Analysis of Coordination Structure around Erbium in Erbium-Doped Fiber

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Erbium (Er)-doped optical fiber amplifier (EDFA), which can amplify optical signals without converting them into electric signals, is an optical component essential for creating today's photonics networks. It is known that the gain characteristic of EDFA is influenced by the Al concentration in Er-doped fiber (EDF), which determines the coordination structure around Er. In this paper, the authors report on the first successful direct analysis of coordination structure of EDF. For the purpose of clarifying the relationship between Al concentration and the coordination structure around Er in the glass network of EDF, the X-ray absorption fine structure (XAFS) analysis using an x-ray beam line in the "SPring-8" synchrotron radiation facility has been applied. By measuring and analyzing the result, the oxygen coordination number around Er increased as Al concentration increased and that the Er-O distances in EDF co-doped with Al are longer than those in EDF without Al-doping, and these results will serve as a guideline for the future development of new amplification fibers.

1. Introduction

An e**rbium**-doped optical fiber amplifier (EDFA) has been widely used in an optical communication system for optical signal amplification in the conventional band (C-band) and longer-wavelength band (L-band)[1]. Silica-based erbium-doped fiber (EDF) is a type of optical fibers in which the core region is doped with erbium (Er). When an optical signal is launched into the core of EDF, accompanied by a pump light, a condition known as population inversion is caused by the pumped Er ions. EDFA is a device that can amplify optical signal lights through the phenomenon of stimulated emission. Because EDFA directly amplifies optical signals in a wavelength division multiplexing (WDM) transmission system for transmission of high-capacity data signals, it is a component essential for building the photonics networks of today. In general, EDFA must have a wide and flat gain spectrum within the amplified band. One well known conventional approach is to obtain a flat gain spectrum using Al co-doped EDF[2], [3]. When the intensity of pump light at a wavelength around 980 nm or 1480 nm is adjusted so as to make the two gain peaks (Gmax) at around 1530 nm and 1558 nm equal in intensity, the minimum gain (Gmin) is found at around 1540 nm. The gain flatness is defined as relative gain deviation: (Gmax-Gmin) / Gmin ×100[%]. As shown in **Fig. 1**, the high concentration of Al doping reduces relative gain deviation. This phenomenon is essentially caused by the change in the coordination structure around Er inside the glass network due to the doping of Al. Numerous papers have been published in the past on the relationships between the coordination structure around rare-earth ions and the emission spectra of various host glasses. Some of the host glasses that have been studied include silica glass[4], [5], [6], phosphate glass[5], [6], [7], borate glass[5], [6], [8], fluoride glass[5], [6], [9], [10], and
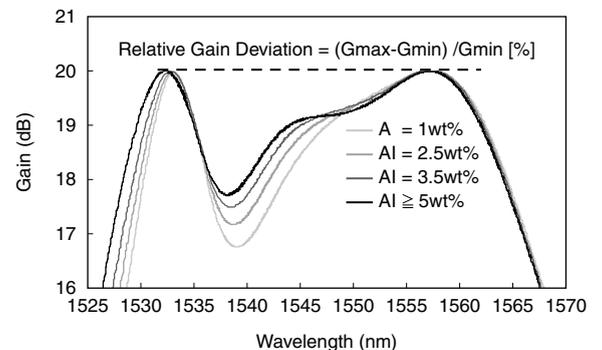
Fig. 1. Gain profiles of EDFs with different Al concentrations

sodium silicate glass[4], [11]. However, these reports deal with multicomponent bulk glasses that have higher Er concentrations (several wt%) than EDF, and no reports have been made on the coordination structure around Er content in EDF. This paper aims to clarify the relationships between Al doping concentrations and the coordination structures around Er in glass networks. In 2006 the authors succeeded in observing the coordination structure around Er in a silica-based EDF by employing X-ray absorption fine structure (XAFS) analysis[12], [13]. In this paper, the authors report on the observation results obtained through the use of the device having a higher detection sensitivity. It has been clarified that Al has effects on Er-O coordination number and Er-O distance, and that Er-O coordination number increases as Al doping concentration increases.

2. EDF sample preparation

Using a commonly used optical fiber production process of modified chemical vapor deposition

(MCVD), several EDF samples were prepared by drawing EDF glass preforms into fibers. **Table 1** lists the chemical compositions of the samples. The dopant concentration of each sample was measured using an electron probe micro analyzer (EPMA).

Table 1. Chemical compositions of EDF samples

Sample No.	Type	Er[wt ppm]	Al[wt%]	Ge[wt%]
1	fiber	510	0.0	0.0
2	fiber	840	0.0	3.9
3	fiber	840	0.4	4.5
4	fiber	1357	1.4	3.4
5	fiber	1022	3.7	3.8
6	fiber	958	6.5	4.1
7	Er-metal	–	–	–
8	Er_2O_3	–	–	–

Figure 2 shows the cross section of an EDF sample. The 14-µm-diameter core is doped with Er at a concentration of about 1000 wt ppm. When the EDF samples are ground into powder to undergo XAFS measurement, the average concentration of Er in the samples will be around 10 wt ppm, which is below the lower detection limit (about 100 wt ppm at a minimum) of the XAFS method.

Therefore, for the purpose of increasing the Er concentration in the ground powder sample to conduct measurement, the cladding was removed from the fiber using hydrofluoric acid (HF solution) to make the outer diameter approximately 20 µm. The length of EDF for each sample was 100 m, and the average Er concentration for ground powder samples was about 500 wt ppm.
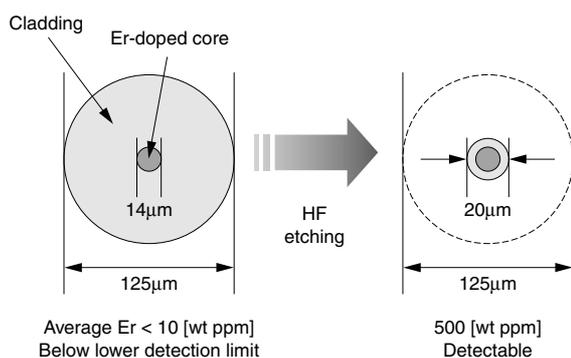
Fig. 2. Cross-section of EDF sample

3. Principle of XAFS

When an X-ray is irradiated on a sample, photoelectrons, that have a bound energy level lower than the X-ray energy, are ejected from the atom. As a result, a steep rise of X-ray absorption called X-ray absorption near edge sructure (XANES) is observed. Moreover, the photoelectrons ejected by X-ray radiation interfere with the photoelectrons scattered from the neighboring atoms. As the result, the wave-like X-ray absorption profile is observed in the higher photon energy side, which is called extended X-ray absorption fine structure (EXAFS). XANES and EXAFS are collectively called XAFS. By analyzing these X-ray absorption spectra data in detail, various kinds of information can be obtained: the bonding distances between atoms irradiated with the X-ray and neighboring atoms, and the types and coordination numbers of neighboring atoms.
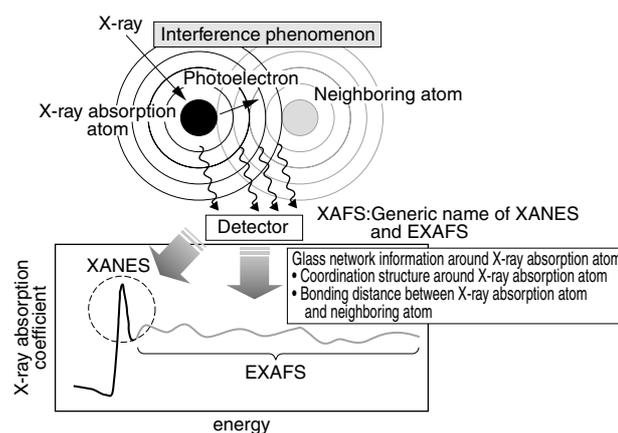
Fig. 3. Principle of XAFS

4. XAFS measurement

The XAFS measurements have been conducted using the two synchrotron radiation beam lines at SPring-8 [14] described in **Fig. 4**. One beam line is the public beam line (BL01B2) and the other one is the industrial consortium beam line (BL16B2) that several companies including Sumitomo Electric are managing.

Before the X-ray is irradiated to a ground powder sample, the X-ray is reflected with the rhodium-coated mirror that has 5 mrad against the direction of X-ray radiation in order to suppress the higher harmonic wave. The intensity of the incident X-ray is monitored by
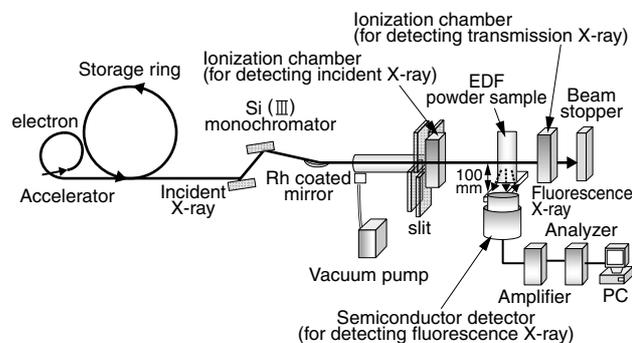
Fig. 4. XAFS measurement system

transmission mode using an ionization chamber. To obtain the XAFS data of a ground powder EDF sample having a low concentration of Er, the fluorescence X-ray has been measured by using the semiconductor detector. In order to measure the fluorescence X-ray efficiently, the semiconductor array with 19 devices having a device area of 1900 mm², which is fifty times larger than conventional ones, has been utilized. The distance between the semiconductor detector and the sample has been set to 100 mm. To measure the XAFS spectra of Er metal and Er_2O_3 having high Er concentrations, the transmission X-ray has been measured by using the ionization chamber located posterior to the samples.

The L_3 absorption edge of Er has been analyzed for XAFS measurement of Er. In order to analyze the coordination structure around Er, EXAFS signal x (k) within the 2 to 14 A^{-1} range has been extracted, and Fourier transform from this EXAFS signal has been made to obtain the radial distribution function (RDF) of Er by using WinXAS [15]. Additionally, X-ray scattering simulation has been made by FEFF8 [16] and using this result, the spectral fitting have been made on this RDF of Er to obtain the coordination structure around Er.

5. Analyses and Results

5-1 XANES analysis

Figure 5 shows the XANES spectra of the prepared samples. For all samples, the absorption peak is observed at around 8.36 KeV. The absorption peak intensity of Er_2O_3 is the highest among all the samples, those of EDF samples are lower than that of Er_2O_3, and that of Er metal is especially low. In addition, the peak absorptions at around 8.4 KeV have been observed except for Er metal. The EDF samples without Al co-doping have lower peak intensities compared with those with Al co-doping. And the peak positions of the EDF samples without Al co-doping are shifted to higher energy regions than those of the Al co-doped EDF samples. These results show that Al co-doping dominantly changes the coordination structure around Er.

5-2 EXAFS analyses

Figure 6 shows the EXAFS oscillation spectra of the prepared samples. Obvious oscillation structures were observed in the range of k/A^{-1} <10. The samples without Al co-doping (samples No.1 and No.2) show oscillation spectra different from those of other samples. In particular, the oscillating spectrum of sample No.1, which is the EDF sample without co-doping of both Al and Ge, is distinctly different from those of the other EDF samples. These differences are due to the fact that Al co-doping affects the bonded atoms around Er, especially the types of nearest neighboring atom.

Fourier transform has been made with the EXAFS oscillation structures so as to obtain the RDF of Er as shown in **Fig. 7**. Especially notable are the peaks in the range between 0.20 nm and 0.24 nm that are due to Er-O bonding; those of the EDF samples with Al co-doping are shifted to longer bonding distance regions than those of the EDF samples without Al co-doping.
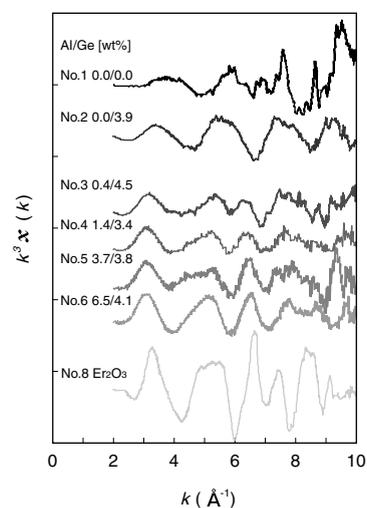
Fig. 6. EXAFS oscillation spectra

Fig. 5. XANES spectra of prepared samples
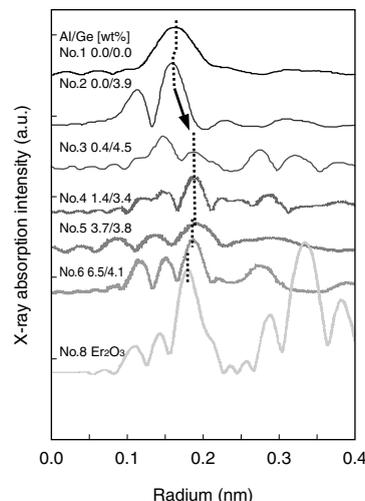
Fig. 7. RDF of Er in prepared samples

5-3 Relationship between coordination structure around Er and concentration of Al

To analyze quantitatively the coordination structure around Er, spectral fitting has been made to the EXAFS oscillation structure shown in **Fig. 6** and the RDF of Er shown in **Fig. 7** by utilizing the result of the X-ray scattering simulation by FEFF8 [16]. The coordination number and bonding distance of Er-O were obtained, as shown in **Table 2**.

Table 2. Coordination number and bonding distance of Er-O in prepared samples

Sample No.	Type	Er [wt ppm]	Al [wt%]	Ge [wt%]	Er-O bonding distace [nm]	Er-O coordination number
1	fiber	510	0.0	0.0	0.203	1.2
2	fiber	840	0.0	3.9	0.204	2.9
3	fiber	840	0.4	4.5	0.236	3.8
4	fiber	1357	1.4	3.4	0.233	6.1
5	fiber	1022	3.7	3.8	0.236	8.2
6	fiber	958	6.5	4.1	0.233	9.5

Figure 8 shows the relationships between Al concentration and Er-O coordination numbers. It is clearly shown that the Er-O coordination number increases as the Al concentration increases. Moreover, Al co-doping changes the Er-O bonding distance as shown in **Fig. 9**. The Er-O bonding distances of the EDF samples without Al co-doping are about 0.20 nm, while those of the EDF samples with Al co-doping are about 0.235 nm.

As described above, it is generally known that Al concentration affects the gain spectrum of EDF. It is assumed from these results that if chemical composition can be tailored so as to allow Er-O coordination number to be changed freely, especially dramatically increased, a new EDF with high pumping efficiency may be developed.

6. Conclusions

It is generally known that the gain characteristics of EDF, especially gain flatness, are changed dramatically by Al concentration. In this experiment, the EDF samples having different chemical compositions were prepared, and the XAFS spectra of these samples were successfully measured and analyzed directly for the first time to clarify the dependence of glass network to chemical composition in EDF. It has been found that the Er-O coordination number of EDF increases as the Al concentration increases, and that Al co-doping significantly changes the Er-O bonding distance. These results indicate that the glass composition is dependent on the coordination number and bonding distance of Er-O, and this finding will serve as a basis for the development of new rare-earth doped fibers. This finding can be applied also to the development of non-rare-earth-doped fibers [17] and new amplification optical fibers that have new chemical compositions.
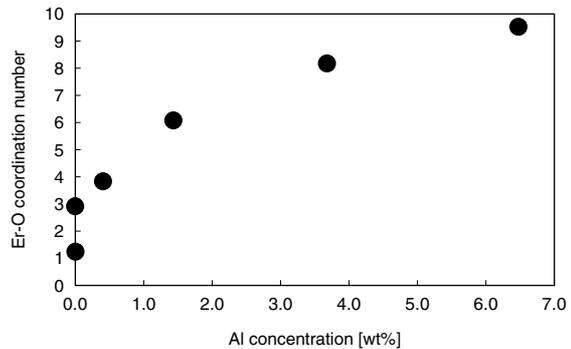
Fig. 8. Relationship between Er-O coordination number and Al concentration of EDF samples
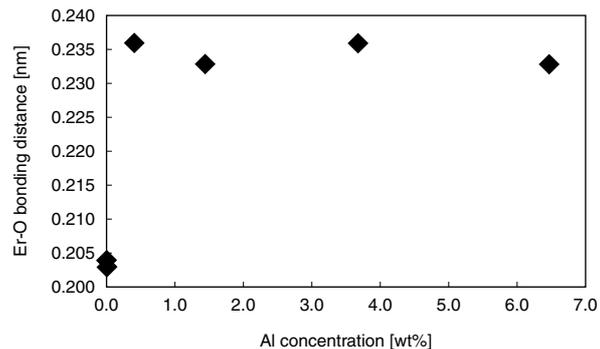
Fig. 9. Relationship between Er-O bonding distance and Al concentration of EDF samples

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