The investigation of Er-doped glasses by two-step hydrolysis with N,N-dimethyl formamide

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Abstract

Characterization of erbium-doped silicate glasses produced by sol-gel method with a drying control chemical additive has been carried out. Both of the absorption and fluorescence spectra of these samples were similar to those of erbium-doped optical fibers prepared by modified chemical vapor deposition. The homogeneous monolithic erbium-doped silicate glasses with concentrations ranging from 500 to 10000 ppm were constantly fabricated. Due to N,N-dimethyl formamide (DMF) in 2-step hydrolysis procedure, the processing time can be reduced significantly. The index of refraction and specific density of the samples were approximately 1.65 and 2.2 g/cm^3, respectively.

KEYWORDS: sol-gel, DCCA, clustering phase, distributing phase, fluoresence

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1 Introduction

Er-doped glasses are of particular interests as optical materials in which silica-based materials with large Verdet constants[1] and lasing ability[2]. Generating and amplifying coherence light of wavelength 1.54 μm are significantly important not only because of its "eye-safe" feature but also its lowest transmission loss in optical fiber communication. Single-mode continuous wave erbium-ytterbium glass laser was demonstrated[3]. Some review papers[4,5] had discussed in detail on fabrication, properties and applications of erbium-doped optical fiber amplifiers and lasers. With various chemical vapor phase deposition (CVD) techniques, such as modified chemical vapor deposition (MCVD) and vapor axial deposition (VAD), codoped Er^{3+}-Al_2O_3 and other codoped silica fibers were fabricated and chacacterized. The codoped Al^{3+} ions tend to broaden the Stark-levels and the fluorescence spectra of $^4I_{13/2}$ to $^4I_{15/2}$ transition[4,6].

The sol-gel process has been known to be one of the promising methods to synthesize high purity silicate glasses and optical fiber preforms[6-11]. This method has been pointed out to have advantages in energy saving and fabricating new multiple compositions of glasses over CVD methods[11]. The sol-gel derived rare-earth doped silicate glasses had been fabricated[1,12-16]. The absorption spectra of various compositions of Pr, Dy, Nd and Er-doped glasses were reported[1]. Most of the Er, Nd, Al-doped glasses were prepared by means of mixing tetramethylorthosilicate (TMOS) or tetraethylorthosilicate (TEOS) as the source of silica with the nitrate or chloride of erbium, neodymium or aluminum, whereas the double metal alkoxides of neodymium and aluminum were employed in the report of Fujiyama et al.[16]. Due to employing Al^{3+}, the disperibility of Nd^{3+} ions can be improved significantly with 4 mol% Nd_2O_3 in silica glass. Fengging Wu et al.[13] used solvent-free sol-gel dipcoating technique to prepare the films with a wide doping concentration of the rare-earths or other spices. They had a final thickness larger than 5 μm and a low loss of 2 dB/km. However, the detail structures about Er or Nd-doped glasses are not clear as yet. Based upon the fluoresence peaks and coordination number of Nd-doped compounds, E. J. A. Pope et al.[15] predicted a tentative structure model for local neodymium environment. But the doping concentration can't be enhanced due to the Er or Nd

clustering effect found by Ainsile et al.[4,17]. Moutonnet et al .[12] tried to synthesize the highly doped Er or Yb glasses (up to $\approx 2x10^{20}$ at./cm^3) by means of vaccum drying. It is difficult to confirm whether the erbium clusters exist or not by the measurement of secondary ion mass spectrometry (SIMS). On the other hand, Moreshead et al.[14] concluded that the short lifetimes of Nd-doped glasses were attributed to concentration quenching of the neodymium and quenching by the high concentration of water in the matrix.

Recently, large-scaled monolithic silicate glasses were successfully produced by means of two-step sol-gel processing[17-19] with DCCA, such as formamide[20-22] and N,N-dimethyl formamide (DMF)[23-26]. In this paper, the Er-doped silicate glasses prepared by the sol-gel processing with control of OH^- ion contents and DMF as a DCCA will be presented. Less than 5 days are needed to obtain 120 °C rod gel from starting solution. We will also prove that the clustering effect of erbium don't exist by the measurement of electron probe X-ray microanalyzer (EPMA). The refractive indexes and densities of Er-doped glasses with different concentrations are shown. The absorption and fluoresence spectra of transition from $^4I_{13/2}$ to $^4I_{15/2}$ are similar to those in erbium doped silica glass optical fibers[4] prepared by the MCVD method.

2. Experimental Procedure

Erbium carbonate was first dissolved in nitric acid and then mixed with deionized water. The aqueous solution of nitric acid and erbium carbonate was mixed with tetraorthosilicate (TMOS) and methanol (MtOH), the mole ratio of TMOS:H_2O:MtOH was 1:10:4. After stirring for 1 hour, DMF was added. Stirring for another 10 minutes, the pH value of the mixture was adjusted to be slightly greater than 5 by slowly dropping 0.1N ammonia water into the solution. The precursors was further polymerized under more basic condition to facilitate the formation of gels. The resultant solution was molded in a 100-ml cylinder and put in an oven which maintained the temperature at 40 °C in order to convert the solution into a wet gel. After 24-hour aging, the temperature was raised at the rate of 5 °C every 6 hours to 120 °C to evaporate the remaining

liquids including MtOH, water and DMF. Finally, the dry gel was sintered at 1050 °C for 2 hours under He atmosphere. The erbium ions contents existing in the solutions in this experiment were 500, 1000, 5000 and 10000 ppm, respectively.

The densities of the rods with different erbium ion concentrations were measured by displacement method using deionized water. The bulk densities could be obtained. The indices of refraction of these were measured by using an Abbe refractometer. Otherwise, the silicate glass rods sintered at 500 °C for 2h were cut into slices for scanning electron microscopic (SEM) observation. The absorption and fluorescence spectra of the sample rods were measured by an optical spectral analyzer (Ando 6310B). The sample rods have dimensions of 5 mm in diameter and 3 cm long. In spectral loss measurement, an optical coupler consisting of an optical fiber of 800 μm in diameter spliced to a quarter-pitch graded-index (GRIN) lens was used to couple and collimate the white light source passing through the sample. The transmitted light was collected by another optical coupler with GRIN lens closed to the sample and then conducted into the optical spectral analyzer. To measure the fluoresence spectra, a green laser beam at wavelength 532 nm (second harmonic generation of diode-pumped Nd:YAG laser, Adlas DPY-325C) was used to excite the erbium glass rods. The pumping laser beam having power of 150 mW and spot size of 0.32 mm was unfocusedly propagated parallel to the glass rod with a distance of about 3 mm from the rod surface. The resultant fluorescence was collected by a 800 μm optical fiber at 90° with respect to the beam direction and analyzed by the optical spectral analyzer.

3. Results and Discussion

The use of DMF and the 2-step hydrolysis reduced the time for obtaining dry gel through conventional drying to less than 5 days in contrast with a week of vaccum drying used by Moutonnet et al.[12]. By controlling the content of ammonia water, our experiment took only a few minutes rather than 2-3 hours to gel the precursor solution in their research. Because the excess OH^- ions of ammonia water can accerlate the rate of polycondensation, the viscosity of sol

drastically increases in a short time. The DCCA can prevent water from attacking the Si-O-Si bond[27] to become two silanol groups hypothesized by Freiman and Michalske[28]. Besides, there exists relatively strong hydrogen bond between the nitrogen atom of DMF and the hydrogen atom of silanol group. Any two silanol groups would prefer to bond together rather than depart from each other in the existing of DMF[29]. Thus, the monolithic gel can have been dried before the cracks take place. The densities of the rods with different concentrations of erbium ions were about 2.19 to 2.21 g/cm^3 which are similar to that of pure fused silica, and the index of refraction about 1.65 as listed in Table I. From the view point of density, the densified glasses had been obtained at 1050 °C for 2h in our processes.

The SEM results of two rod samples sintered at 500 °C for 2h with 500 and 10000 ppm Er^{3+} ions are shown in Fig. 1. There exist some white precipitates in these samples. These observation can be explained by so-called viscous flow mechanism proposed by G. C. KUZYNSKI[30] for sintering of glasses. As the viscosity at 500 °C is too high to densify the gel, the second phase may appear. Hence, the precipitates could disappear as the sintering temperature was raised up to 1050 °C. The SEM of densified rod (1050 °C) with Er^{3+} ions of 10000 ppm was also shown in Fig. 2 to indicate that no precipitates were observed. To understand whether the clustering of Er^{3+} ions could happen around the white precipitates, Fig. 3 shows the measurement of electron probe X-ray microanalyzer (EPMA) around these precipitates. A homhgeneous erbium distribution has been obtained with no coagulation situation of erbium ions. The clustering effect[31] existing in the Nd-doped samples of 15 wt% produced by CVD can't be found in our sol-gel samples. Maybe the concentrations of our samples are too low to cause the clustering. The clustering phenomenum is known to be avoided by incorporating Al_2O_3 in silica[4]. Because the soluble erbium ions in glass depend on the host glass(SiO_2-Al_2O_3, SiO_2-GeO_2) very much, it is possible to achieve high solubility of erbium in glass types where network modifiers are replaced. The amorphous phases (no crystalline XRD peaks were observed at the sweeping velocity of 4° and 0.5°/min) are visible.

Figure 4 presents the spectral loss of the sample containing 5000 ppm Er^{3+} ions. Peaks around 1250 and 1380 nm are attributed to the absorption of the overtones of OH vibrational normal modes. The absorption peak around 980 nm attributed to transition between $^4I_{15/2}$ and $^4I_{11/2}$ is commonly used to pump erbium ions to the upper levels in fiber lasers and amplifiers. The absorption peak most concerned around 1530.1 nm is attributed to the transition from $^4I_{15/2}$ to $^4I_{13/2}$. The normalized absorption spectrum normalized to the 1530.1 nm peak and the fluorescence spectrum normalized to the 1535.8 nm peak are shown in Fig. 5. Although these spectra are similar to those of erbium doped optical fibers[4], there is a larger shift of 5.7 nm between the absorption and fluorescence peaks compared with that of 2 nm in 500 ppm Er^{3+} content optical fibers[4].

4. Conclusions

We had successfully prepared Er-doped silica glasses by using two-step hydrolyzing sol-gel procedure which have good optical properties. The processing time from starting solution to obtain dry gel is reduced significantly by contrilling the OH^- ion contents and choosing DMF as DCCA. The viscou flow mechanism can explain why the second phase appears at 500 °C, but disappears at 1050 °C. By the measurement of EPMA, the homogeneous distribution of Er^{3+} ions can be observed, even at the concentration of 10000 ppm Er^{3+} ions.

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6. References

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Table captions

Table I Refractive indices and densities of the gel-derived glasses with different concentrations of Er^{3+} ions.

Erbium concentration (ppm)	Density (g/cm3)	Refractive index
500	2.2	1.6470
1000	2.2	1.6498
5000	2.2	1.6574
10000	2.4	1.6528

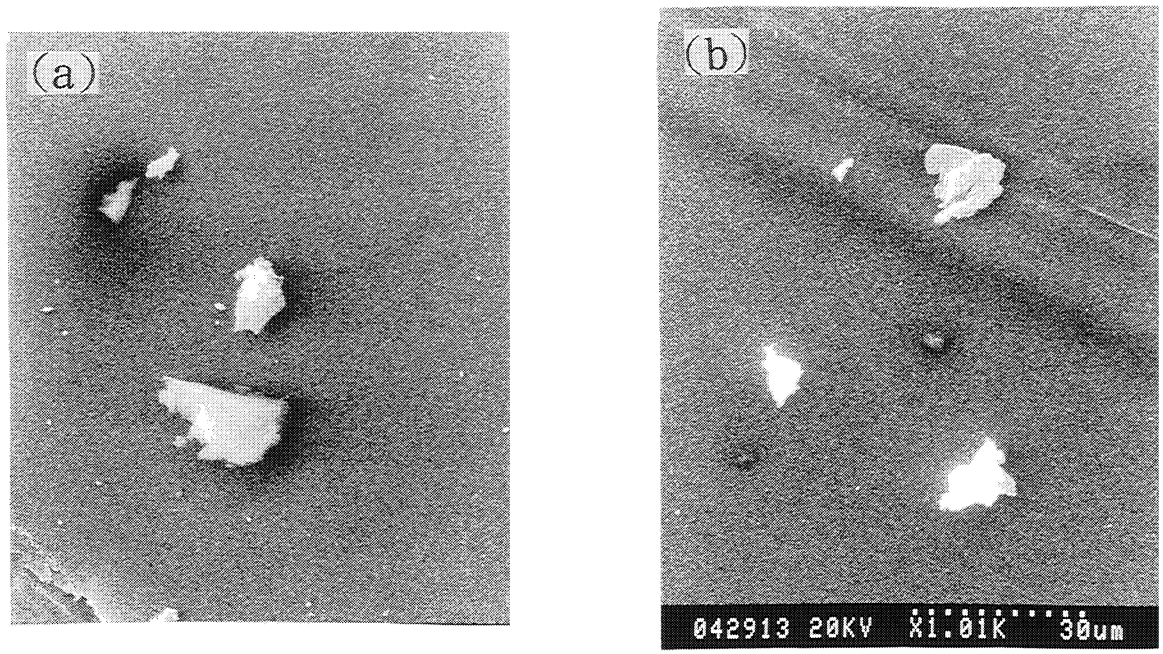

Fig. 1 The SEM photographs of the rod samples sintered at 500 °C for 2h with (a) 500 and (b) 10000 ppm Er^{3+} ions.

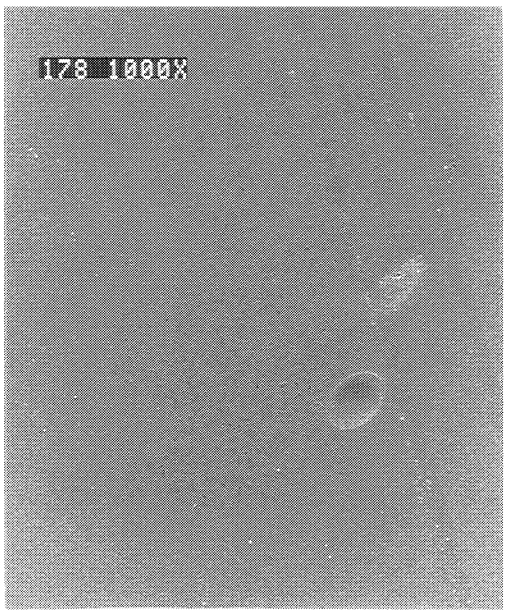

Fig. 2 The SEM photograph of the densified rod sample with 10000 ppm Er^{3+} ions sintered at 1050 °C for 2h.

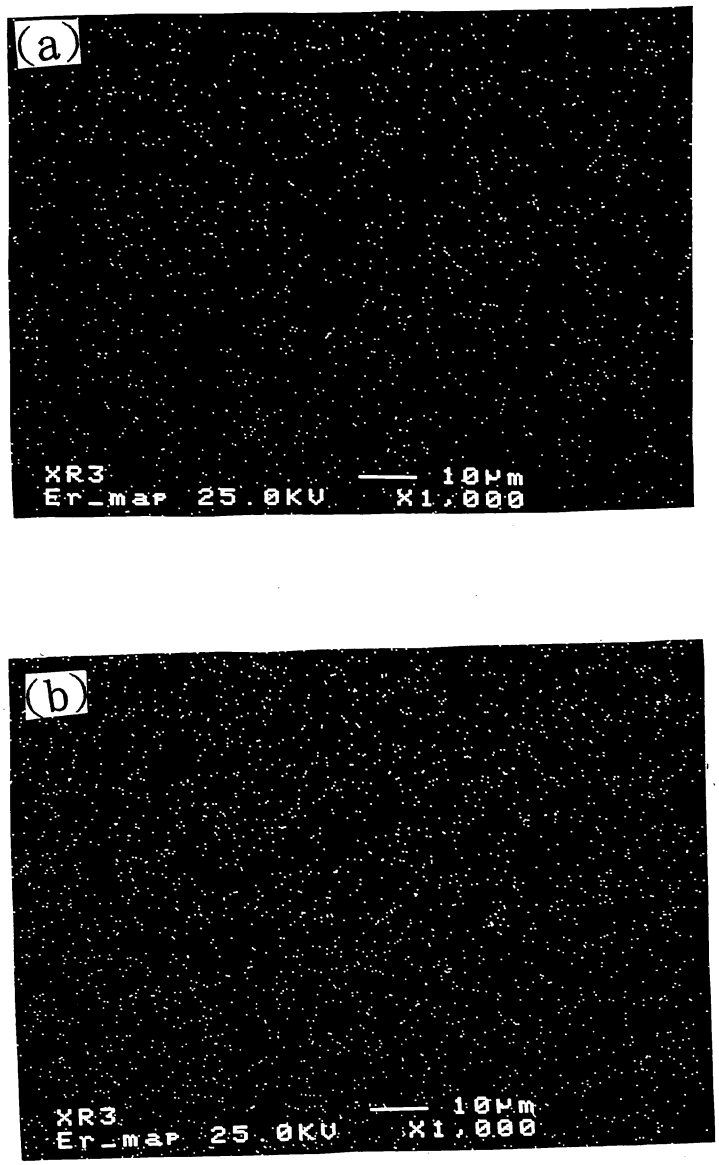

Fig. 3 The EPMA photographs of the samples corresponding to (a) Fig.1a and (b) Fig.1b.

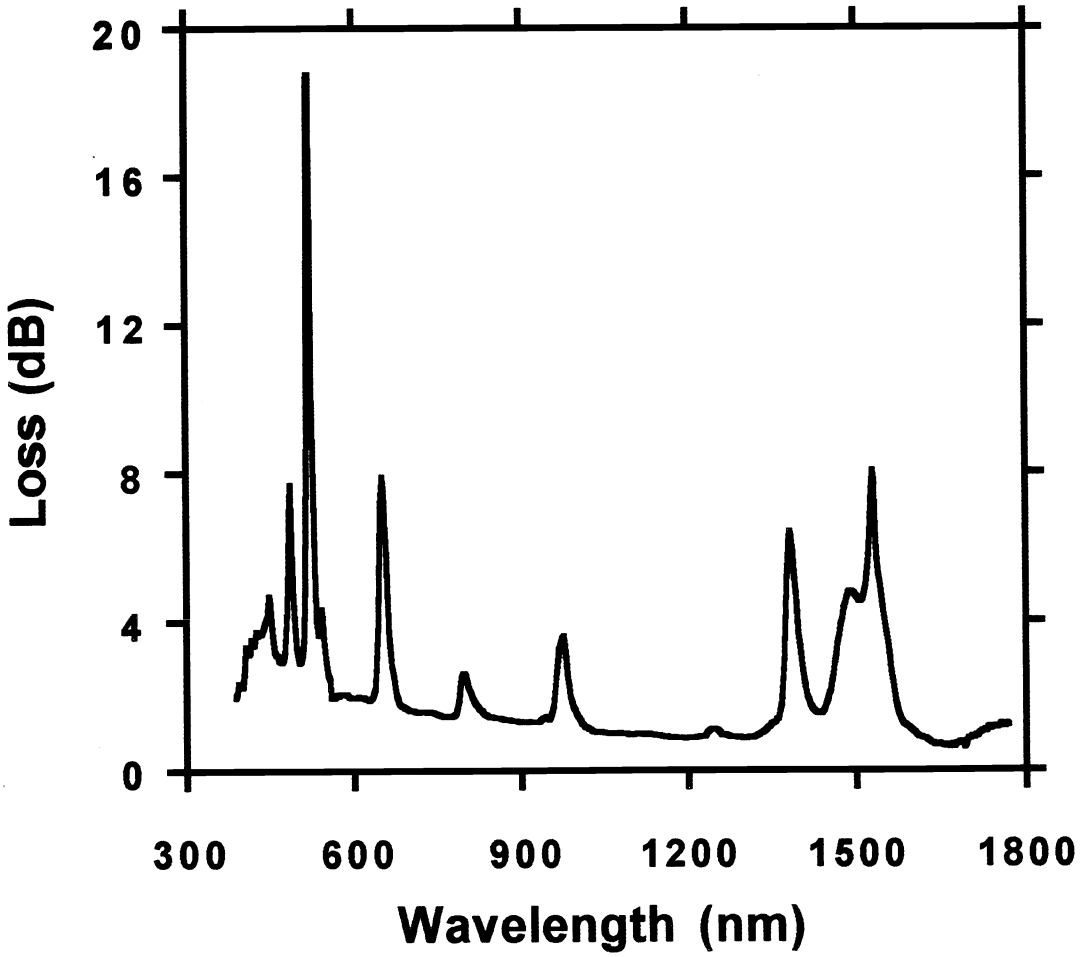

Fig. 4 The spectral loss of the sample with 5000 ppm Er^{3+} ions.

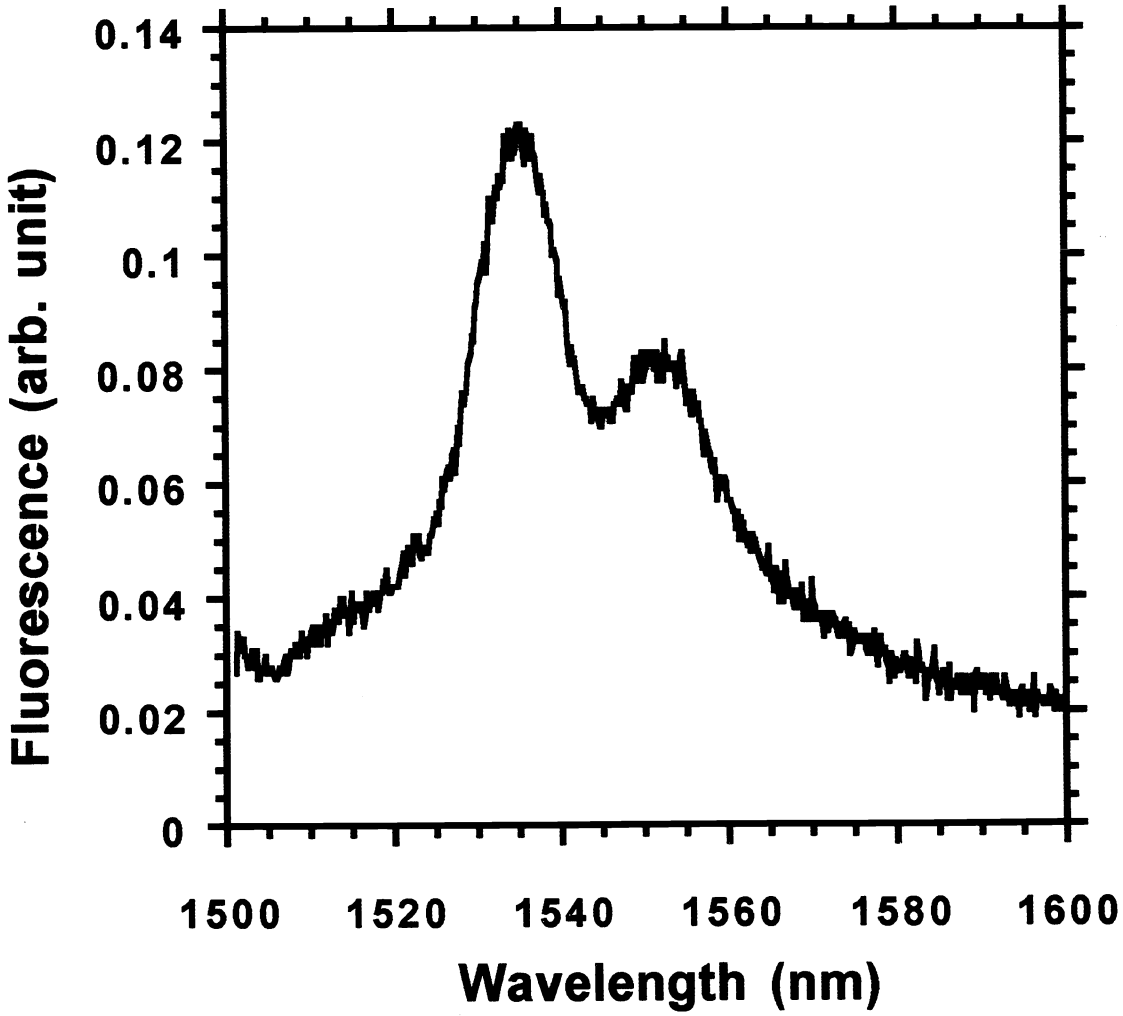

Fig. 5 The absorption and fluorescence spectra of the sample with 5000 ppm Er^{3+} ions.