Industrial Applications of Rare Earths in Fiber Optics, Luminescent Solar Concentrators and Lasers*

RENATA REISFELD**

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Abstract

Luminescent solar concentrators which concentrate light from large plate surfaces to the plate's edges are promising devices for lowering the price of photovoltaic electricity. Plates based on neodymium and ytterbium doped glasses covered by thin glass layers incorporating organic dyes are promising materials for efficient luminescent solar concentrators.

Fluoride glasses incorporating rare earths are proposed as integrated systems for fiber optic communications in the visible and infrared parts of the spectrum. Such devices may be obtained from rare earths in fluoride glasses in direct contact with undoped glass of the same composition without the light-emitting lanthanide.

Storage of energy in the lowest quartet state of manganese(II) and transfer of energy to neodymium(III) provides another opportunity for improving the performance of lasers.

New laser materials based on the combination of rare earths and organic dyes will also be discussed.

Introduction

At the previous conference on the Technology of the Lanthanides and Actinides in Venice, Sept. 1983, 'Future Applications in Spectroscopy and Non-radiative Phenomena of Rare Earths in Glasses' [1], was presented. Many topics discussed then have materialized during the time between the two conferences. For example large plates for luminescent solar concentrators (LSC) doped by the rare earths Nd(III) and Yb(III) and by Cr(III), and borosilicate plates doped by uranyl have been prepared and tested by Dr Neuroth of Schott [2].

We shall discuss below how such luminescent solar concentrators can be improved further by radiative trapping of energy from thin films of organic dyes deposited on the luminescent glass plates.

Most of today's optical fibers are made of silica glass and while useful in many applications they transmit visible light only and absorb in the infrared part of the spectrum where Rayleigh scattering is at its lowest.

Since transmission loss is perhaps the most important single performance parameter of optical fibers it remains an active area of research and development. Substantial long-term development activity on low-loss fibers focuses on mid-IR-fibers and the research in this area made noteworthy advances in recent years. Fibers based on fluoride glasses can transmit light 10–100 times more efficiently than silicate glasses. Zirconium fluoride optical glass is now available which transmits light up to 5–7 μm with little loss of transmission. Losses lower than 1 dB/km at 2.55 or 2.6 μm were announced by several companies. One prospect for commercialization of this technology will probably be repeaterless transoceanic cable systems. Applications with more short-term potential might include sensing, spectroscopy, power-delivery for medicine and industrial processing. Promising research for this application is concentrated on fluoride glasses. However one of the serious problems remaining is the coupling of the laser beam to the very thin fiber. We shall discuss a possibility of manufacturing the laser source within the fluoride fiber and thus overcome this difficulty. If such a fiber can be made into a laser the advantages of low cost will be met. The coherent source can exploit best the high intrinsic bandwidths of optical fibers and thus it is promising in various high bandwidth light wave system applications in addition to its potential in long distance applications. Coherent systems have been already shown to have very interesting potential for advanced local area networks.

Luminescent Solar Concentrators

The operation of a luminescent solar concentrator is based on the absorption of solar radiation in a collector containing a fluorescent species in which the emission bands have little or no overlap with the

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**Enrique Berman Professor of Solar Energy.

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absorption bands. The fluorescence emission is trapped by total internal reflection and concentrated at the edges of the collector which is usually a thin plate [3]. LSCs have the following advantages over conventional solar concentrators: they collect both direct and diffuse light; there is good heat dissipation of non-utilized energy by the large area of the collector plate in contact with air so that essentially 'cold light' reaches the photovoltaic cells; tracking the sun is unnecessary; the luminescent species can be chosen to allow matching of the concentrated light to the maximum sensitivity of the photovoltaic cell [1, 3–5].

The performance of LSCs which absorb light in a large plate area and convert it to luminescence which ultimately concentrates at the edges of the plate, has been discussed in refs. 2–4.

The optical efficiency of an LSC may be expressed by

$$\eta_{opt} = \eta_{tr}\eta_{abs}\eta_{fl}\eta_{st}\eta_{par} \quad (1)$$

where η_{tr} is the efficiency of the trapped fluorescence due to internal reflections, η_{abs} is the efficiency of the absorbed light, η_{fl} is the fluorescence efficiency, η_{st} is the Stokes efficiency and η_{par} is the efficiency including parasitic losses.

The highest efficiency for a singly doped rare earth glass is 12% for an Nd-doped tellurite glass obtained in our laboratory. In general, the optical efficiencies of LSCs containing rare earths can be obtained from the calculated absorption and fluorescence efficiency [5]. These values are helpful for determining which specific material should be studied for LSCs.

As the intrinsic absorption of inorganic ions is low since its origins are parity forbidden (and sometimes spin forbidden) transitions, an additional increase in plate efficiencies of LSCs doped by inorganic ions can be obtained by nonradiative [6] and radiative [7] trapping of strong luminescence emitted by organic dyes incorporated in thin polymer or glass films covering the plates. About 40% efficiency has been shown in systems where an Nd-doped plate is covered by a specific organic dye [8]. The dye efficiently absorbs the solar light. The resulting fluorescence is trapped in the glass. The high concentration of emitting photons amplifies the absorption of Nd(III) which is then followed by intensive luminescence.

Laser Sources for Fiber Optics

Already in 1880 Bell talked over a distance of 1300 feet (approximately 400 m) by means of his photophone. However, at that time electrical connections were more flexible and economical. The attempts at communication by means of light waves failed in part from lack of coherent sources. The development of fiber optics together with coherent semiconductor lasers and rare earth lasers promise cheap and simple broad-band communications over a variety of distances, in computers, switching systems, aircraft and space craft as well as between points hundreds of kilometers apart. The economic and social context is one of limited space required for copper wires, increasing cost of copper and other materials and the need for more circuits and more bandwidths. As already mentioned there is an increase in a variety of fiber waveguides based on fluoride glasses. We present below the laser properties of several rare earths doped into these glasses which emit in the range of maximum transparency of the fibers.

We propose that glasses doped by appropriate rare earth ions having the desired laser emission be drawn into fibers which will be a part of long fibers made of undoped glass. As will be shown below such intrinsic laser sources can be produced and be a part of integrated fiber optics.

The laser action of a glass or crystal [9] depends on the laser peak cross-section and the threshold power for lasing.

The formula for peak cross-section is

$$\sigma = \frac{\lambda^4 A}{8\pi c n^2 \Delta\lambda} \quad (\mathrm{cm}^2) \quad (2)$$

where λ = emission wavelength (cm), $\Delta\lambda$ = full width at half height of emission band (cm), n = refractive index, and A = radiative transfer probability (s^{-1}). Threshold power (W/cm^2) for transverse pumping is

$$P_{thr} = \frac{hc(L_0 + L_{res}) \times 10^{-7}}{2\lambda_p \tau_f l F \sigma \alpha_p} \quad (3)$$

where L_{res} = resonant power loss due to self-absorption at the laser wavelength which is defined as

$$L_{res} = 2l\sigma N\beta_y/Z \quad (4)$$

where N = number density of lasing ions, β_y = Boltzmann factor for the terminal laser level, Z = partition function, and l = length of laser.

In Nd(III) the terminal level $^4I_{11/2}$ for the 1060 nm luminescence is positioned at $\approx$2000 cm^{-1}, then $\Delta E/kT = 10$ at room temperature and the Boltzmann factor is 4.5×10^{-5}. For a 1 cm long minilaser at representative values of N and σ: $L_{res} = 0.2$–0.1%; L_0 = nonresonant loss which is mainly due to the absorption of the medium and loss at mirrors: it is usually taken to be 0–1.5%; λ_p = pumping wavelength: for Nd(III) it is 806 nm of LED having 25 nm bandwidth; τ_f = lifetime of lasing level; F = Boltzmann population function of the lasing level which in case of glasses having an inhomogeneous broadening is taken as 1; α_p = absorption coefficient of the pumped level which is obtained by dividing the optical density of the sample at the pumping wavelength by its thickness.

The energies used for pumping can be obtained from the existing light emitting diodes or semiconducting lasers obtainable today in arrays.

A high efficiency laser array was recently demonstrated to pump rare earth doped lasers Nd(III), Ho(III) and Er(III) [10].

The cross-section σ and threshold power P_{thr} for these ions were calculated by Eyal based on the relevant literature data. Tables I, II and III present the cross-sections and laser properties respectively of Nd(III), Ho(III) and Er(III) in glasses the formulae of which are presented below.

Formulae of the Glasses (references to the specific glasses are given in Tables I–III)

ZBLA: $34BaF_2$, $57ZrF_4$, $4AlF_3$, $3LaF_3$, $(Nd,Er,Ho)F_3$.

PGZ: $22ZnF_2$, $46PbF_2$, $30GaF_3$, $2LaF_3$, $(Nd,Er)F_3$.

BZYTZ: $9BaF_2$, $27ZnF_2$, $27.5ThF_4$, $6ZrF_4$, $22.5YF_3$, $5NaF$, $3LiF_3$, $(Er,Ho)F_3$.

BIZYT: $30BaF_2$, $30InF_3$, $20ZnF_2$, $(10-x)YF_3$, $10ThF_4$, $xHoF_3$.

BZYTL: $19BaF_2$, $27ZnF_2$, $27ThF_4$, $21LuF_3$, $1HoF_3$, $5YbF_3$.

ZnTe: $35ZnO$, $65TeO_2$, $(Ho,Nd)F_3$.

ED-2: $60SiO_2$, $27.5Li_2O$, $10CaO$, $2.5Al_2O_3$, $0.16CeO_2$ mol.%, $2.012Nd_2O_3$ wt.%.

GLS: $3Ga_2S_3$, $0.85La_2S_3$, $0.15Nd_2S_3$.

The threshold powers can be significantly lowered by transferring energy from other ions. The existence of these ions increases the possibility of pumping due to higher absorption. The threshold powers presented in Table IV are significantly lower, as a result of energy transfer, than those of singly doped ions.

TABLE I. Cross-sections and Laser Properties of Nd(III) in Glasses

Glass	Reference	Nd (mol.%)	Transition	λ (μm) laser	Lifetime (ms)	A (s^{-1})	$\sigma \times 10^{20}$ (cm^2)	λ (nm) pump	α_{pump} (cm^{-1})	P_{thr} (W/cm^2)
ZBLA	27	0.5	$^4F_{3/2} \rightarrow {}^4I_{11/2}$	1.05	0.445	1100	2.90	806	0.90	106
ZBLA	27	0.5	$^4F_{3/2} \rightarrow {}^4I_{13/2}$	1.30	0.445	340	0.90	806	0.90	343
PGZ	28	2.0	$^4F_{3/2} \rightarrow {}^4I_{11/2}$	1.05	0.19	1470	2.90	806	3.60	64
PGZ	28	2.0	$^4F_{3/2} \rightarrow {}^4I_{13/2}$	1.31	0.19	371	0.86	806	3.60	209
ZnTe	29	1.6	$^4F_{3/2} \rightarrow {}^4I_{11/2}$	1.05	0.13	3200	3.60	806	4.73	55
ZnTe	29	1.6	$^4F_{3/2} \rightarrow {}^4I_{13/2}$	1.31	0.13	760	1.40	806	4.73	143
GLS	30	2.6	$^4F_{3/2} \rightarrow {}^4I_{11/2}$	1.08	0.10		7.95	806	14.50	11
GLS	30	2.6	$^4F_{3/2} \rightarrow {}^4I_{13/2}$	1.37	0.10		2.70	806	14.50	31
ED-2	31	0.7	$^4F_{3/2} \rightarrow {}^4I_{11/2}$	1.06	0.30		2.90	806	1.27	108
ED-2	31	0.7	$^4F_{3/2} \rightarrow {}^4I_{13/2}$	1.34	0.30		0.72	806	1.27	450

TABLE II. Cross-sections and Laser Properties of Ho(III) in Glasses

Glass	Reference	Ho (mol.%)	Transition	λ (μm) laser	Lifetime (ms)	A (s^{-1})	$\sigma \times 10^{20}$ (cm^2)	λ (nm) pump	α_{pump} (cm^{-1})	P_{thr} (W/cm^2)
ZBLA	32	2	$^5I_7 \rightarrow {}^5I_8$	2.0	4.2	84.0	0.44	540	1.43	278.5
ZBLA	32	2	$^5I_6 \rightarrow {}^5I_8$	1.2	2.5	140.3	0.39	540	1.43	528.0
ZBLA	32	2	$^5I_6 \rightarrow {}^5I_7$	2.9	2.5	24.0	1.31	540	1.43	39.3
ZBLA	33	2	$^5I_7 \rightarrow {}^5I_8$	2.0	13.5	67.0	0.41	540	1.43	115.6
ZBLA	34	2	$^5I_7 \rightarrow {}^5I_8$	2.0	11.7	87.0	0.48	540	1.43	91.7
ZBLA	34	2	$^5I_6 \rightarrow {}^5I_8$	1.2	3.5	158.0	0.44	540	1.43	334.3
ZBLA	34	2	$^5I_6 \rightarrow {}^5I_7$	2.9	3.5	27.6	1.52	540	1.43	24.2
BIZYT	33	0.5	$^5I_7 \rightarrow {}^5I_8$	2.0	14.2	63.0	0.37	540	0.33	431.1
BIZYT	33	0.5	$^5I_6 \rightarrow {}^5I_8$	1.2	3.5	140.0	0.41	540	0.33	1578.4
BIZYT	33	0.5	$^5I_6 \rightarrow {}^5I_7$	2.9	3.5	24.0	1.50	540	0.33	108.0
BZYTZ	35	0.125	$^5I_7 \rightarrow {}^5I_8$	2.0	11.5	79.0	0.45	540	0.08	1750.0
BZYTZ	35	0.125	$^5I_6 \rightarrow {}^5I_8$	1.2	3.8	148.0	0.41	540	0.08	5815.0
BZYTZ	35	0.125	$^5I_6 \rightarrow {}^5I_7$	2.9	3.8	29.1	1.58	540	0.08	377.2
ZnTe	36	2.0	$^5I_7 \rightarrow {}^5I_8$	2.0	2.5	204.0	0.63	540	2.60	179.8
ZnTe	36	2.0	$^5I_6 \rightarrow {}^5I_8$	1.2	0.4	357.0	0.52	540	2.60	1361.2
ZnTe	36	2.0	$^5I_6 \rightarrow {}^5I_7$	2.9	0.4	69.0	1.82	540	2.60	97.3

TABLE III. Cross-sections and Laser Properties of Er(III) in Glasses

Glass	Reference	Er (mol.%)	Transition	λ (μm) laser	Lifetime (ms)	A (s^{-1})	$\sigma \times 10^{20}$ (cm^2)	λ (nm) pump	α_{pump} (cm^{-1})	P_{thr} (W/cm^2)
ZBLA	37	1	$^4I_{11/2} \rightarrow {}^4I_{15/2}$	0.98	6.0	89.9	0.15	975	1.00	454.5
ZBLA	37	1	$^4I_{11/2} \rightarrow {}^4I_{13/2}$	2.80	6.0	18.6	1.11	975	1.00	15.3
ZBLA	38	2.66	$^4I_{11/2} \rightarrow {}^4I_{15/2}$	0.98	6.0	111.0	0.20	975	2.70	125.8
ZBLA	38	2.66	$^4I_{11/2} \rightarrow {}^4I_{13/2}$	2.80	6.0	24.0	1.28	975	2.70	4.9
PGZ	39	2	$^4I_{11/2} \rightarrow {}^4I_{15/2}$	0.98	6.0	127.0	0.18	975	2.10	179.7
PGZ	39	2	$^4I_{11/2} \rightarrow {}^4I_{13/2}$	2.80	6.0	28.5	1.20	975	2.10	6.7
BZYTZ	35	0.125	$^4I_{11/2} \rightarrow {}^4I_{15/2}$	0.98	7.4	98.0	0.20	975	0.13	2118.0
BZYTZ	35	0.125	$^4I_{11/2} \rightarrow {}^4I_{13/2}$	2.80	7.4	30.0	1.96	975	0.13	54.0
BZYTL	40	1.0	$^4I_{11/2} \rightarrow {}^4I_{15/2}$	0.98	6.0	110.5	0.22	975	1.01	308.8
BZYTL	40	1.0	$^4I_{11/2} \rightarrow {}^4I_{13/2}$	2.80	6.0	22.8	1.54	975	1.01	11.0

TABLE IV. Effect of Added Ion on Laser Threshold Power of Er(III) and Ho(III) in Fluoride Glasses

Glass	Reference	Ion	λ (μm) laser	$\sigma \times 10^{20}$ (cm^2)	λ (nm) pump	α_{pump} (cm^{-1})	P_{thr} (W/cm^2)	Added ion	Concentration (mol.%)	λ (nm) pump	α_{pump} (cm^{-1})	P_{thr} (W/cm^2)
BZYTL	40	Er	0.98	0.22	975	1.00	308.8	Yb	5.00	973	20.00	15.40
BZYTL	40	Er	2.80	1.54	975	1.00	11.0	Yb	5.00	973	20.00	0.55
BZYTZ	34	Er	0.98	0.20	975	0.081	2118.0	Yb	5.00	973	20.00	13.80
BZYTZ	34	Er	2.80	1.96	975	0.081	54.0	Yb	5.00	973	20.00	0.35
BZYTZ	34	Ho	2.00	0.45	540	0.081	1750.0	Er	5.00	520	15.00	10.00
BZYTZ	34	Ho	1.20	0.41	540	0.081	5841.8	Yb	5.00	973	20.00	13.30
BZYTZ	34	Ho	2.90	1.58	540	0.081	377.2	Yb	5.00	973	20.00	0.86
BIZYT	34	Ho	2.00	0.37	540	0.325	431.1	Er	5.00	520	15.00	9.70
BIZYT	33	Ho	1.20	0.41	540	0.325	1578.4	Yb	5.00	973	20.00	14.20
BIZYT	33	Ho	2.90	1.50	540	0.325	108.0	Yb	5.00	973	20.00	0.97

The mechanism of energy transfer in fluoride glasses between Mn(II) and Nd(III) [11], and Nd(III) and Yb(III) [12] has been elaborated recently.

New Crystal Lasers

The utilization of energy transfer in crystal lasers enables us to obtain lasing at room temperature which is not observed in singly doped ions. Some recent examples are outlined below.

Holmium

Room temperature lasing of Ho(III) has been also obtained by codoping a variety of dielectric crystals by Er(III), Tm(III) and Yb(III) [13].

The lasing at 2.12 μm at room temperature was observed recently in yttrium aluminate garnet ($Y_{0.89}Tm_{0.10}Ho_{0.01})_3(Al_{0.99}Cr_{0.01})_5O_{12}$ codoped by Tm(III) and Cr(III) [14].

A cw double cross pumping of $^5I_7 - {}^5I_8$ laser transition of Ho(III) at 2.086 μm results in efficient room temperature cw lasing in Cr,Tm,Ho:YScAl–garnet and Cr,Tm,Ho:YScGa–garnet crystals [15].

Figure 1 shows an energy level diagram. The ^2E of Cr(III) is in resonance with the $^3F_3$ level of Tm(III) which is at high concentration. The first nonradiative relaxation to the $^3F_4$ state is followed by successive energy jumps to the $^5I_7$ level of Ho(III), thus an effective energy pumping is supplied by Cr(III) [14].

Room temperature 2 μm lasing of Ho(III) was recently obtained in GdScGa–garnets of the composition $Cd_{2.813}Tm_{0.17}Ho_{0.017}Sc_yCr_{0.05}Ga_{4.95-y}O_{12}$. The

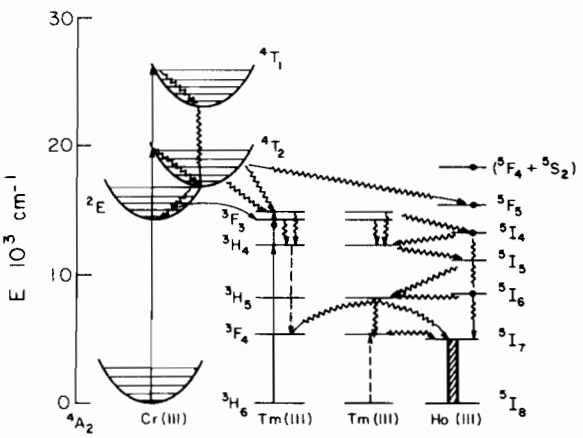

Fig. 1. A scheme of triple energy transfer Cr(III) → Tm(III) → Ho(III).

efficiency of lasing at 2.08 μm at room temperature was 0.85% [16].

The fluoride host has been favoured over the oxide by some investigators [17]. For Ho(III) in $YLiF_4$, the lifetime of the $^5I_7$ laser level is 12 ms and the multiphonon transition lower than in oxide glasses [18].

Erbium

Er(III) in $YLiF_4$ (YLF) can provide a convenient room temperature solid-state laser source in the eye-safe region of the spectrum. The performance characterization and optimization of Er,YLF $^4S_{3/2} \rightarrow {}^4I_{9/2}$ laser operation at 1.73 μm has been described recently. An output energy was obtained with an overall efficiency of 0.0024 [19].

Laser operation at 1.7 μm due to $^4S_{3/2} \rightarrow {}^4I_{9/2}$ has been achieved in $YAlO_3$ doped by Er(III) [20]. The emission is tunable to one of the manifolds of the terminal level by means of an etalon introduced into the laser resonator.

An efficient room temperature operation of a laser at $^4I_{11/2} \rightarrow {}^4I_{13/2}$ at 2.8 μm of Er(III) and $^5I_7 \rightarrow {}^5I_8$ of Ho(III) at wavelength around 2 μm was reported in garnets where the sensitization of luminescence of rare earths was facilitated by energy transfer from Cr(III) [21].

Single-mode Fiber Lasers

The suggestion of preparing fluoride active fibers doped by rare earth ions has a good chance of being realised in the near future [22–24]. Our optimism is based on the fact that a construction of active fibers based on silica was demonstrated [25]. When the rare earths are doped into single-mode fiber lasers a number of advantages are achieved. As a consequence of the high pumping intensities in the small diameter cores <8 μm, very low threshold 100 mW and large gain can be achieved. The small fiber diameter minimizes also the thermal effects. Moreover, continuous laser operation is possible in systems which have previously only operated in the pulsed mode.

In a specific case of a silicate fiber doped by Nd(III), a lasing threshold of 100 mW was indeed obtained using a semiconductor laser pump. A 17 dB gain has been measured in a short length of Nd(III)-doped fiber indicating the potential of high gain optical fiber amplifiers.

Q-switching of the fiber lasers [26] using an acousto-optic modulator or a rotating chopper is also possible and peak powers of several watts have been observed in pulses ranging from 50 ns up to 1 μs.

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