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Growth and spectroscopic characteristics of Yb:GSO single crystal

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Abstract

For the first time, a high optical quality 10 at.% Yb³⁺-doped gadolinium oxyorthosilicate laser crystal Gd₂SiO₅ (GSO) was grown by the Czochralski (Cz) method. The segregation coefficient of Yb³⁺ was studied by the inductively coupled plasma atomic emission spectrometer (ICP-AES) method. The crystal structure has monoclinic symmetry with space group $P2_1/c$; this was determined by means of an x-ray diffraction analysis. The absorption spectra, fluorescence spectra and fluorescence decay curves of Yb³⁺ ions in a GSO crystal at room temperature were also studied. Then, the spectroscopic parameters of Yb:GSO were calculated. The advantages of the Yb:GSO crystal include high crystal quality, quasi-four-level laser operating scheme, high absorption cross-sections and particularly broad emission bandwidth (~72 nm). The results indicated that the Yb:GSO crystal seemed to be a very promising laser gain medium in diode-pumped femtosecond laser and tunable solid state laser applications when LD pumped at 940 and 980 nm.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recent advances in high-performance InGaAs laser diodes in the 900–1100 nm range have stimulated interest in diode-pumped Yb³⁺ lasers [1]. Compared to other rare-earth ions, Yb³⁺ ion has a relatively simple electronic structure with just two manifold levels, the ${}^{2}F_{7/2}$ ground state and the ${}^{2}F_{5/2}$ excited state, so it exhibits some advantages, such as low quantum defect, low thermal load, no excited state absorption and no up-conversion losses. In the past decade, much attention have been given to searching for new host materials doped with trivalent

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ytterbium ions, namely Yb:YAG [2], Yb:KYW [3], Yb:GdVO₄ [4], Yb:SYS [5], Yb:YAB [6], Yb:GGG [7] and Yb:CaF₂ [8]. In particular, the well-known diode-pumped Yb:YAG lasers have reached a high level of development and wide laser application. However, numerous ytterbium-doped materials are subject to a somewhat difficult growth, a relatively narrow emission band, or a relatively low thermal conductivity.

A main drawback of current Yb³⁺ lasers comes from the quasi-three-level laser operating scheme at room temperature. The ground state manifold is also the laser terminal level, the Yb³⁺ laser terminal level is thermally populated and that causes strong re-absorption at the emission wavelengths and then leads a high laser pumping threshold power. It is still a challenge to make the Yb³⁺ lasers work with a quasi-four-level laser operating system like the Nd³⁺ counterparts, which requires a large splitting of the fundamental manifold ${}^{2}F_{7/2}$ of Yb³⁺. In order to limit the thermal population of the terminal level, a relatively strong crystal field is expected, which increases the Stark splitting of the Yb³⁺ ${}^{2}F_{7/2}$ ground manifold as much as possible. Thus, a low-symmetry crystal structure and multi-types of substitutional site are essential for ytterbium-doped host materials [9].

Gadolinium oxyorthosilicate crystal Gd_2SiO_5 (GSO) is a well known silicate that has been studied as a host for Tb^{3+} , Eu^{3+} , Pr^{3+} , Er^{3+} and especially Ce^{3+} ions, with applications as phosphors and excellent scintillators, etc [10–15], but to the best of our knowledge, up to now spectroscopic investigations and laser properties have never been reported for Yb^{3+} -doped Gd_2SiO_5 crystal.

In this paper, a high optical quality 10 at.% Yb^{3+} -doped gadolinium oxyorthosilicate laser crystal Gd₂SiO₅ (Yb:GSO) was grown by the Czochralski (Cz) method for the first time. The segregation coefficient of Yb^{3+} was studied by the inductively coupled plasma atomic emission spectrometer (ICP-AES) method. The crystal structure was determined by means of x-ray diffraction analysis. Absorption spectra, fluorescence spectra and fluorescence decay curves of Yb^{3+} ions in a GSO crystal at room temperature were also studied. Then, spectroscopic parameters of Yb:GSO have been compared with those of Yb:YAG crystal.

2. Experimental details

2.1. Crystal growth

The Yb:GSO crystal was grown by the Czochralski method from an inductively heated iridium crucible. The Yb concentration in the melt was 10 at.% with respect to Gd. The starting materials were SiO₂, Gd₂O₃ and Yb₂O₃ powders with at least 99.995% purity. The powders were weighed, mixed and isostatically (200 MPa) pressed into tablets; then, the tablets were sintered at 1400 °C for 24 h before they were loaded into the iridium crucible. The total weight was 600 g, and the chemical reaction formula is as follows:

$$(1 - x)Gd_2O_3 + SiO_2 + xYb_2O_3 = Gd_{2(1-x)}Yb_{2x}SiO_5$$

with x = 10 at.%.

Nitrogen with purity of 5 N was used as the growth atmosphere. The pulling rate was $1-3 \text{ mm h}^{-1}$ and the rotation rate of the seed was 15-30 rpm. The GSO seed was 4.5 mm in diameter.

2.2. X-ray diffraction, segregation coefficient and spectra measurements

The segregation coefficient of Yb in the GSO crystal was measured using the inductively coupled plasma atomic emission spectrometer (ICP-AES) method. The sample was cut from



Figure 1. Photograph of 10 at.% Yb:GSO crystal grown by Czochralski process.

the crystal adjacent to the seed crystal position, and then was ground to fine powder in an agate mortar.

The crystal structure was examined with a D/MAX 2550V powder x-ray diffractometer (XRD). The unpolarized absorption spectrum of Yb:GSO was measured with a UV/VIS/NIR spectrophotometer (Model V-570, JASCO). The fluorescence spectrum was measured with a Jobin–Yvon TRIAX 550-type spectrophotometer, and the pumping source was a 940 nm laser. All measurements were performed at room temperature.

3. Results and discussion

3.1. Crystal quality, segregation coefficient and structure

It is well known that the GSO crystal has a cleaving property [12]. In order to prevent the crystal from cracking, the GSO seed axis was oriented at 60 °C relatively to the [010] axis and parallel to the cleavage plane (100) in this study, and a pulling rate of 1.5 mm h⁻¹, crystal rotation rate of 25 rpm and a post-growth cooling rate of 40 °C h⁻¹ were used as the growth parameters. In addition, it is well known that Y doping in the GSO host tends to suppress cracking [12]; 10 at.% Yb doping in GSO is also a factor of producing high optical quality crystals. As a result, the as-grown Yb:GSO crystal boule was up to 90 mm in length and 30 mm in diameter (see figure 1); it was colourless, of high optical quality, crack-free and without inclusions. When the 20 mW He–Ne laser beam passed through the crystal, the light beam was almost unseen by the eye, which indicated very few scattering particles in the Yb:GSO crystal.

The concentrations of both Gd and Yb atoms at the top of as-grown Yb:GSO crystal were measured by the ICP-AES method, then the Yb content was calculated with respect to Gd sites at the top of the boule. The distribution coefficient of Yb³⁺ in Yb:GSO crystals can be calculated from the following formula:

$$k_m = C_t / C_0, \tag{1}$$

where C_t is the Yb³⁺ concentration at the growth starting position in the crystals, and C_0 is the initial Yb³⁺ concentration in the melt.

We can calculate that the segregation coefficient of ytterbium ion in Yb:GSO crystal is equal to 0.86, according to 10 at.% of C_0 and 8.6 at.% of C_t . Apparently, the solubility of ytterbium ion in the Yb:GSO host lattice is high; this enables us to grow Yb:GSO crystals with high Yb doping level, which are potential candidates for use as compact, efficient thin chip lasers.



Figure 2. Unpolarized absorption spectrum of a 10 at.% Yb:GSO crystal at room temperature.

The crystal structure of the as-grown Yb:GSO was examined with the XRD (Cu target, K α). This demonstrated that the symmetry of the Yb:GSO crystal still maintains the primitive monoclinic structure with space group of $P2_1/c$. The unit cell parameters are similar to the published data of pure GSO crystal [13]. We find that the change of lattice parameters is insignificant. There should not be very significant distortions of the microstructures in Yb:GSO, as the ionic radius of Yb³⁺ (0.868 Å) is slightly smaller than that of Gd³⁺ (0.938 Å).

In the GSO host lattice, there are two non-equivalent crystallographic sites of Gd^{3+} [14], labelled site Gd_1 and site Gd_2 , which are coordinated with seven and nine oxygen atoms, respectively. Site Gd_1 is bonded to three isolated oxygen ions, to two bridging oxygen ions in one [SiO₄] tetrahedron and one bridging oxygen ion in two [SiO₄] tetrahedra. Site Gd_2 is bonded to one isolated oxygen ion, to two bridging oxygen ions in two [SiO₄] tetrahedra and through one oxygen ion in four [SiO₄] tetrahedra. The distance $Gd-O_{min}$ is 2.27 Å, which is much shorter than that of $Gd-O_{max}$ (2.76 Å) [14]. In Yb:GSO crystals, ytterbium ions occupy both Gd sites. It should be noted that site Gd_1 for Yb³⁺ has larger crystal-field splitting and local C_s symmetry, while site Gd_2 has smaller energy level splitting and approximate C_{3v} symmetry [15].

From the structure point of view, the low-symmetry $P2_1/c$ monoclinic structure of the GSO host, the wide band gap (~6.1 eV), two non-equivalent distorted host sites and a large distribution of Yb–O distances are favourable for creating a strong crystal-field strength in the GSO host. The Yb³⁺ ion has a strong-field coupling characteristic: the 4f shell of the Yb³⁺ ion is affected by the strong crystal field, and this results in a larger crystal-field splitting of the Yb³⁺ manifolds. Thus, Yb-doped GSO crystal laser operating is a potentially useful quasifour-level laser scheme, which results in easy population inversion and a low threshold value.

3.2. The absorption and LD-excited IR emission spectra

The room-temperature absorption spectrum of a 10 at.% Yb^{3+} -doped GSO crystal is shown in figure 2. The absorption in the wavelength range from 890 to 1030 nm of the Yb:GSO crystal is regarded as the role of ytterbium ion. From figure 2, we can observe that the absorption spectrum is mainly composed of four strong bands around 897, 922, 940 and 976 nm, and other two weak absorption bands around 1010 and 1028 nm. Apparently, the absorption peak



Figure 3. IR fluorescence spectrum of a 10 at.% Yb:GSO crystal at room temperature.

around 976 nm belongs to the zero-line transition between the lowest levels of ${}^{2}F_{7/2}$ and ${}^{2}F_{5/2}$ manifolds. Others correspond to the typical transitions from the ground state ${}^{2}F_{7/2}$ to other sublevels of ${}^{2}F_{5/2}$ of Yb³⁺ in the GSO host. The absorption peaks at 940 and 976 nm are both well matched with the emission wavelength of commercially available high-power InGaAs laser diodes. The absorption coefficient of 940 and 976 nm is 3.37 and 5.18 cm⁻¹, respectively, with absorption linewidth (FWHM) of 16 and 19 nm in turn.

The IR fluorescence spectrum of a 10 at.% Yb^{3+} -doped GSO crystal excited under the InGaAs LD source with a wavelength of 940 nm at room temperature is presented in figure 3. In order to illustrate the fluorescence bands, the fluorescence curve of Yb:GSO is decomposed by Lorentzian multi-peak fits. As a result, the broad fluorescence curve mainly includes four bands around 1013, 1031, 1048, and 1088 nm, whose fluorescence bandwidth is 27, 10, 31 and 17 nm in turn, corresponding to the transitions from the lowest level of ${}^{2}F_{5/2}$ to the other levels in the ${}^{2}F_{7/2}$ manifold except the lowest. The fluorescence intensity of peaks is increasing along the longer wavelength side of the emission spectrum. Among these four fluorescence bands of Yb:GSO, the fluorescence intensity at 1088 nm is the strongest.

In order to complete the lifetime characterization of a 10 at.% Yb³⁺-doped GSO crystal, a fluorescence decay measurement was carried out by a computer-controlled transient digitizer. A decay curve of emission at 1088 nm at room temperature is presented in figure 4. The relationship in the figure displays single exponential behaviour of the decay, and the fluorescence lifetime could be obtained from the fitting line. As a result, the experimental lifetime value of the excited manifold ${}^{2}F_{5/2}$ of Yb³⁺ has been measured to be 1.11 ms for Yb:GSO.

The room-temperature fluorescence and absorption spectra are shown together in figure 5. Compared to other Yb-doped hosts, the overlapping between emission and absorption spectra of Yb:GSO is much weaker, indicating high quantum efficiency.

As Yb^{3+} ions are doped highly in the GSO host, the re-absorption by Yb^{3+} ions will be more serious at the wavelength overlapping. The absorption located at wavelength 976 nm is so strong that concentration quenching of the Yb^{3+} fluorescence at the zero line would be caused. In this IR fluorescence spectrum, we do not observe the fluorescence corresponding to the zero-phonon transition; contrarily, there is a shallow concave at wavelength 976 nm in



Figure 4. Room-temperature fluorescence decay curve of Yb:GSO crystal at 1088 nm.



Figure 5. The overlap between fluorescence and absorption spectra of Yb:GSO crystal.

the fluorescence curve, due to marked re-absorption processes by Yb^{3+} ions in the 10 at.% Yb^{3+} -doped GSO crystal.

In the case of Yb³⁺ ions occupying two crystallographic sites (site Gd₁ and site Gd₂), with a strong crystal-field strength and the thermal spreading of the spectrum at room temperature, the shapes of the absorption and fluorescence spectra become quite broad, and obviously increasingly complex, involving additional bands [9]. Although it is difficult to distinguish the energy-level diagrams of the two sites through such complex spectra at room temperature, we can estimate the maximum splitting of the ytterbium manifolds. The energy is scaled to zero at the fundamental transition wavelength around 976 nm, to identify different processes. As previously said, site Gd₁ has larger crystal-field splitting, and we can deduce that only site Gd₁ is concerned with the emission band at the longest wavelength around 1088 nm. Thus, the emission band around 1088 nm is due to transition from the lowest levels of the ²F_{5/2} manifold to the highest levels of the ²F_{7/2} manifold in site Gd₁. As a result, the ytterbium energy-level diagram in site Gd₁ was approximately deduced, and is shown in figure 6.



Figure 6. Energy-level diagram of Yb^{3+} in GSO crystal.

From the energy-level diagram, we can estimate that the overall splitting of the ${}^{2}F_{7/2}$ manifold reaches about 1067 cm⁻¹, which is one of the largest known values. However, the overall splitting is about only 785 cm⁻¹ in the case of Yb:YAG crystals. This proves that ytterbium experiences quite a strong crystal-field interaction in the GSO host. Thus, Yb:GSO appears as an interesting laser medium approaching a quasi-four-level laser operating scheme like the Nd³⁺ counterparts, which results in easy population inversion and a low threshold value.

3.3. Spectroscopic parameters

The absorption cross-section of Yb^{3+} is calculated according to the expression

$$\sigma_{\rm abs} = \alpha/N,\tag{2}$$

where α is the absorption coefficient of Yb³⁺, and $N = 1.60 \times 10^{21}$ ion cm⁻³ is the concentration of Yb³⁺ ions.

The emission cross-section of Yb³⁺: ${}^{2}F_{5/2}-{}^{2}F_{7/2}$ transition can be calculated by the reciprocity method (RM) [16]:

$$\sigma_{\rm em}(\lambda) = \sigma_{\rm abs}(\lambda) \frac{Z_l}{Z_u} \exp[(E_{\rm ZL} - hc/\lambda)/kT], \qquad (3)$$

where σ_{abs} is the absorption cross-section at wavelength λ . Z_l and Z_u are partition functions for lower and upper levels. k is Boltzmann's constant, and E_{ZL} is the zero-line energy, which is defined to be the energy separation between the lowest of the upper and the lower crystalfield states. For Yb:GSO crystal, the zero line λ_{ZL} is equal to 976 nm and the value of Z_l/Z_u is 1.0 [16]. The emission cross-section of Yb³⁺ can also be calculated and the Füchtbauer– Ladenburg formula [17]:

$$\sigma_{\rm em}(\lambda) = \frac{\lambda^5 \cdot I(\lambda)}{8\pi n^2 c \tau_{\rm rad} \int \lambda \cdot I(\lambda) \, d\lambda},\tag{4}$$



Figure 7. The absorption cross-section σ_{abs} and the emission cross-section σ_{em} of a 10 at.% Yb:GSO crystal.

Table 1. Spectroscopic parameters of Yb:GSO compared with Yb:YAG.

Parameter	15 at.% Yb:YAG				10 at.% Yb:GSO			
Main absorption peaks λ_{abs} (nm)	915	941	969	1029	897	922	940	976
Absorption bandwidth (nm)	11	16	5	10	22	23	16	19
Absorption cross-section $\sigma_{abs} (10^{-20} \text{ cm}^2)$	0.37	0.71	0.40	0.1	0.26	0.32	0.20	0.31
Fluorescence peak (nm)	1030		1048		1012	1031	1048	1088
Fluorescence bandwidth (nm)	10		10		27	10	31	17
Emission cross-section (10^{-20} cm^2)	1.63		0.27		0.20	0.39	0.31	0.42
Fluorescence lifetime (ms)	1.15				1.11			

where $I(\lambda)$ is the intensity of corrected emission spectrum, τ_{rad} is the radiative lifetime value of the excited manifold ${}^{2}F_{5/2}$ of Yb³⁺, *c* is the velocity of light and *n* is the refractive index. The radiative lifetime obtained from Judd–Ofelt analysis is practically the same as experimentally obtained, and is equal to about 1.09 ms, n = 1.75.

The absorption cross-section σ_{abs} and the emission cross-section σ_{em} of Yb:GSO crystal were calculated and are shown in figure 7. Here, in order to analyse the spectroscopic parameters of a 10 at.% Yb³⁺-doped GSO crystal, we compare the results with those of a Yb:YAG single crystal [18], which are listed in table 1.

According to table 1, the absorption bandwidth of Yb³⁺ in the GSO host is much greater than that in Yb:YAG. The absorption bandwidth of Yb:GSO at 940 and 976 nm is about 16 and 19 nm, respectively, and the absorption cross-section σ_{abs} has been estimated at 0.20×10^{-20} and 0.31×10^{-20} cm², respectively. Broad absorption bands are necessary to increase the diode-pumping efficiency, because laser diodes typically emit in a 5 nm wide spectral range, and present a thermal shift of the peak wavelength [9]. One can recognize here that these two absorption bands of Yb:GSO crystal are strong and broad enough to match well the emission wavelength of efficient diode-pumping using high-performance InGaAs laser diodes.

As shown in figure 7, the emission cross-section $\sigma_{\rm em}$ of the fluorescence peaks including 1012, 1031, 1048 and 1088 nm is 0.20×10^{-20} , 0.39×10^{-20} , 0.31×10^{-20} and 0.42×10^{-20} cm², respectively. These four fluorescence bands can serve as the possible laser output.

Although there is a weak re-absorption at 1010 and 1028 nm, it does not have too much effect on the laser output at these two fluorescence bands. In particular, the emission band at 1088 nm possesses the largest emission cross-section for the smallest thermal populating of the terminal laser level which brings about the smallest re-absorption losses. As a result, the laser output around 1088 nm becomes the most efficient one with easy population inversion and a low threshold value. It should be noted that the particularly broad emission bandwidth of Yb:GSO crystal reaches about 72 nm, which is far bigger than that of Yb:YAG. Apparently, Yb:GSO crystal is very suitable to be used for generating ultra-short pulses and as a tunable laser medium when LD pumped at 940 and 980 nm, because of its especially broad emission band.

4. Conclusion

A high optical quality 10 at.% Yb³⁺-doped gadolinium oxyorthosilicate laser crystal Gd₂SiO₅ (GSO) was grown by the Czochralski (Cz) method for the first time. The segregation coefficient of Yb³⁺ in the GSO host lattice is equal to 0.86. The crystal structure of Yb:GSO has monoclinic symmetry with space group $P2_1/c$. Ytterbium experiences quite a strong crystal-field interaction in the GSO host, and the overall splitting of the ²F_{7/2} manifold reaches about 1067 cm⁻¹, which is one of the largest known values. Yb:GSO appears as an interesting laser medium approaching a quasi-four-level laser scheme, which results in easy population inversion and a low threshold value.

Yb:GSO crystal has high absorption cross-sections and a particularly broad fluorescence bandwidth. Such broad bands are similar to those of disordered materials such as glasses. The absorption cross-section σ_{abs} of Yb:GSO at 940 and 976 nm is high, and equal to 0.20×10^{-20} and 0.31×10^{-20} cm², respectively. The emission cross-section σ_{em} of the fluorescence peaks at 1012, 1031, 1048 and 1088 nm is 0.20×10^{-20} , 0.29×10^{-20} , 0.30×10^{-20} and 0.42×10^{-20} cm², respectively. The particularly broad emission bandwidth of the Yb:GSO crystal reaches about 72 nm, which is far bigger than that of Yb:YAG. Results indicated that Yb:GSO crystal seemed to be a very promising laser gain medium for generating ultra-pulses and in tunable solid-state laser applications when LD pumped at 940 and 980 nm.

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