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Spectroscopic properties of erbium doped silica glasses obtained by sol-gel method

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Abstract

The spectroscopic properties of erbium doped silica glasses obtained by sol-gel technology have been investigated. The emission properties of Er^{3+} ion are discussed on a basis of the absorption and emission spectra. The transmission and emission characteristics of Er doped silica fibers are presented. The efficient emission in the mid-ir region (at 1.55 μm) was observed. It has been found that, for the high concentration (1000 ppm) Er doped fiber, the 1.55 μm emission was completely quenched. Instead of this emission, the efficient green anti-Stokes emission (after laser diode pumping at 980 nm) was observed. © 1998 Elsevier Science S.A.

Keywords: Erbium doped silica glasses; Spectroscopic properties; Sol-gel method

1. Introduction

A great progress has been observed in last years in development of Er doped glasses appropriate for fiber lasers and telecommunication amplifiers operating at 1.55 μm [1]. Among different inorganic glasses the best candidates for efficient mid-ir sources are heavy fluoride and oxide glasses. The basic criteria are the efficient emission at 1.55 μm, lack of hydroxyl groups exhibiting absorption in this region and significant diminishing of multiphonon transitions. The most efficient commercial composition is a five-component glass ZBLAN (ZrF_4: BaF_2: LaF_3: AlF_3: NaF) [2]. This glass can be obtained either by the melting technique or by the sol-gel method [3,4].

The sol-gel technology allows to produce the transparent, monolithic quartz samples at relatively low temperature (below melting) with high concentration of rare earth ions. The optical properties of Er doped sol-gel silica glasses obtained at low temperatures (i.e. aerogels) were reported by Xu et al. [5]. Such glasses may be easily produced however they contain high amount of hydroxyl groups – greatly reducing the emission quantum yield of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, important for telecommunication purposes. The essential problem is obtaining thermally densified silica glasses with contamination of water below 2 ppm. Only from such sol-gel glasses it is reasonable to draw fibers. Recently [6] we have reported a new preparation technique for thermally densified sol-gel silica glasses doped with Er^{3+} ions sintered in freon atmosphere.

In this work we report optical properties of Er doped silica glasses obtained by sol-gel method. The emission characteristics around 1.55 μm was measured in a bulk and fiber for two different concentrations of active ions (100 and 1000 ppm). We have found that more concentrated sample did not demonstrate the emission at 1.55 μm. The fibers obtained from this glass have shown the efficient green anti-Stokes emission after pumping with 0.98 μm laser diode. It is concluded that Er doped silica glasses obtained by sol-gel technology may be suitable for optical amplifiers.

2. Experimental

The Er^{3+} silica gel glass samples were obtained according to the procedure described by us earlier [6]. The rods of silica quartz were formed and then the cores of

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PCS-type 200 μm diameter optical fibers were drawn. Absorption spectra were measured using Cary Varian 2300 spectrophotometer. Emission spectra were measured using Jobin-Yvon TRW 1000 spectrophotometer. As excitation sources were used an excimer laser Lambda Physics, an argon laser ILA 120 and a semiconducting diode laser 980 nm.

3. Results and discussion

3.1. Absorption

The optical absorption spectra of Er^{3+} doped silica gel glass with concentration 0.1 mol % were measured at room temperature and are demonstrated in Fig. 1. The spectrum consists of ten absorption bands corresponding to the electronic transitions from the ground $^4I_{15/2}$ state to the excited states $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^2H_{9/2}$, $^4G_{11/2}$, and $^2G_{9/2}$ states, respectively. The most intense bands are combined with the hypersensitive $^4I_{15/2}\rightarrow{}^2H_{11/2}$ and $^4I_{15/2}\rightarrow{}^2G_{11/2}$ transitions. There is observed a strong absorption band associated with the second overtone of OH group at 1400 nm.

The attenuation of Er doped silica sol-gel fiber was measured in the range 450–1700 nm. It is shown in Fig. 2. In general this spectrum differs significantly from the absorption spectrum of Er doped silica sol-gel glass especially in the mid-ir range (1100–1700 nm), where occur the strong absorption bands associated with the second overtone of –OH vibration which overlap with the $^4I_{13/2}$ state of Er^{3+} ion. Similarly the $^4I_{11/2}$ state located at the range of 900–1000 nm is overlapped by the third overtone of OH vibration. The most important fiber parameter characterizing its usefulness is the attenuation parameter measured at 1.55 μm. Its magnitude is equal to 16.000 dB km^{-1} which is similar to other Er doped fibers applied in optical amplifiers. In the range between 450 and 900 nm there appear a several intense and well resolved bands corresponding to the Er^{3+} absorption transitions. They are shown in the figure.

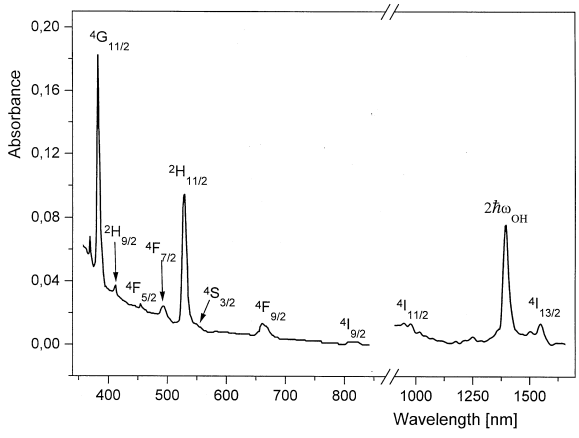

Fig. 1. Absorption spectrum of Er doped silica gel glass.

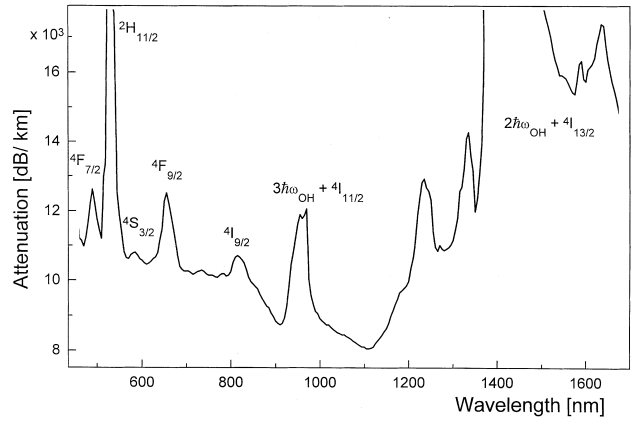

Fig. 2. Attenuation of Er doped silica gel fiber.

3.2. Emission

The emission spectra of Er^{3+} doped silica gel bulk glass were measured at 300 K upon argon laser excitation (488 nm). It is illustrated in Fig. 3. In the visible range we have observed the emission band at 540 nm assigned to the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition.

The ir emission spectrum of Er^{3+} doped silica fiber sample at 1.55 nm corresponding to the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition was excited with laser diode 980 nm. It is shown in Fig. 4. We have observed it only for low concentrated fiber (100 ppm) (see Fig. 4). For the second fiber with higher concentration we could not observed the ir emission. However, we have found that such fiber demonstrated the intense green emission resulting from the up-conversion process. The observed spectrum is shown in Fig. 5. One can observe the three well resolved bands centered at 500, 520 and 540 nm. The first band corresponds to the $^4F_{7/2}\rightarrow{}^4I_{15/2}$, the second band to the $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and the third to the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transitions. The principal

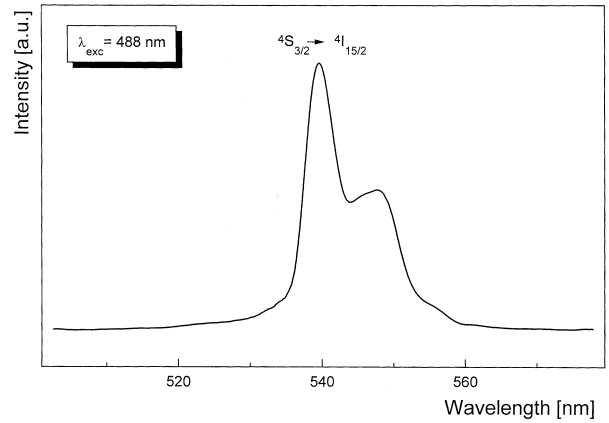

Fig. 3. Emission spectrum of Er doped silica gel glass under argon laser excitation.

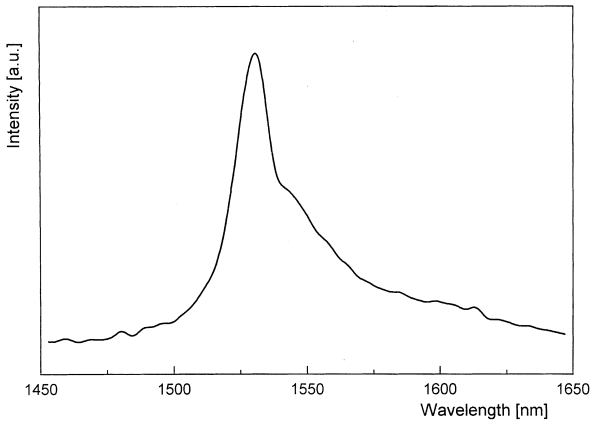

Fig. 4. Emission spectrum of Er doped silica gel fiber obtained under 980 nm excitation.

difference between the spectrum observed under argon laser excitation and that measured after up-conversion process is that there appear two additional bands at 500 and 520 nm. The anti-Stokes green emission was earlier observed by Xu et al. [5], however only in the case of Er^{3+} doped xerogel with red excitation of krypton laser (647.1 nm). They did not find the emissions at 500 and 520 nm. The mechanism of the up-conversion process observed in the Er^{3+} doped silica gel fiber is shown in Fig. 6. In the first step, there takes place absorption of two photons of energy corresponding to 980 nm from the ground $^4I_{15/2}$ to the $^4I_{11/2}$ levels of two different Er^{3+} ions. In the second step one of the Er^{3+} ions (occuring in the excited state) absorbs the energy of the second excited Er^{3+} ion due to the cooperative interaction and brings it to the higher energy $^4F_{7/2}$ level. Such process can occur for the closely distanced Er^{3+} ions. The emission we observed occurred from the $^4F_{7/2}$ level and the two lower lying $^4F_{7/2}$ and (metastable) $^4S_{1/2}$ states. They are populated by the fast

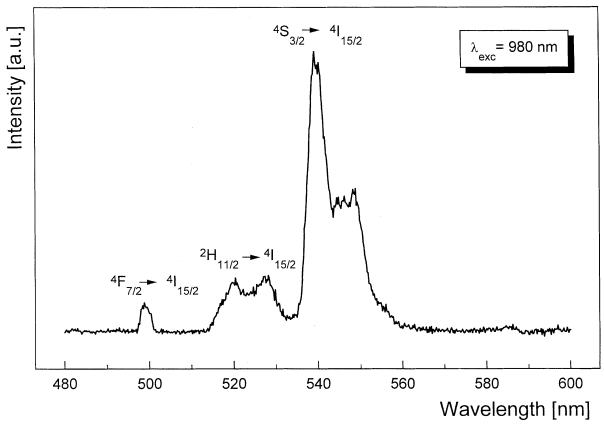

Fig. 5. Anti-Stokes green emission of Er doped silica gel fiber under 980 nm excitation.

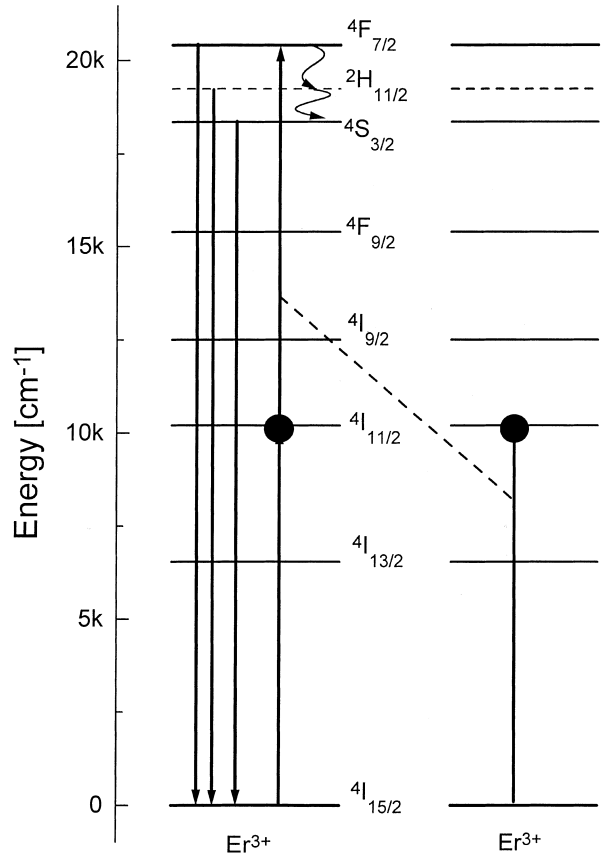

Fig. 6. Partial energy level diagram of Er^{3+} ions and proposed mechanism of up-conversion.

multiphonon relaxation. The most intense is the fluorescence band corresponding to the $^4S_{1/2} \rightarrow {}^4I_{15/2}$ transition.

4. Conclusions

The spectroscopic properties of Er doped silica gel glasses in a bulk glass and in fibers are reported. The measurements were performed for two different concentrations of active ions. The attenuation parameter for the 100 ppm fiber was determined to be 16.000 dB km^{-1}. It was found that under 980 nm excitation with laser diode the Er doped fibers exhibit intense emission at 1.55 μm at low concentration of Er^{3+} ions (100 ppm). For higher concentration (1000 ppm) we did not observe an emission at 1.55 μm, but instead of it the intense green emission. The up-conversion emission observed in fiber was essentially different to that measured by Xu et al. [5] for monolithic silica xerogel samples. We have observed at room temperature not only emission from the $^4S_{3/2}$ level but also from higher laying $^2H_{11/2}$ and $^4F_{7/2}$ levels. Its occuring is most probably due to the great reducing of multiphonon relaxation. Further studies of the dynamics of up-conversion process in fibers are in progress. It is

interesting to note that the green emission of Er doped silica fiber excited by laser diode may be applied as an intrinsic fiber-optic temperature sensor [7]. The results reported therein demonstrate that the Er doped fibers obtained from the silica gel glass may be appropriate for optical amplifiers.

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