Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials, Tsukuba, 1992, pp. 369-371

Generation of Intense Green and Blue Emission in Energy Upconversion Devices Having Optical Confinement Structure

Yoh Mita, Nobuaki Ando and Shigeo Shionoya

Tokyo Engineering University
1404 Katakura, Hachioji, Tokyo 192

Blue and green light sources having high brightness and simple structure have been fabricated by combining rare earth ion-doped upconversion material and 980nm emitting laser diodes. The upconversion efficiencies have been considerably improved by putting the material small in size into a reflective cavity. Conversion efficiencies as high as 0.5 % and 4 % have been obtained for blue and green emission, respectively, under 30mW laser light excitation.

1. Introduction

Frequency upconversion devices were once extensively invesigated nearly two decades ago[1)2)]. However, little attention has been paid thereafter, since infrared to visible coversion efficiency was generally low. The limited conversion efficiency is principally due to energy dissipation in the form of infrared emission as well as to low availability of excitation energy. In a typical green-emitting upconversion device composed of Er^{3+}-containing phosphors and a GaAs:Si light emitting diode (LED), over 70% of incoming excitation energy is wasted in the form of infrared light. A substantial improvement of the upconversion devices was proposed by one of the present authors at this Conference held 19 years ago[3)]. The improvement was realized by replacing the phosphor layer with a single crystal and by adopting an optical confinement structure. It was also shown that reduction in the upconversion material size is favorable for improvement of the conversion efficiency. However, since GaAs:Si LED used as an excitation source had low output power and was not small enough, the conversion efficiency of the green light was low compared to that of green emitting GaP diodes.

Novel blue and green emitting upconversion devices, which utilizes a 980nm emitting laser diode (LD) as exciting source, are presented here. Transparent upconversion materials such as fluoride glass or single crystals are used as host for rare earth ions. The material are highly doped with sensitizer Yb^{3+} ions as well as Er^{3+} or Tm^{3+} activator ions. Since the absorption peak of Yb^{3+} ions has good match with laser diode light, very high excitation density can be realized upon proper focusing of the exciting laser light. Luminescence processes leading to the upconversion, as well as device characteristics, have been investigated. Problems for improving the upconversion efficiency are discussed.

2. Device construction and characteristics

A cross section of a novel upconversion device is schematically illustrated in Fig.1. The upconversion material is irradiated with focused laser diode light having 980nm wavelength emission. The material is placed in a reflective cavity: The exciting laser diode light enters the cavity through a small opening and visible emission comes out through a dichroic filter that can transmit visible emission but reflects infrared emis-

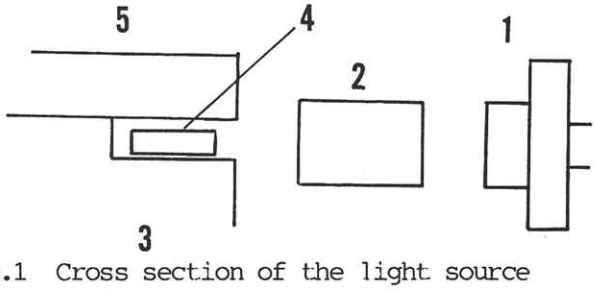

Fig.1 Cross section of the light source
1. laser diode 2. SELFOC lens
3. reflective cavity 4. upconversion material
5. dichroic filter

sion of the upconversion material as well as the exciting light. Many kinds of upconversion materials have been tested. In the case of blue emission, Tm^{3+} and Yb^{3+}- containing fluoride glass presents better results compared to powder phosphors or vitroceramic material. The best result for the green emitting device has been obtained by adopting $BaY_2F_8:Er^{3+},Yb^{3+}$ small crystals. In this report, results on blue-emitting fluoride glass are given.

The upconversion efficiency is strongly dependent upon material size as well as material chracteristics. Since effective volume participating the upconversion process is very small and conversion efficiency generally increases with increasing excitation power density, a smaller size is more favorable to efficient emission. Since infrared emission of Yb^{3+} ions is the principal energy dissipation route, use of the optical confinement structure that can reflect back the emission is also favorable to improvement of the efficiency.

The conversion efficiency has been obtained from measurements of illumination intensity. The best results that have been obtained are 0.5% and 4% for the blue and the green emissions, respectively.

3. Luminescence and related characteristics

Optical absorption spectrum near 1.0μm region were measured to examine the upconversion processes. As can be seen from Fig. 2, the absorption peak due to Yb^{3+} ions in the fluoride glass is situated at 975.5nm wavelength with 39.1 cm^{-1} peak intensity. Laser diode emission wavelength used in the experiments is indicated with an arrow. It can be seen that the large absorption constant of Yb^{3+} ions, combined with good match with the laser diode emission and sharp focusing, presents favorable condition for realizing high excitation density. Near infrared emission spectra were measured for both thin and thick glass samples. The emission peak shifts toward longer wavelength in a thicker sample, showing strong reabsorption effect. It can be expected from this result that reabsorption of Yb^{3+} emission may take place under proper optical confinement structure. This reabsorption also leads to extending the excited lifetime of Yb^{3+} ions[3].

Emission spectrum under LD light excitation is given in Fig. 3 along with optical absorption spectrum. Energy levels of both Tm^{3+} and Yb^{3+} ions and relevant transitions are given in Fig. 4. Although the emission extends from ultraviolet to infrared region, the major part of the absorbed energy is dissipated in the form of infrared emission, particularly emission from Yb^{3+} ions. Energy flow diagram obtained for a fluoride glass platelet is shown in Fig. 5.

4. Discussions

The adoption of 980nm emitting LD as an excitation source, which is in good match with Yb^{3+} ion absorption peak, togather with sharp focusing to a small volume upconversion material, can present very high excitation density in the material. According to a a simple theory, cubic dependence upon excitation intensity is expected for the blue emission and quadratic dependence for the green emission. Hence, the blue emission is expected to be inverse quadratically proportional to the sample volume, while inversely proportional dependence is expected for the latter. In practice, however, excitation power dependence as well as volume dependence is considerably low compared to these expected relations, presumably due to saturation effect. Under higher excitation intensity, moreover, the green emission color turns to yellow owing to higher excitation intensity dependence of the Er^{3+} red emission. These saturation effects may impose an upper limit in conversion efficiency.

It can be seen from the experimental results that the greater part of the excitation energy is lost in the form of infrared emission. For this reason, proper optical confinement structure is desirable, in which the infrared emission is reflected back and may be reabsorbed. It was also shown in the previous paper that material with smaller

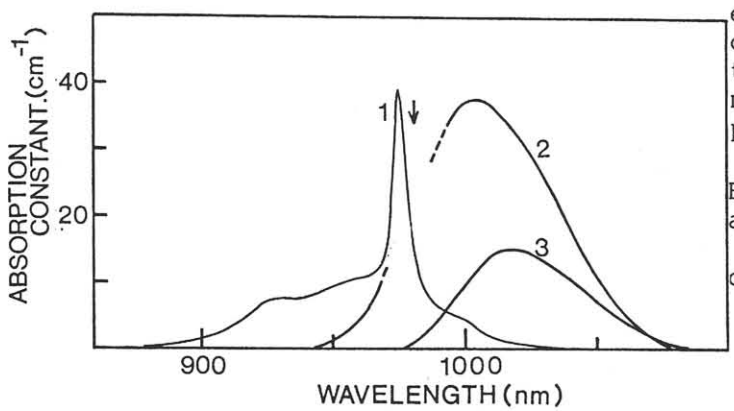

Fig.2 Optical absorption and emission spectra at 1.0um wavelength region for fluoride glass containing 20mol% Yb^{3+} and 0.05mol% Tm^{3+} ions
Curve 1. Optical absorption spectrum
Curve 2. Emission spectrum measured for thin sample
Curve 3. Same for 3mm thick sample

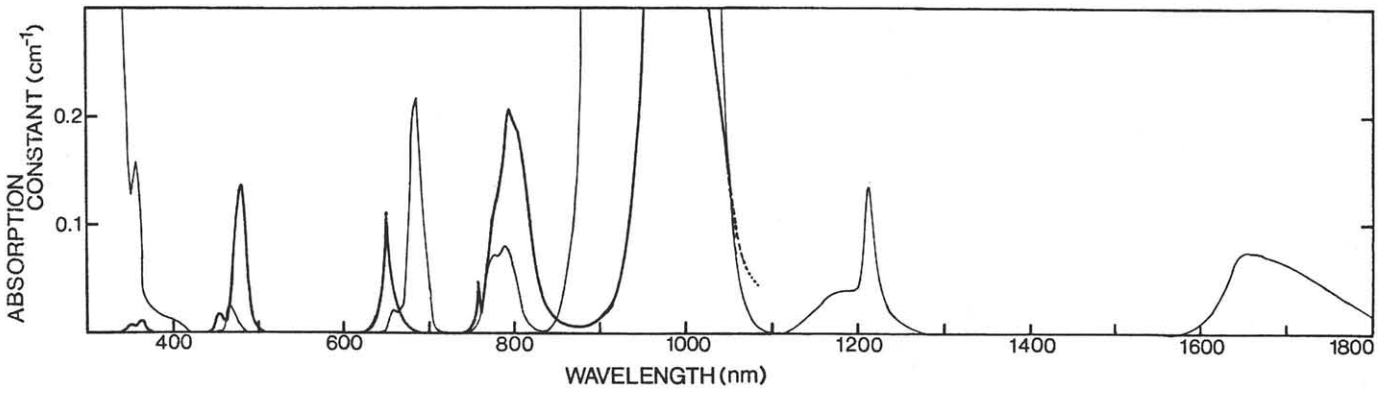

Fig.3 Optical absorption and emission spectra
Thin curve: Optical absorption spectrum measured for glass containing 0.2mol% Tm^{3+} ions
Solid curve: Emission spectrum for glass containing 0.05mol% Tm^{3+} ions

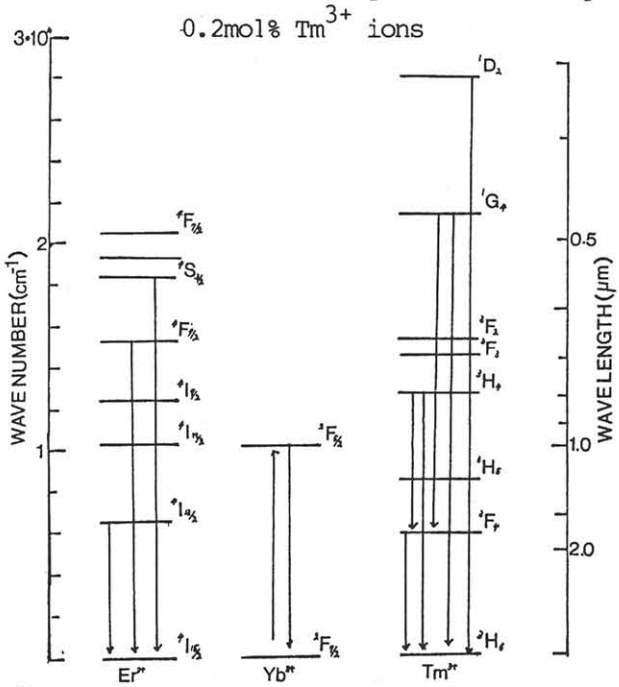

Fig.4 Energy levels and relevant transitions of Tm^{3+} and Yb^{3+} ions

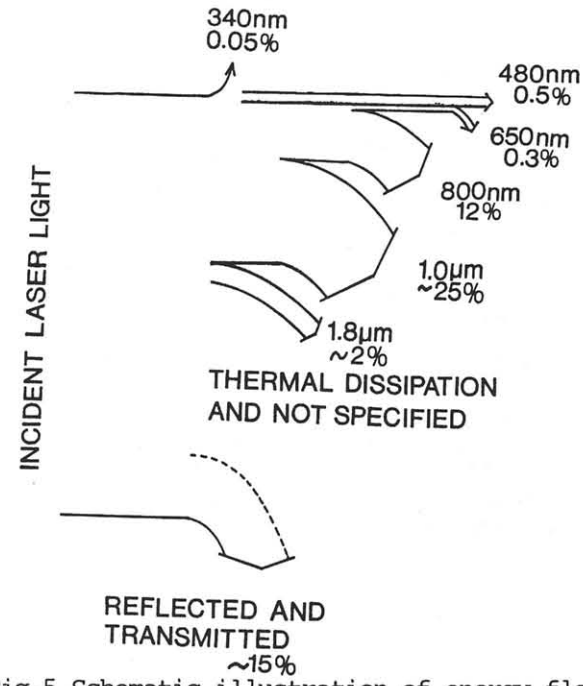

Fig.5 Schematic illustration of energy flow for a blue emitting glass platelet

nonradiative decay rate is favorable[3].

The light sources reported here have a small volume that can be possibly reduced to a size comparable to that of laser diodes. Complicated adjustment technique such as optical alignment or phase matching is not required in use of light sources. The device can present shorter wavelength visible emission with high conversion efficiency comparable to that of SHG of laser diode light. Although the emission is incoherent in nature, high brightness emission from a tiny emitting area is favorable for many application purposes. Still higher conversion efficiency can be expected by proper improvement in device geometry as well as by optimization of the material properties.

The authors would express thanks for Prof. H. Yamamoto for his valuable discussions, Drs. K. Kobayashi and T. Suzuki of NEC Corp. for presenting laser diodes and Sumita Optical Glass Inc. for presenting fluoride glass samples. They are also thankful to K.Hirama, T. Sakai and other members in the University for cooperation in experimental studies.

References:
1) F.Auzel:J. Luminescence 45(1990)341.
Proc. IEEE 69(1973)758.
2) Y.Mita: J.Appl.Phys.43(1972)1772.
3) Y.Mita et al.: Suppl. Jpn. J. Appl. Phys. 43(1974)81.
Y.Mita and E. Nagasawa; NEC Res. and Develop. No.33(1974)61.