ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 692–696

Journal of ALLOYS AND COMPOUNDS

Towards composite solid state laser materials

F. Auzel

France Télécom, DTD/BAG, Groupe Optique des Terres Rares, BP 107 F-92225 Bagneux, France

Abstract

The largest recent advance in the field of solid state materials is the exponential development of the Erbium doped fibre amplifiers, the so-called EDFAs, which are already implemented in many telecommunication systems. One is already interested in the evolution of such amplifiers towards more compact devices which could be obtained through Erbium doped wave guide amplifiers. The conditions for wave guide amplifiers are first discussed showing that it will be difficult to limit the active length to less than a few tenths of a centimetre in usual glasses without having to increase the active ion concentration up to the point where self-quenching reduces prohibitively the quantum efficiency of the amplifying transition. This leads us to consider new glassy materials where the inhomogeneous linewidth of the active ions shall be reduced in order to correlatively increase the gain cross-sections. An historical review of such an approach will be presented. Then we show that composite materials of the vitroceramic type where the active rare earth ion stays only in the microcrystalline phase, provide materials with reduced inhomogeneous broadening and with crystal type optical spectra though obtained by glass technics. Evaluations of the gain cross-sections indicate increases of at least 100%. Such composite materials may so pave the way for wave guide amplifiers.

Keywords: Active waveguide; Erbium cross-sections; Transparent vitroceramics; Rare-earth clusters

1. Introduction

Though the present size and specification of usual Erbium Doped Fiber Amplifiers (EDFA) are well suited for long distance systems, they are still too bulky and too costly to be usable in the distribution network where there is a need to compensate for the inherent losses of multiway splitters. Clearly optical amplifiers need size reduction and technology simplification in order to be generalised in the optical distribution network. One way to undertake this problem is to look towards Erbium doped short waveguide amplifiers. In this paper we shall consider the basic limitations imposed by physics and likely solutions which may be taken into account even before any practical realisation of the waveguides themselves.

The shortening of the active length will be obtained only if one of the following conditions is fulfilled: the active ion concentration–cross-sections product can be increased by three orders of magnitude.

From basic principles, it is shown that because of the rather weak interaction with the surroundings, the ion cross-sections do not vary a lot when changing the glass host and that the ion–ion interactions will fundamentally limit the active ion concentration.

A tentative solution is the development of transparent RE doped vitroceramics with high volumic percentage of the crystallite phase. A comparison of results for nanometric and micrometric crystallite types of transparent vitroceramics shall be given.

2. Typical specifications of present optical fiber amplifiers

2.1. Comparison and specifications for semiconductor and EDFA optical amplifiers

The competition between semiconductor and EDFA optical amplifiers, was won by the latter not because of the gain values which are about equivalent (30–40 dB), but essentially because of two specific characters of EDFA: namely the gain saturation power, which reaches +11 dBm in EDFA to be compared to −3 to +8 dBm in semiconductors and the polarisation effect defined as the ratio of the gain for two orthogonal polarizations which is 0 db for fiber and 1–4 dB for semiconductor amplifiers.

2.2. Typical lengths and doping concentrations for fiber amplifiers

It is interesting to define an upper limit to the gain (G_{lim}) of an Erbium doped optical amplifier, whatever the tech-

0925-8388/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(98)00419-8

nology and the pumping efficiency, by simply considering the single path gain for total inversion, which of course can never be reached: if such value is found lower than the expected gain, then it shall be hopeless whatever the pumping. It is given by:

$$G_{\mathrm{lim}} = 10 \log_{10}(\exp(\sigma N L)) \tag{1}$$

where σ is the induced emission cross-section, N the active ion concentration and L is the length of the optical amplifier. For typical values of Erbium in a fiber, with $\sigma = 5 \times 10^{-21}$ cm^2, $N = 1.4 \times 10^{18}$ cm^{-3} ($\cong$200 ppm), $L = 10$ m, one obtains:

$$G_{\mathrm{lim}} = 10 \log_{10}(\exp 7) = 30.4\ \mathrm{dB} \tag{2}$$

Such a value, with the above length and concentration, being a limit, will of course never be reached whatever the pumping and if a higher gain is required, it is certainly an impossible task. Defining such a limit is useful in finding the minimum requirements for a given gain value. Let us consider the analogue of the compact waveguide amplifier we are interested in.

3. The fundamental parameter for optical fiber amplifier

3.1. The cross-section–concentration product necessary for a compact waveguide amplifier

Assuming that a compact waveguide amplifier should have a length of about 1 cm, that is a length 1/1000 of the typical one for an EDFA, and in order to keep a gain of 30.4 dB, one needs from (2) to still have: $\sigma N L = 7$, that is an increase in σN by a factor of 1000 or:

$$\sigma N = 7\ \mathrm{cm}^{-1} \tag{3}$$

This is to be compared to 7×10^{-3} cm^{-1}, the usual value for fiber.

3.2. The basic limitations for cross-section and concentration increase in glasses

Because Rare-Earth (RE) 4f–4f transitions are forbidden at first order, the integrated cross-sections over frequencies, that is the oscillator strength is about constant $\cong 10^{-6}$ except for the so-called hypersensitive transitions characterized by $\Delta J \leq 2$. The case of interest to us is the Er^{3+} transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ at 1.54 μm. It could be an hypersensitive one, however because $\Delta J = 1$ is also the selection rule for the magnetic dipole transition which is allowed, a large part of the oscillator strength for the above transition is of magnetic dipole origin and so independent of the host. It can be concluded that there is not much chance of finding a material with an oscillator strength much larger than the ones we already know. Consequently high cross-sections can only be found in materials showing narrow effective line width Δ_{eff} with:

$$\Delta_{\mathrm{eff}} = \frac{1}{\sigma_{\max}} \int \sigma(\nu)\mathrm{d}\nu$$

In glasses the narrower effective linewidth shall be obtained for narrower inhomogeneous width.

As for the concentration increase, the limitations are firstly at the chemical level; either because one-constituent glass offers too tiny a space for the large RE ions (1 Å), which are rejected by the glass; this is the case for pure silica glass, where concentration is chemically limited to about 100 ppm (0.7×10^{18} cm^{-3}) and this directs us towards multicomponent glasses; or because the RE elements behaving usually as glass modifiers and not as glass formers tend to devitrify glasses when they are incorporated at too high concentrations. The highest chemical concentration that we know for a phosphate glass reaches 3×10^5 ppm (2.2×10^{21} cm^{-3}).

The concentration limitation also takes place at the physical level usually before the maximum chemical concentration is reached. This is due to the ion–ion interactions giving rise to ‘concentration quenching’ which is excitation independent. There is also clustering of ions revealed by energy transfers with one out of both considered ions being in an excited state; the role of this effect is excitation dependant. Energy transfers by dipole–dipole interactions can take place at distances reaching 20 Å, whereas the cluster effect, by definition, exists for nearby ions separated by distances less than 6 Å and for this reason is very effective.

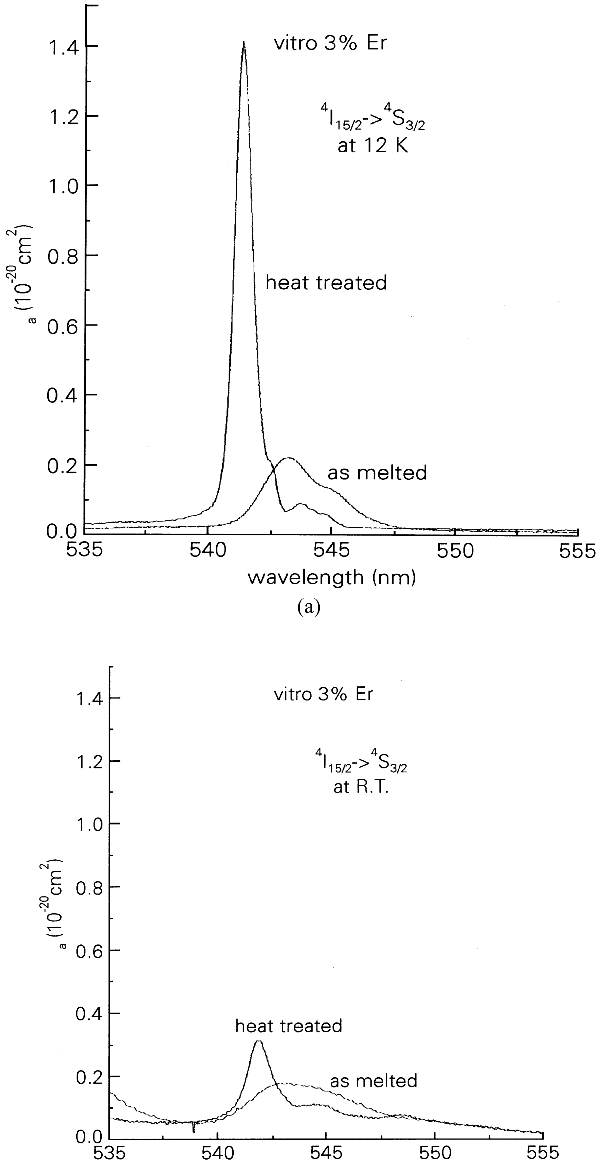
4. Proposed hints for solutions

4.1. Inhomogeneous line-width reduction in glassy materials

In order to increase the useful cross-section, as observed above, one can decrease the inhomogeneous linewidth. We had proposed a long time ago to consider oxyfluoride vitroceramics (GeO_2–PbF_2–REF_3; SiO_2–PbF_2–REF_3), where the doping RE ions embedded in a fluoride microcrystalline phase surrounded by an oxide glassy phase [1]. The crystallites were larger than the wavelength and these vitroceramics were not transparent, which was a useful property for the visualization application considered at the time. However fluorescent properties of such materials were excellent because cross-sections were those of crystals and efficiencies were high enough because the non-radiative transitions of the RE ions were reduced, being ruled out by the lower energy photons of the surrounding fluoride and not by the oxygenic glassy host. We had proposed [1], provided the crystallite’s size could be reduced, to use such vitroceramics for lasers because they were the first known glassy material having the RE doping only in the crystalline phase.

Since then, such vitroceramics have been modified in order to become transparent, with the idea to obtain bulk up-conversion lasers [2,3] or Pr^{3+} amplifiers [4].

We have obtained transparent vitroceramics in the system: (GeO_2–PbO–PbF_2–ErF_3/NdF_3) [5], displaying the typical spectra of PbF_2 crystals instead of the one of the initial glass as shown in Fig. 1. At 300 K the cross section is multiplied by a factor of two and six at 12 K. TEM pictures of the vitroceramic structure show that the crystallites have a diameter of about 85 Å with a volumic filling factor of 2% for a 3% Er-doped initial glass.



(a)

(b)

Fig. 1. Comparison of absorption cross-section spectra at (a) 12 K and at (b) 300 K, for the initial Er-doped (GeO_2–PbO–PbF_2) glass as melted and for the corresponding vitroceramics after heat treatment. After [5].

Because we are interested here in short path amplifiers, we want to increase the crystalline phase with respect to the glassy one. This leads us to consider fluoride vitroceramics (ZrF_4–LaF_3–AlF_3) doped with Er^{3+} [6]. Such vitroceramics are obtained by spinodal decomposition and show large size crystallites which, are constituted of the phase $Zr(La,Er)_3F_{15.}$ They show spectra reflecting the reduced inhomogeneous linewidth of the crystal and not the inhomogeneous linewidth of the initial glass before the heat treatment which provokes the demixing, see Fig. 2. Because the masses of the of the glass phase constituents are very close to the ones of the crystallites, the obtained vitroceramic is still transparent though it presents some added scattering losses. Such a vitroceramic, being crystallized at about 70–90% of its volume, shows a large active path length. Moreover, as shown in Fig. 3, the cross-section is increased, both because the spectrum is somewhat narrower than for the initial glass by reduction of the inhomogeneous width, but also because the integrated cross-section is increased by the change in the RE ion environment. The cross-section at 1.5 μm can be doubled in such a matrix and reaches 10^{-20} cm^2.

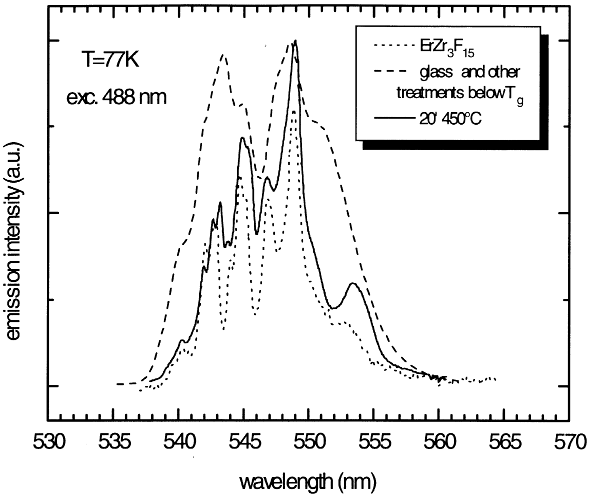


Fig. 2. Comparison of the $^4S_{3/2}$ emission spectra of Er^{3+} at 77 K in the original glass before heat treatment (- - -); the vitroceramic as obtained after heat treatment (———); a reference sample of crystalline powder of $ErZr_3F_{15}$ (· · ·). From [6].

4.2. Increase of the useful concentration by reduction of the ion–ion clustering effect

As shown in Fig. 3, the other way to increase the gain is to increase *N* without increasing to much self-quenching and clustering. Because the self-quenching is linked to the diffusion towards other unwanted ions with absorption in the same range as Er emission, or OH radicals, or clusters

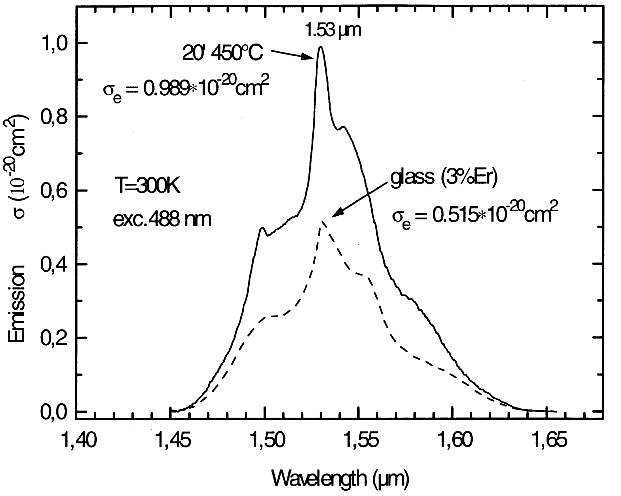


Fig. 3. Comparison of emission spectra and cross-sections for the initial glass (- - -) and the vitroceramic (———). After [6].

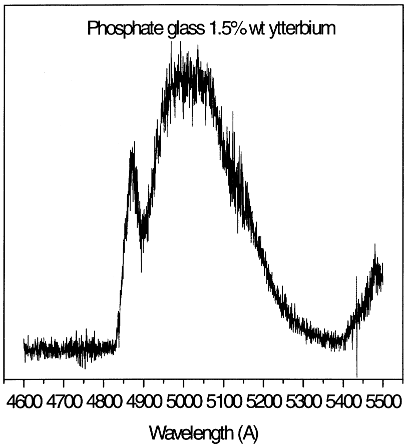


Fig. 4. Blue cooperative emission from Yb^{3+} clusters in a phosphate glass at 77 K.

of Er ions, it is important that, besides controlling the purity of the glass during fabrication, one can also control the amount of clustering.

4.3. Definition of a doping cluster; obtaining of the cluster signature by a cooperative luminescence experiment

We have proposed to obtain the signature of the RE clusters in an unambiguous way by using Yb^{3+} ion cooperative luminescence as a clustering probe [7]. Such effect involves only close-by ions (<6 Å) whereas energy transfers are known to arise even at distances of 30 Å for which a cluster is difficult to define. The Yb ion is particularly useful for such a probe because this ion possesses only two levels at about 10^4 cm^{-1} in the near infra-red and no levels in the visible. Because cooperative luminescence corresponds to the emission at 0.5×10^4 cm^{-1} from two simultaneously excited Yb ions inside a clustered pair, the corresponding visible emission is a clear signature of the existence of a pair; see Fig. 3 and also Fig. 4. A systematic study of such signatures has allowed us to obtain glasses with reduced amounts of clustering and useful concentrations up to 2×10^{21} cm^{-3} before the $^4I_{13/2}$ lifetime was reduced by 1/2.

4.4. Present best results in waveguide amplifiers and what could be gained with proposed hints

In silica glass waveguide amplifiers, gains of 9.4 dB have been obtained with $L=23$ cm in S shape for $N=3800$ ppm [8], this corresponds to $\sigma N=0.13$ cm^{-1} and to $G_{lim}=13$ db. This shows that the obtained gain is not far from the limit and improvement without increasing σN is not expected.

In phosphate glass a gain of $G=10$ db has been obtained [9] for $N=4\times10^4$ ppm and $L=4$ cm. This corresponds to $\sigma N=1.4$ cm^{-1} and to $G_{lim}=24$ db. It shows that the obtained result is still far from the gain limit and some engineering improvements are still possible.

From the results of Section 4.1 Section 4.3 one can expect an increase of a factor of two for cross-sections and a factor of seven for concentration with respect to the values considered for the phosphate amplifier wave guide of [9].

The simultaneous increase in cross-section and in concentration could eventually be a problem within the microcrystals. This is not really linked to the clustering process because in the crystallites, contrary to the glass case, the distances are well defined through the crystal structure itself. We have to consider the basic self-quenching properties of the micro-crystal itself and choose the microcrystal nature in the function of the rule that we had defined for the crystal field in the so-called stoichiometric materials [10,11].

5. Conclusion

From the above examples and results it is shown that wave guide amplifiers with RE ions are possible for cm length, on the condition that: (i) multicomponent glasses are used with concentration increases up to 2×10^{21} cm^{-3}; (ii) OH radicals and clusters are avoided; (iii) heat treatments are used, turning the glass into vitroceramics nucleated from the RE ions. Of course this implies that the scattering losses may be reduced down to an acceptable level with respect to the gains.

Acknowledgements

It is a pleasure to acknowledge the collaboration of Fabienne Pellé, Michel Mortier and Philippe Goldner on various aspects of this subject.

References

[1] F. Auzel, D. Pecile, D. Morin, J. Electrochem. Soc. 122 (1975) 101.

[2] Y. Wang, J. Ohwaki, Appl. Phys. Lett. 63 (1993) 3268.

[3] K. Hirao, K. Tanaka, M. Makita, N. Soga, J. Appl. Phys. 78 (1995) 3445.

[4] P.A. Tick, N.F. Borelli, L.K. Cornelius, M.A. Newhouse, J. Appl. Phys. 78 (1995) 6367.

[5] M. Mortier, F. Auzel, Proceedings of the 9th CIMTEC–World Ceramics Congress and Forum on New Materials (Florence, Italy, June 14–19, 1998). P. Vincengini (Ed.), SX-2: LD8.

[6] F. Auzel, K.E. Lipinska, P. Santa-Cruz, Optical Materials 5 (1996) 75.

[7] F. Auzel, D. Meichenin, F. Pellé, P. Goldner, Optical Materials 4 (1994) 35.

[8] K. Hattori, T. Kitagawa, M. Oguma, M. Wada, J. Temmyo, M. Horiguchi, Electron. Lett. 29 (1993) 357.

[9] D. Barbier, ''Compact 1.54 μm optical planar amplifier'', leaflet issued by GEEO, F-38031 Grenoble cedex France, 1996.

[10] F. Auzel, Mater. Res. Bull. 14 (1979) 223.

[11] F. Auzel, J. Dexpert-Ghys, M. Morin, Mater. Res. Bull. 16 (1981) 1521.