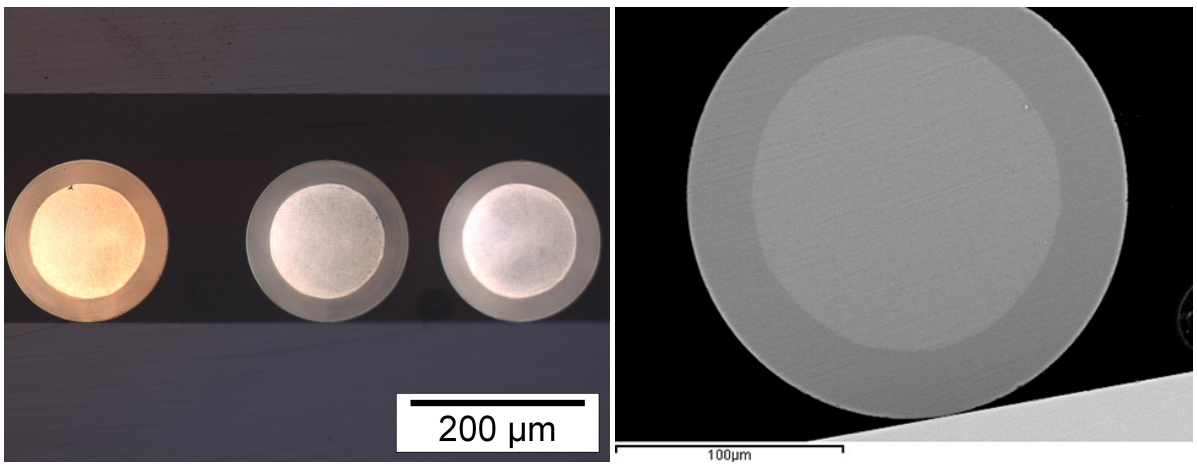
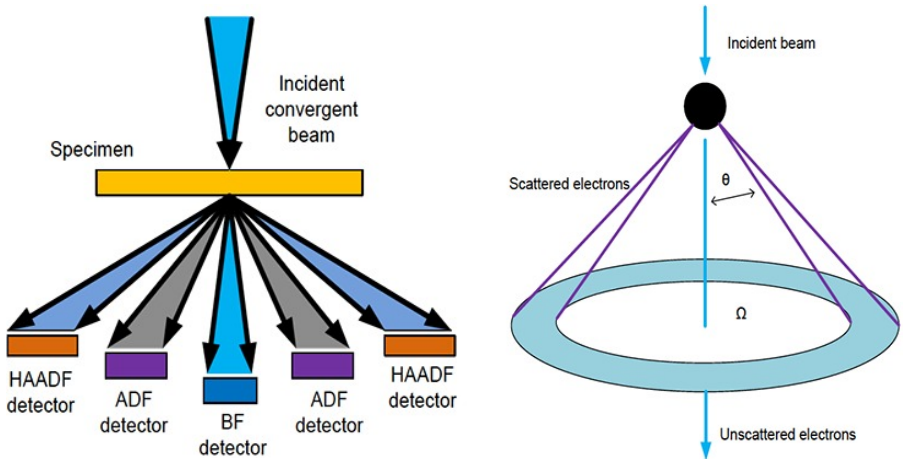


Figure 1. Optical and SEM micrographs of active fibers with core diameter of 150 µm in plan view; Core and clad are visible due to refractive index and chemical contrast.



(a) (b)

Figure 2. (a) Schematic of the HAADF, conventional ADF and BF detectors in a STEM (b) Electron scattering by a single isolated atom in STEM [13]

FIB technique can damage the specimen and make artifacts. However, the ion milling process containing Ar beam with the energy of 2-4 KeV has much smaller energy than that of the FIB system (30 KeV). It should be mentioned that when the Ar beam polishes the specimen, the Si and O atoms are easier to remove than Yb atoms. It may result in an increase of the doping density in the core area by removing relatively more Si and O atoms.

3. RESULTS AND DISCUSSION

Fig. 3 demonstrates the TEM micrographs (BF) showing the nanostructure and diffraction patterns of a fiber core produced by granulated silica derived from the sol-gel process. A well-developed amorphous structure is observed in the fiber core and the electron diffraction pattern shows diffused rings as would be expected for an amorphous phase [10]. However the question arises regarding the homogeneity and elemental distribution of the dopant (Yb) and co-dopants (i.e P and Al) in nano and atomic scales. For this purpose, as described previously, STEM was implemented to investigate the fiber core if it is structured into ultra fine substructures, clusters or nano phase segregations. An ultra precise chemical mapping was performed to individualize the different chemical phases even if they are restricted to ultra small quantities where we have an electron beam with a HAADF STEM resolution of o.18 nm. Fig. 4 demonstrates the elemental distribution images associated with Si, O, P, Al, and Yb, respectively. It can provide useful information on the dopant and co-dopants localization in the nanostructure. It is noteworthy that an extremely homogeneous

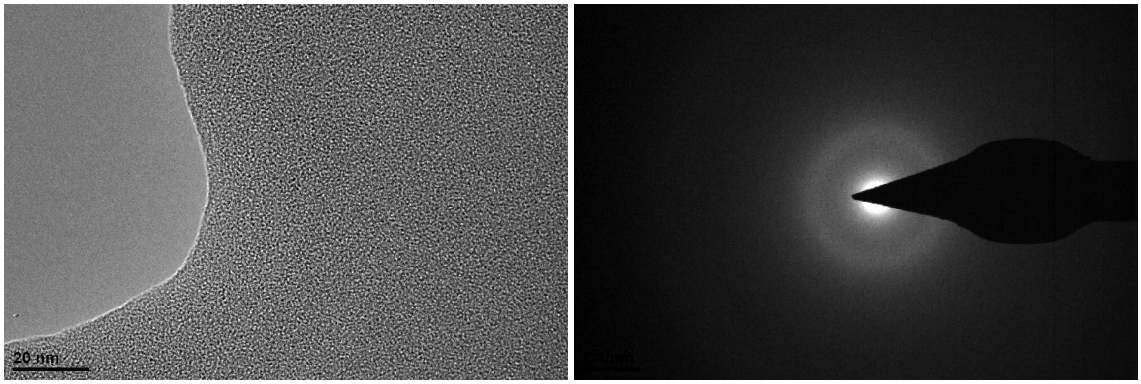


Figure 3. TEM micrograph showing the nanostructure and diffraction pattern of a fiber core produced by granulated silica derived from the sol-gel process

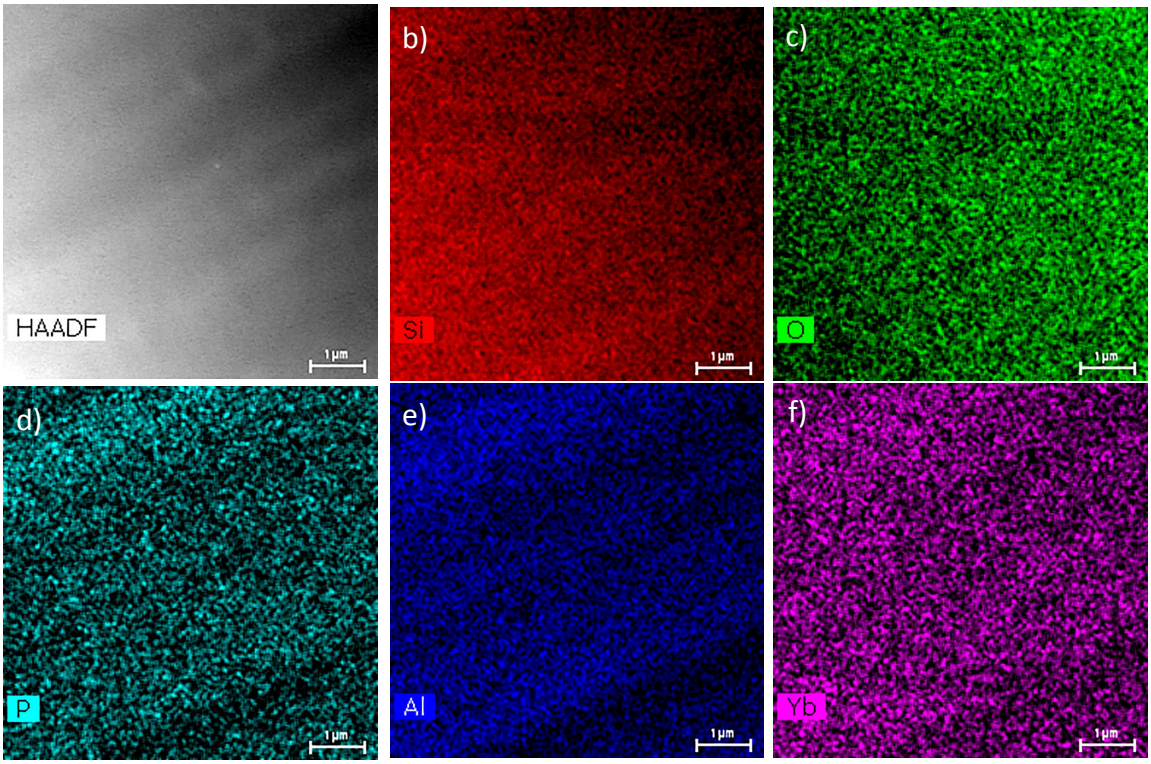


Figure 4. STEM micrograph showing the nanostructure and elemental distribution a doped fiber core

distribution of dopants is observed in the substructure in nano-scale (see Fig. 4 d-f). In order to obtain a clue of dopants homogeneity in atomic scale, Fig. 5 shows acquired HAADF image in an extremely high magnification. As previously mentioned, according to the "Z contrast" imaging theory, the brightness of each dot in the STEM-HAADF image mode is roughly proportional to the Z^2 where Z is atomic number [8].

Considering the rational hypothesis of a flat investigated area within the field of view at such high magnification, we can conclude that the bright areas on the micrographs represent Yb atoms and clusters since the Yb atom species are the only heavy dopant in the core. The atomic numbers of other elements and dopants (i.e. Al, P, Si, and O) are much lower than Yb. Furthermore, Figure 5a shows that at such atomic scale magnification, some Yb atoms tend to cluster together while some are randomly distributed in the core. Given the fact that Yb ionic diameter is around 0.5 nm and the average cluster size in the observation area is around 4 nm. Consequently, it can be concluded that Yb clusters are formed by the average of 8 atoms or in another word; Yb clusters are formed by less than 10 atoms. The Yellow circles (each one represents an Yb atom) on Fig. 5a indicate the size of the clustered area in the core structure.

According to the best knowledge of authors, it is a valuable achievement of the present work. In order to validate this hypothesis, the EDX spectrum was performed in both suspected clustered area and free cluster zone (see Fig. 6) The green color shows the EDX spectrum of the clustered area while the blue spectra indicates that of the free cluster area. The strong Si and O signals come from the fiber host, SiO_2. The Cu signals come from the copper grid holder supporting the TEM specimen of the fiber. The only distinction in the two spectra is the visible signal from Yb elements within the clustered area. It results in the dominating contrast (Fig. 5a) in STEM-HAADF image given the fact of its larger atomic number, Z.

Concerning the sample preparation, since all STEM micrographs are the 2D projections of 3D objects, the thin specimens are required in order to avoid the vertical distribution issue (Yb distribution along the beam direction). However, it can be observed in STEM micrographs that the single Yb atoms are not clearly separated from each other. Firstly, It may result from the high doping level of the fiber, which makes the Yb atoms likely to cluster and overlap even in very thin regions of the sample. Fibers produced with lower Yb doping level may help to detect individual Yb atoms.

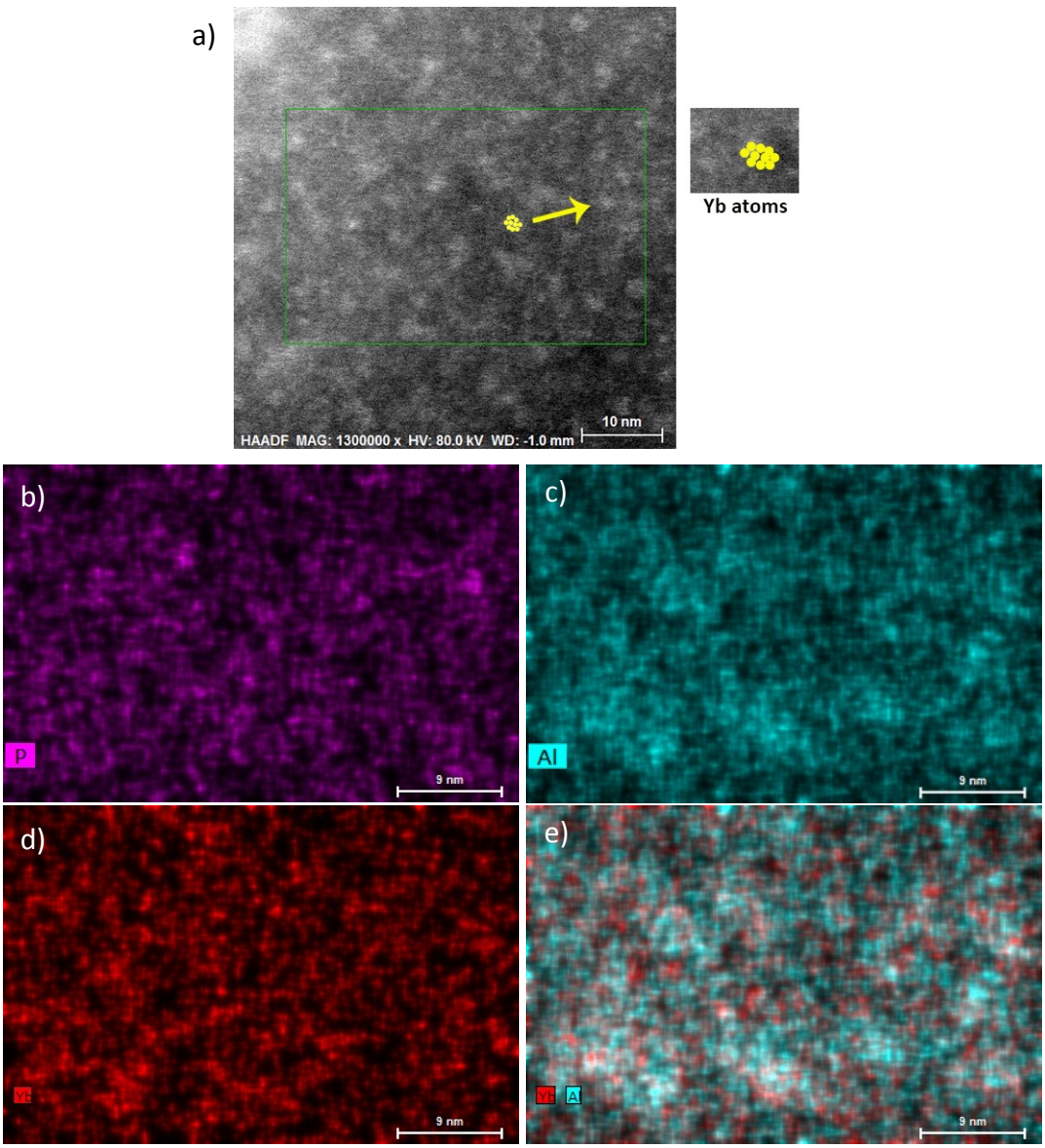


Figure 5. (a) HAADF-STEM micrograph (Yellow circles represent Yb atoms) and (b-d) elemental mapping acquired at ultra high magnification from a fiber core

Secondly besides the original Yb distribution in the core, whether the ion milling leads to Yb atom migration is still an uncertainty. Thus it can be proposed that a STEM specimen prepared by a gentle ion milling should be investigated in order to minimize the influence of high-energy ion beam. Ultimately, in addition to all above-mentioned facts, another problem encountered in both of the above micrographs is the resolution due to nature of a glassy sample, which is a great insulator. Higher resolution techniques are needed in the future to achieve more details about the distribution of individual Yb atoms. A new technique for identifying individual dopant atoms within the fiber core is under progress by the authors.

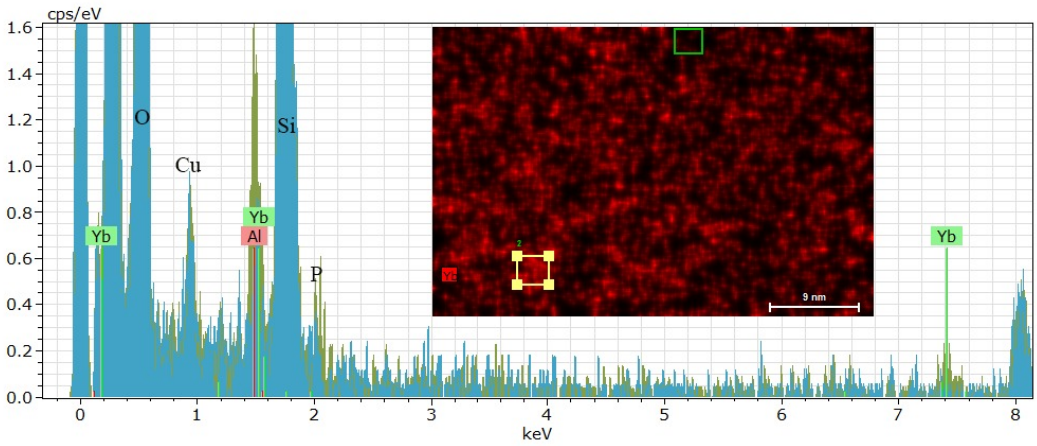


Figure 6. EDX spectra from a clustered area (green) and a free cluster zone (blue): the visible signal from Yb atoms within the clustered area.

4. CONCLUSIONS

The granulated silica derived from the sol-gel process was implemented for fabrication of Ytterbium-doped active fibres. Then, in order to analyze the homogeneity of the Yb doped fibers, the distribution of dopants and in particular Yb atoms is observed in a range of nano and atomic scales by HAADF-STEM technique. In order to prepare specimens appropriate for STEM with atomic resolution, tripod polishing method and ion milling have been employed. According to the STEM micrographs, the dopants and co-dopants are homogeneously distributed in the observation area in nano-scale. While in the atomic scale we observed some Yb clusters in the range of 10 atoms within the core structure. It proves our suitable protocol for material development and fiber drawing parameters. But further work is required in order to obtain more details on the distribution of individual Yb atoms.

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