Growth and upconversion properties of erbium doped $LiNbO_3$ single crystal fibers

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Abstract

Erbium(Er) doped $LiNbO_3$(Er:$LiNbO_3$) single crystal fibers were grown free of cracks along the c-axis by micro-pulling down method. The Er^{3+} concentration was distributed homogeneously along the growth axis. The samples for optical characterization were cut from as-grown single crystal fibers and polished. When the 980nm light was incident on the sample, upconversion phenomena were observed at the green range of wavelength 510~570 nm. In addition, the intensity of upconversion was remarkably increased by increasing the concentration of Er_2O_3 dopant in as-grown Er:$LiNbO_3$ crystals.

Er^{3+} 첨가 LiNbO3 fiber 단결정의 성장 및 upconversion 특성

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요 약

Micro-pulling down 법으로 congruent(Li_2O_3/Nb_2O_5 = 48.6/51.4)한 조성에 Er_2O_3를 각각 1mol%과 3mol%을 첨가한 Er:$LiNbO_3$ 단결정을 c-축 방향으로 성장시켰다. 성장된 결정 내에서 Er^{3+}은 균일한 분포를 나타내었다. 결정은 분홍색을 띄었으며, 첨가 원소인 Er_2O_3의 농도증가에 따라 더욱 짙은 색을 나타내었다. 또한 성장된 결정에는 crack 이 존재하지 않았다.. 결정의 광학적 측정을 위해 결정을 2mm 로 절단한 후 연마를 하였다. 결정에 980nm 파장의 빛을 입사 시켰을 때 초록색 영역(510~570 nm)에서 upconversion 현상이 일어났으며, Er_2O_3의 첨가농도가 증가할 수록 upconversion intensity 가 증가함을 확인할 수 있었다.

1. Introduction

Erbium(Er) doped $LiNbO_3$(Er:$LiNbO_3$) has recently gained attention through the development of light amplifier based on optical fibers[1]. And the work for near infrared(NIR) pumped blue/green lasers has been studying for the development of short-wavelength solid lasers[2], which have many technical applications including data storage, laser printing, underwater communications and full color laser display etc.[3]. $LiNbO_3$ is a very well-known crystal due to its unique physical properties of the ferro-electric material, which also shows piezo-electric, elastic-optic and photo-refractive effects[4, 5]. Some of these properties are drastically affected by the presence of impurities and the growth conditions[6]. Thus with a combination of the nonlinear optical properties of $LiNbO_3$ and the spectral properties of Er^{3+}, the crystal can simultaneously emit the second harmonic light through quasi-phase matching[7] and green light through upconversion at room temperature[2]. However it has a different physical mechanism between second harmonic generation and upconversion[8]. For such a optical properties, Er:$LiNbO_3$ single crystal fibers of high quality without subgrain boundaries are generally required. Yoon et al.[9] had developed the micro-pulling down(μ-PD) method. The characteristics of the method has high pulling down rate, low thermal strain compared with other growth method and it is possible to grow a crystal from incongruent melt composition[10].

In this work, we have grown Er:$LiNbO_3$ single crystal fibers by the μ-PD method. Further more this study was aimed at the dependence of the upconversion intensity on the doping concentration. We investigated the upconversion phenomena of green fluorescence in a Er:$LiNbO_3$ single crystal fibers exposed to light at the

wavelength of 980nm which correspond to energy transitions of the Er^{3-} ions and compared the upconversion intensities under the two different conditions.

2. Experimental procedure

The starting materials were Li_2CO_3 and Nb_2O_5 powders of 99.99% purity. They were thoroughly mixed in a ball mill at a congruent composition(Li_2O_3/Nb_2O_5 = 48.6/51.4). Doped material were prepared by mixing the raw materials with 1mol% and 3mol% of Er_2O_3(99.99%), respectively.

Er:$LiNbO_3$ single crystal fibers were grown by the μ-PD method. Figure 1 shows a schematic diagram of μ-PD apparatus and growth conditions are summarized in Table 1.

The raw materials were melted in the Pt crucible and allowed to pass through the micro nozzle. The single crystal fibers were formed by attaching the seed crystal to the tip pulled down at constant velocity. The alignment of the seed to the micro nozzle was controlled by the micro X-Y stage. Crystal diameter was maintained constant by controlling the temperature of the main and after heaters during growth process.

Several test plates(2mm thick) were cut from as-grown fiber crystals and polished for optical characterization. The fluorescence spectra were recorded with a SPEX/fluorolog-T2 spectrofluorometer system. It was obtained with a pulsed 980nm Xenon lamp and the single monochromater. All spectral measurements were performed at room temperature. Er^{3+} compositional distribution in the samples was determined by electron probe microanalysis(EPMA).

3. Results and discussion

The Er:$LiNbO_3$ single crystal fibers were grown with Er_2O_3 concentration of 1 and 3mol%, respectively. The crystals were transparent, changing from colorless to pink in color depending on increase of the Er^{3+} concentration in crystal. The crystals had a uniform shape and were grown free of cracks.

Figure 2 shows the distribution of Er^{3+} ions along the grown c-axis in 3mol% Er_2O_3 doped crystals. The concentration of Er^{3+} are almost identical to the initial melt composition, which means that the very little segregation occurred during crystal growth. This is probable because the nature convection was restricted in the micro-nozzle and the Er_2O_3 constituent in Er:$LiNbO_3$ melt became unity along the growth axis leading to the homogeneous composition throughout the fiber [11].

Figure 3 shows the upconversion process described using three-level ions. Sequential two-photon upconversion relies on two photons at different wavelength, "a" and "b", to populate the upper emitting level of the ions. Photon "a" promotes the ground state ion to the metastable intermediate state, while photon "b" promotes the ion from the metastable state to the upper emitting level[12].

Figure 4 shows when the 980nm light was incident on the sample, green fluorescence spectra were observed with an incident power of 450W. It was observed that the fluorescence peak was strong with increasing the Er_2O_3 concentration. It shows that the Er:$LiNbO_3$ really possesses strong upconversion emission, at the green light of wavelength 510~570 nm. Among the peaks, the 550 nm peak was the most intense one. The dominant peaks around 550 nm were due to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition, whereas the small peaks around 530 nm were due to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition. For the same

pump intensities, the measured fluorescence intensity for the 3mol% Er_2O_3 doped crystals was about 3.5 times larger than that for the 1mol% Er_2O_3 doped crystals.

Figure 5 shows the upconversion mechanism for sequential two-photon absorption of Er^{3+} ions in Er:$LiNbO_3$ crystals. The ground-state-absorption(GSA) and the excited-state-absorption(ESA) refer to photon wavelengths corresponding to the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and $^4I_{11/2} \rightarrow {}^4F_{7/2}$ transitions, respectively, where $^4I_{15/2}$ is the ground state and $^4I_{11/2}$ is the metastable state, and the emission from $^4S_{3/2}$ produces visible radiation. It is characterized that the ESA ions decay through rapid non-radiation processes from the $^4F_{7/2}$ level to the $^4S_{3/2}$ level in upconversion phenomena[13]. In Er:LiNbO3 crystals, it is believed that the green upconverted fluorescence corresponding to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions was emitted.

4. Summary

$LiNbO_3$ single crystal fibers doped with a high concentration of Er_2O_3 were grown free of cracks by micro-pulling down method. And it was demonstrated the visible dual-wavelength light generation in Er:$LiNbO_3$ and observed green upconverted fluorescence when the samples were exposed to the light with 980 nm wavelength. For the 980nm exposure the dominant mechanism for the upconverted fluorescence was proved to be the sequential two-photon excitation. The intensity of upconversion was increased by increasing the concentration of Er_2O_3 in Er:$LiNbO_3$. Thus, it is expected that the Er^{3+} concentration in $LiNbO_3$ had an effect on the intensity of upconversion.

Acknowledgments

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List of Figures and Tables

Table.1. W. S. Yang

Starting materials	Li_2CO_3, Nb_2O_5, Er_2O_3
Melt composition (Er:Li:Nb)	1:48.6:52.4, 3:48.6:52.4
Crucible	Pt, 2×0.5×0.5 cm^3
Nozzle diameter	0.5 mm
Pulling-down rate	0.5~2 mm/min
Pulling-down axis	<001>
Crystal Diameter	0.3 ~ 0.5 mm
Atmosphere	Air

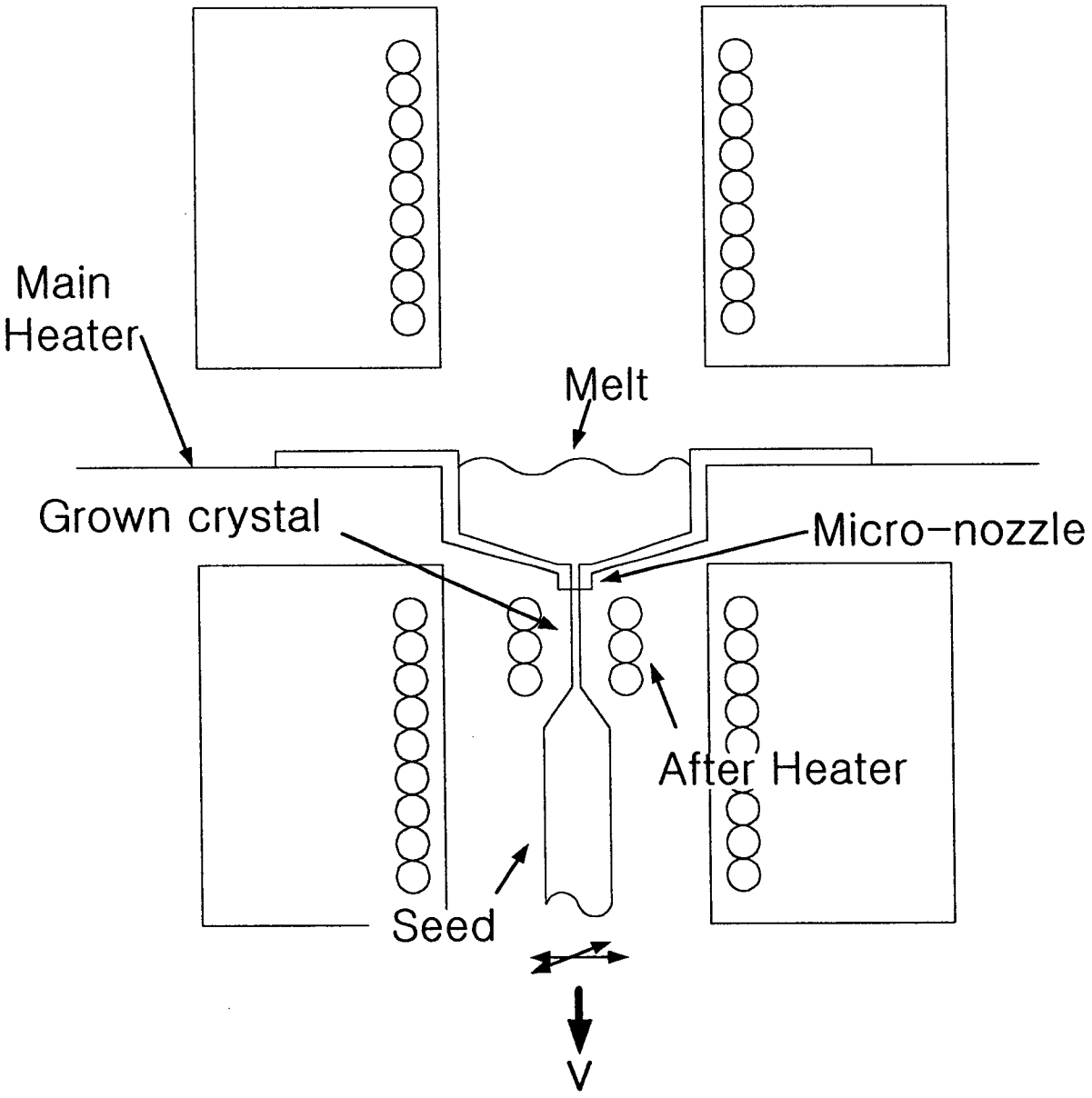
Main
Heater
Melt
Grown crystal
Micro-nozzle
After Heater
Seed
V

Fig. 1. W. S. Yang

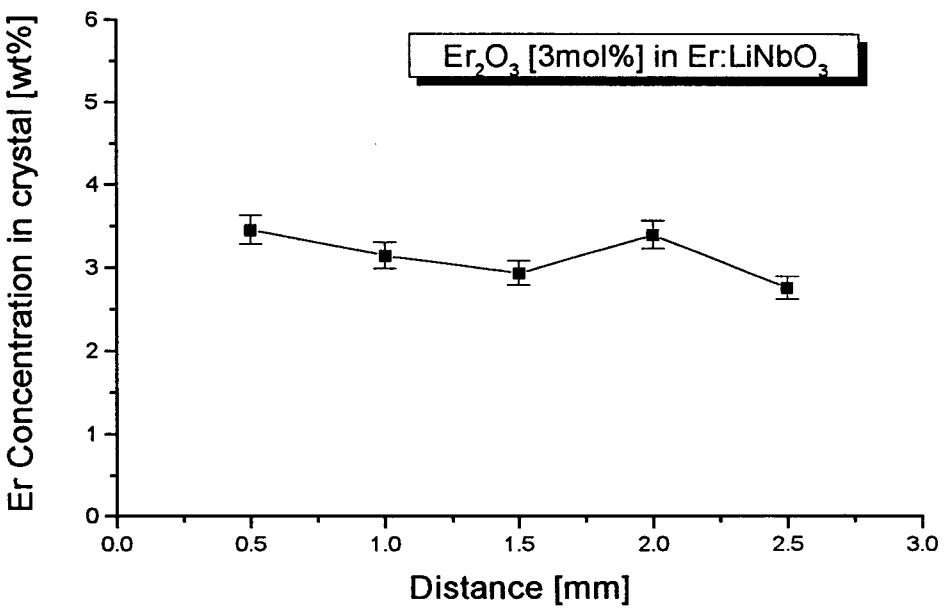
Er2O3 [3mol%] in Er:LiNbO3
Er Concentration in crystal [wt%]
Distance [mm]
0
1
2
3
4
5
6
0.0
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 2. W. S. Yang

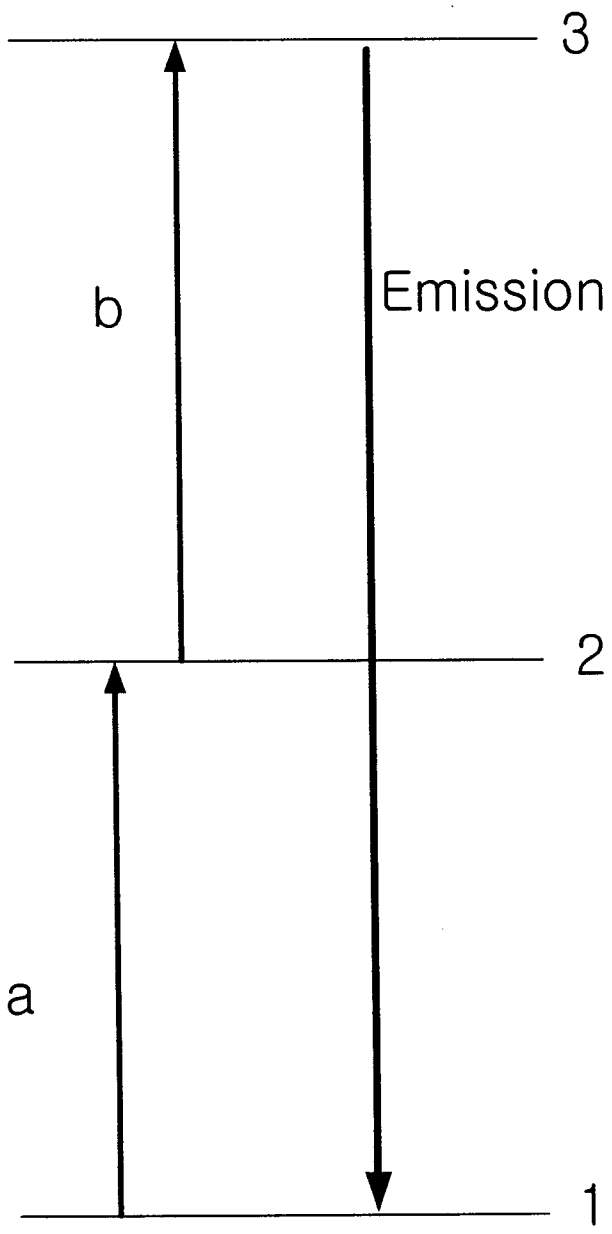

Fig. 3. W. S. Yang

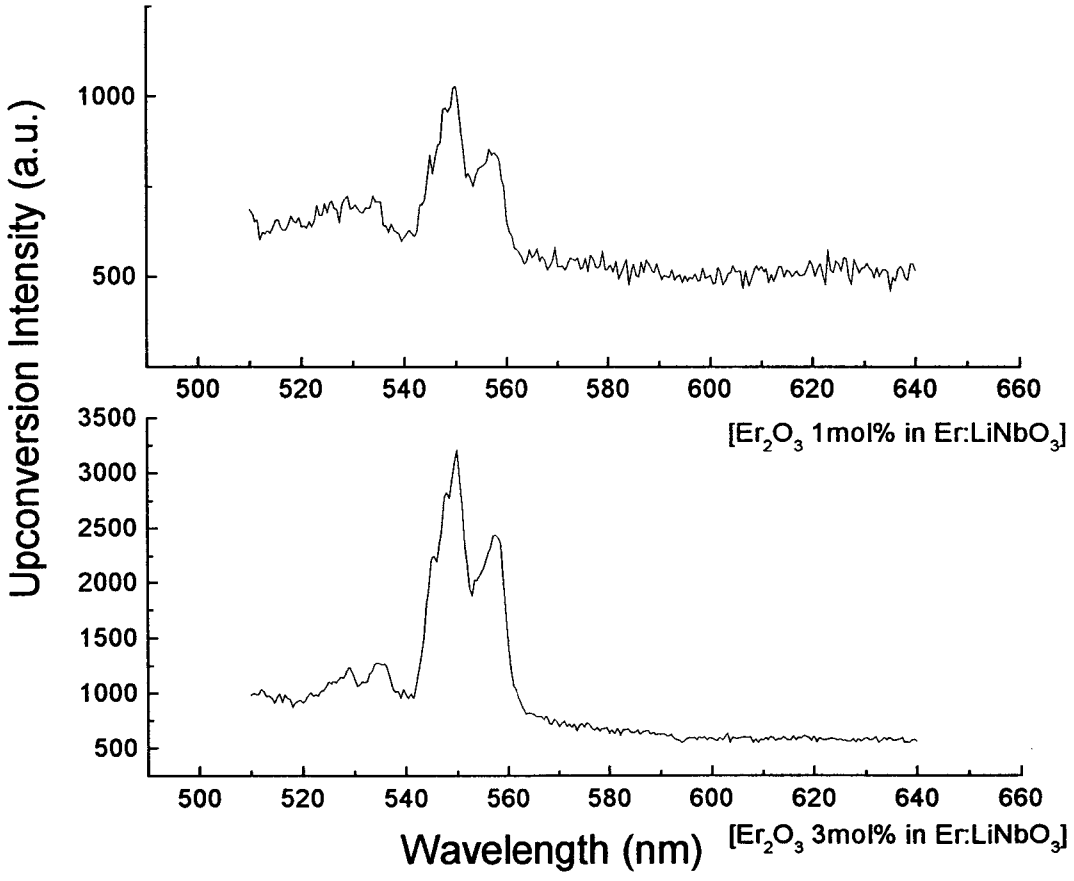
Upconversion Intensity (a.u.)
1000
500
500 520 540 560 580 600 620 640 660
[Er2O3 1mol% in Er:LiNbO3]
3500
3000
2500
2000
1500
1000
500
500 520 540 560 580 600 620 640 660
Wavelength (nm)
[Er2O3 3mol% in Er:LiNbO3]

Fig. 4. W. S. Yang

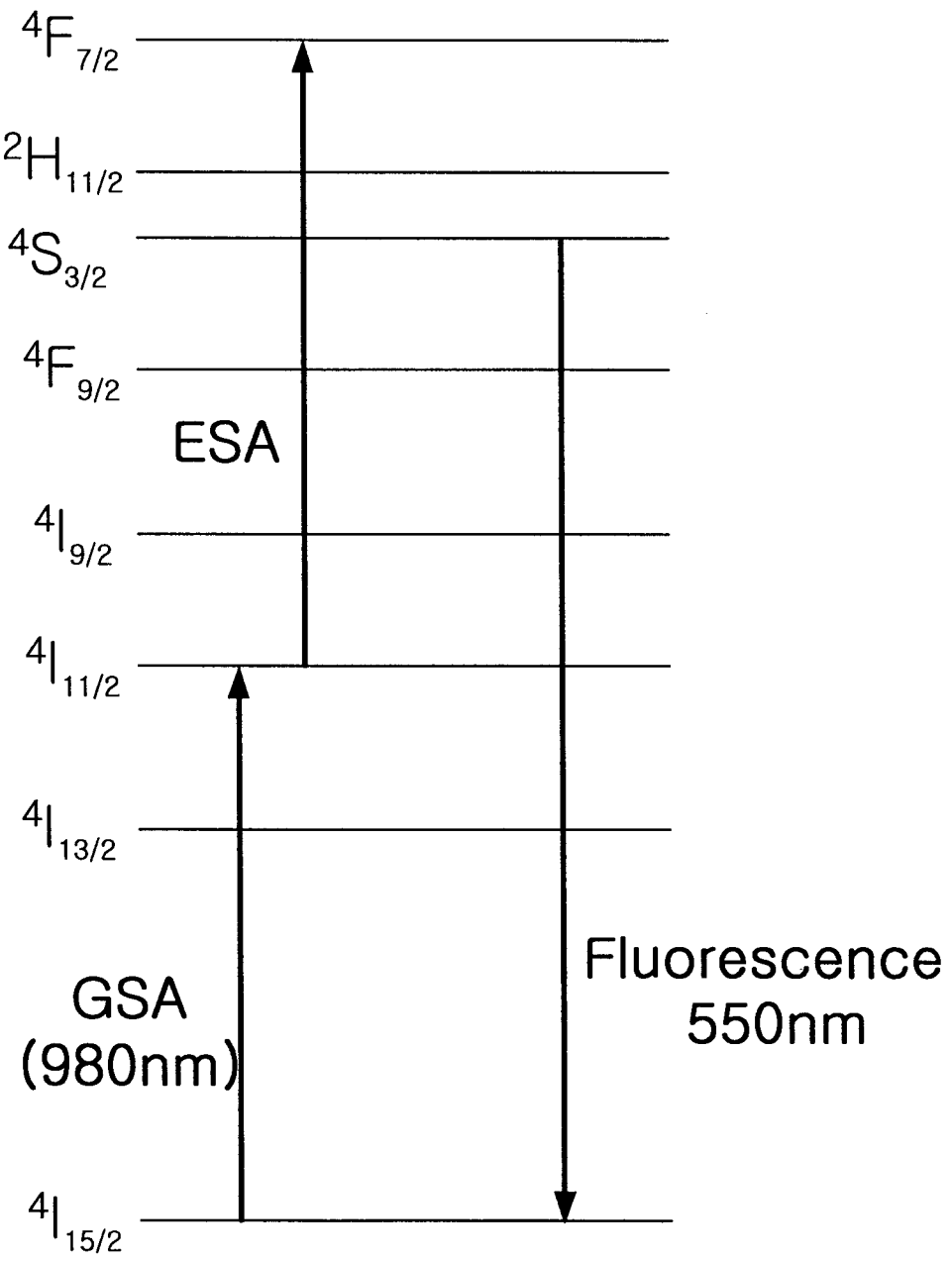
$^4F_{7/2}$
$^2H_{11/2}$
$^4S_{3/2}$
$^4F_{9/2}$
ESA
$^4I_{9/2}$
$^4I_{11/2}$
$^4I_{13/2}$
GSA
(980nm)
Fluorescence
550nm
$^4I_{15/2}$

Fig. 5. W. S. Yang