Crystal Growth and Characterization of New Laser Crystal $Bi_4Si_3O_{12}$: Nd

N. SENGUTTUVAN*, K. OOTSUKA*, N. KIDOKORO*,
M. ISHII*,+, M. KOBAYASHI**, T. TAIRA***,
Y. SATO***, S. KURIMURA*** and M. IMAEDA****

The Bridgman growth of Nd doped BSO single crystals and their optical and laser properties are investigated. Good quality crystals were grown with Nd concentration varying from 0.5 to 5.0 at%. Uniformity of Nd distribution in the crystals has been characterized by determining the absorption coefficient at different stages of crystallization. It has been found that the absorption coefficients at the peak wavelengths of 743 and 809 nm were 34 and 19 cm^{-1}, respectively, for 5.0 at% Nd doping. The distribution coefficient, k, of Nd in BSO was also determined by means of chemical analysis and it was found to be about 1.1. Fluorescence lifetime measurement was carried out and the lifetime of fluorescence intensity, τ_0 was calculated to be 267.7 μs. Thermal conductivity of the grown crystals as a function of Nd concentration has also been measured.

1. Introduction

Laser diode pumped solid-state lasers are increasingly attractive because of their compactness, high efficiency and applications in the field of military, industry, medical treatment, remote sensing, optical memory and scientific research. Neodymium (Nd) has been a well-known activator dopant in many laser materials such as Nd:YAG, Nd:YVO$_4$, and Nd:Glass. Despite tremendous applications of Nd:YAG, the major disadvantage of this material is that the distribution coefficient of Nd in YAG is only 0.18. This leads to low dopant level in the crystal which in turn limits the pump absorption. Higher concentration of 4.5 at% was reported for Nd doped YAG crystals grown by flux method, but only small samples are available.[1] For Nd:YVO$_4$, the distribution coefficient is little high at 0.63.[2] Some spectroscopic parameters of typical solid-state laser materials are given in Table 1.

$Bi_4Si_3O_{12}$ (BSO) has recently been found to be an ex-

---

* Shonan Institute of Technology
** KEK, High Energy Accelerator Research Organization
*** Institute of Molecular Science
**** NGK Insulators, Ltd.
+ Corresponding author; email: ishii@mate.shonan-it.ac.jp

平成 12 年 10 月 19 日受付

cellent scintillation detector. The larger absorption and faster decay characteristics of BSO scintillators make them more suitable for radiation detector applications in nuclear and high-energy physics experiments. Undoped and Ce doped BSO crystals have been studied for crystal growth and scintillation properties.[3],[4] Undoped BSO crystals have been shown to have excellent optical transmittance. Single crystals as long as 200 mm were produced successfully with good reproducibility.[5] Its isomorphous, $Bi_4Ge_3O_{12}$ (BGO) has been studied for laser applications by means of doping with Nd^{3+} ions.[6] As Nd^{3+} is to be doped in to Bi^{3+} sites no charge compensation is required. Moreover the ionic radii of Nd and Bi are close enough (1.04 and 0.96 Å, respectively) to allow heavy doping. These factors could make BSO more attractive for laser host applications. The present study aims at investigating crystal growth and possible applications of BSO:Nd as laser host material. However, so far no paper has been published on crystal growth of Nd doped BSO crystals though BGO:Nd has been studied for laser and magneto-optic properties.[6] The advancements in the diode laser pumping technology also make BSO more attractive because the use of conventional flashlamp as the pumping source may lead to more absorption of pump light owing to large Bi^{3+} absorption coefficient.

In the present investigation, crystal growth of BSO:

Table 1. Characteristics of some laser materials in comparison with Nd:BSO.

Material	Dopant concentration	Absorption			Emission	
		Wavelength (nm)	Coefficient (nm)	Width (nm)	Wavelength (nm)	Lifetime (μs)
Nd:YAG	1.0 at%	808.0	8.5	1.5	946, 1064.4	230
Nd:YVO$_4$	1.1 at%	809.0	31.1	2.8	1064.3, 1342	90
Nd:Glass	5.0 at%	800.0	3.0	13	1054	315
Nd:BSO*	5.0 at%	809.7	19.0	17	1064	267.7

*Results are described in the present paper.

Nd by vertical Bridgman method with different doping levels of Nd has been studied. The optical absorption coefficients of these crystals have been measured. Inductively coupled plasma (ICP) mass spectroscopic analysis was carried out to determine the Nd concentration in the grown crystals. Fluorescence lifetime measurement has also been carried out. Thermal conductivity of the grown crystals has been measured by laser flash heat method.

2. Crystal Growth

We used 6N pure Bi$_2$O$_3$ and ultra high purity (>6N) SiO$_2$ (non-crystalline) as starting materials. Nd was added as Nd$_2$O$_3$ at concentrations of 0.5, 1.5, 2.5, 5.0, 7.5 and 10.0 at% to the raw material. The starting materials were weighed according to the formula (Bi$_{1-x}$Nd$_x$)$_4$Si$_3$O$_{12}$ (x is from 0.005 to 0.100). These chemicals were dried at 300°C for 3h before weighing accurately. A total of 300 g of charge was weighed and mixed in a ball mill coated with polyethylene for 6h. The mixture was then fired at 850°C for 3h. After firing, it was ground to powder and mixed again in the ball mill for 3h. It was then pressed into cylindrical rod of about 26 mm in diameter using cold isostatic press (CIP) at 2000 ton/cm^2 and sintered at 950°C for 12h before loaded into a cylindrical platinum crucible. The Pt crucible was 25 mm in diameter, 150 mm in length and 0.3 mm in thickness and was provided at the conical bottom with smaller pipe of 5 mm in diameter to hold the seed crystal. The crucible with the charge was loaded in the furnace and positioned in such a way that the top of the seed was at the melting point of BSO at a furnace temperature of 1075°C. The charge was kept at the molten state for about 12h before being lowered. The lowering rate for all the experiments in the present investigation was 0.5 mm h^{-1}. The

crystals were grown along ⟨100⟩ direction in all the growth runs. After completion of the growth cycle, the crystals were cooled to room temperature over a period of 30 h.

The grown crystals were 25 mm in diameter and about 90 mm in length and are shown in Fig. 1. The crystals were violet colored, mostly clear without cracks though some segregation has been found to form along the surface and at the top for the case of smaller Nd concentration[7]. Up to 1.5 at% of Nd doping, the crystals are similar to the undoped crystals. They are very clear inside with some segregation on the surface and at the top. This segregation phenomenon has been explained previously in our recent publication.[4),8)] When the crystal was grown with further doping (7.5 and 10.0 at% of Nd) it posed big problems as the grown crystals were found to have multiple cracks and second phase. For the 7.5 at% of Nd, the crystal was found to contain second phases inside the crystal. There are small areas where the crystal is transparent and other areas are opaque. For 10.0 at% of Nd, the crystal was found to have segregation at top which is similar to the undoped BSO crystals in addition to the presence of second phase. The presence of segregation inside the crystal at the cone part led to polycrystalline growth at the bottom. The crystal also has many macroscopic defects such as voids and inclusions. The outer surface of the crystal was not smooth having many cracks and voids.

3. Characterization

3.1 Distribution coefficient

The concentration of Nd in the crystal is visibly well distributed. Samples were obtained at different stages of crystallization to check the uniformity of Nd distribution. Inductively coupled plasma mass spectroscopy

Crystal Growth and Characterization of New Laser Crystal $Bi_4Si_3O_{12}$: Nd (N. Senguttuvan et al.)

0.5 at%

(a)

2.5 at%

(b)

5.0 at%

(c)

7.5 at%

(d)

10.0 at%

(e)
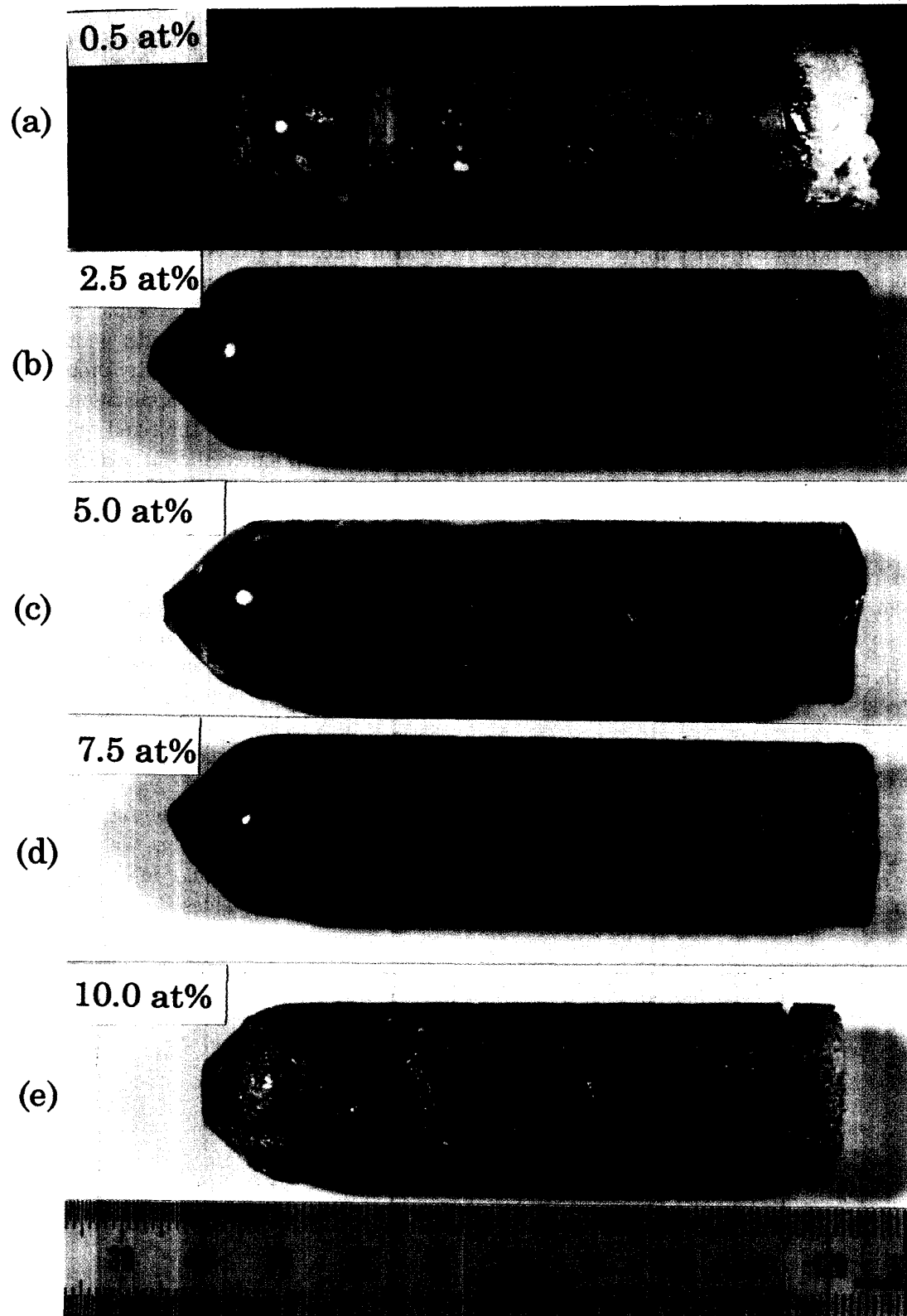
Fig. 1. As grown crystals of Nd doped BSO; (a) 0.5 at% Nd, (b) 1.5 at% Nd, (c) 2.5 at% Nd, (d) 3.5 at% Nd, (e) 5.0 at% Nd and (f) 7.5 at% Nd.

analysis was carried out on crystals grown with 2.5, 3.5 and 5.0 at% of Nd. These crystals were cut at different positions (bottom and top) of the crystal to chemically determine the Nd concentration in the grown crystal. The distribution coefficient, k, was calculated using the relation

$$C_s = k\,C_0\,(1-g)^{k-1} \qquad (1)$$

where C_s is the concentration of Nd in the solid, C_0 is the initial concentration of Nd, k is the distribution coefficient and g is the amount of crystallization. The value of k was found for different crystals grown with different Nd concentration in the melt and the values are given in Table 2. From this result, we can see that the distribution coefficient is not sensitive to the Nd concentration in the melt.
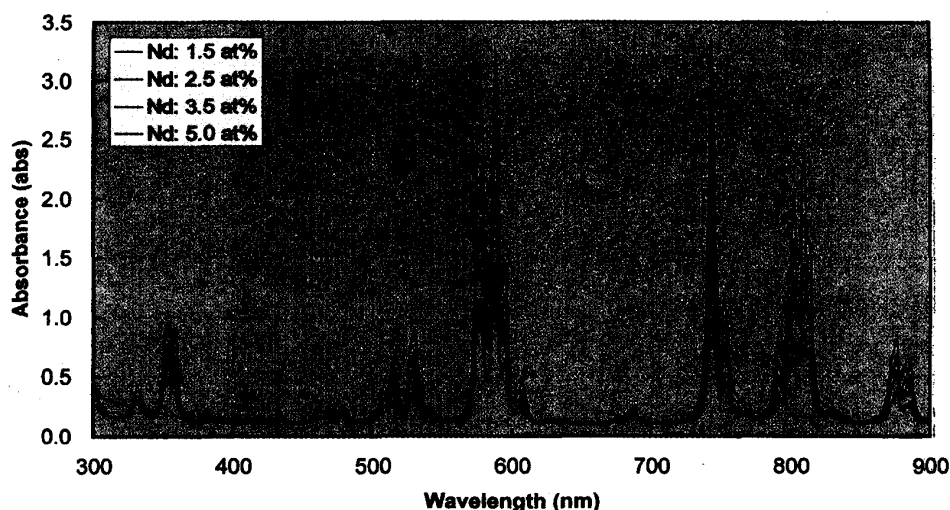
3.2　Optical absorption

The grown crystals were cut and polished into wafers of 3.5 and 0.8 mm thickness. Three samples were obtained from each ingot at three parts of crystallization—bottom, middle and top. Optical transmittance

and absorption were recorded on these samples using Hitachi U3210 spectrophotometer. The overall transmittance of 3.5 mm thick crystals was about 80% irrespective of the amount of dopant. Fig. 2a shows the absorption spectra of different BSO:Nd crystals grown with different Nd concentration. As can be seen from the figure, the absorbance increases steadily as the Nd concentration in the crystal is increased. The full width at half maximum (FWHM) for the aborbance peak around 800 nm has been found to be about 17 nm, which is quite broad when compared to Nd:YAG and Nd:YVO$_4$ crystals. This broader width is essential for more absorption of pump energy prompting its usefulness in the microchip laser applications.

A few samples were subjected to precise measurement of absorption coefficient using Hitachi U3500 at 0.2 nm resolution. The absorption coefficient, α, was calculated for all the samples (with 0.5, 1.5, 2.5, 3.5 and 5.0 at% of Nd doped into the BSO crystals) across 0.8 mm thickness and is plotted in Fig. 2b. When Nd concentration was plotted against α, it was found that the value of α increased linearly for smaller Nd concentration. As the Nd concentration increased the absorption coefficient was found to be saturated, probably due to Nd–Nd interaction. This result is shown in Fig. 3. The absorption coefficient has been found to be 34 and 19 cm^{-1} at the peak absorption wavelengths of 743 and 809 nm, respectively, for 5.0 at% Nd doping. The absorption coefficient, α, was plotted against the amount of crystallization, g in Fig. 4. The smaller absorption coefficient values shown in this figure is due

Table 2.　Distribution coefficient of various Nd doped BSO crystals.

Nd concentration in the melt (at%)	Distribution coefficient, k
2.5	1.1
3.5	1.3
5.0	1.1

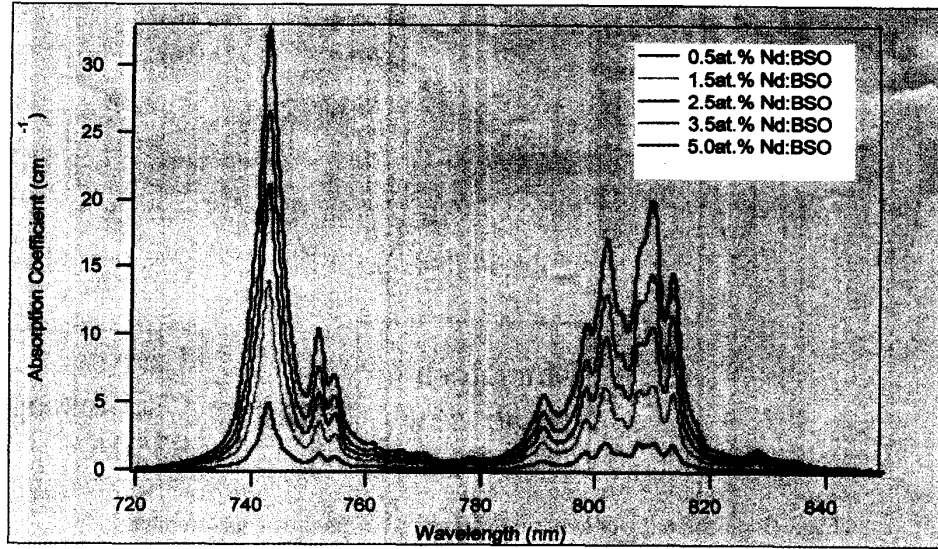**Fig. 2a.**　Absorbance spectra of BSO crystals doped with different Nd concentration (sample thickness: 3.5 mm).

Crystal Growth and Characterization of New Laser Crystal $Bi_4Si_3O_{12}$:Nd (N. Senguttuvan et al.)

Fig. 2b. Absorption coefficient of Nd:BSO crystals in the wavelength region of 720–840 nm (sample thickness: 0.8 mm).
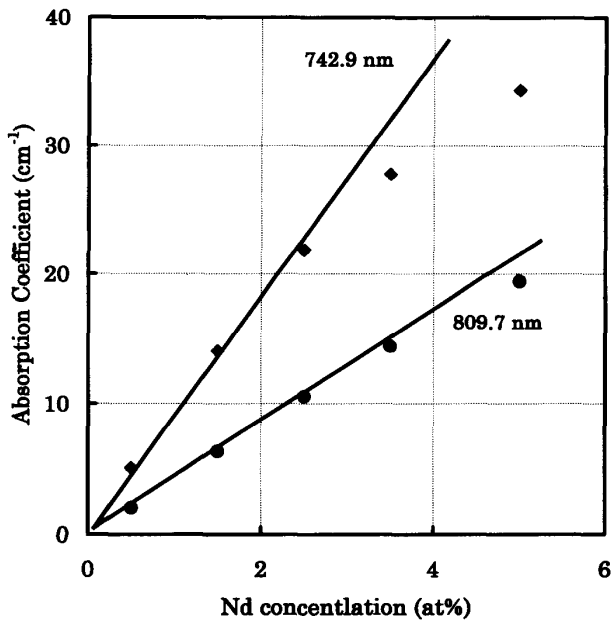

Fig. 3. Variation of absorption coefficient, α with Nd concentration in BSO crystal (sample thickness: 0.8 mm).
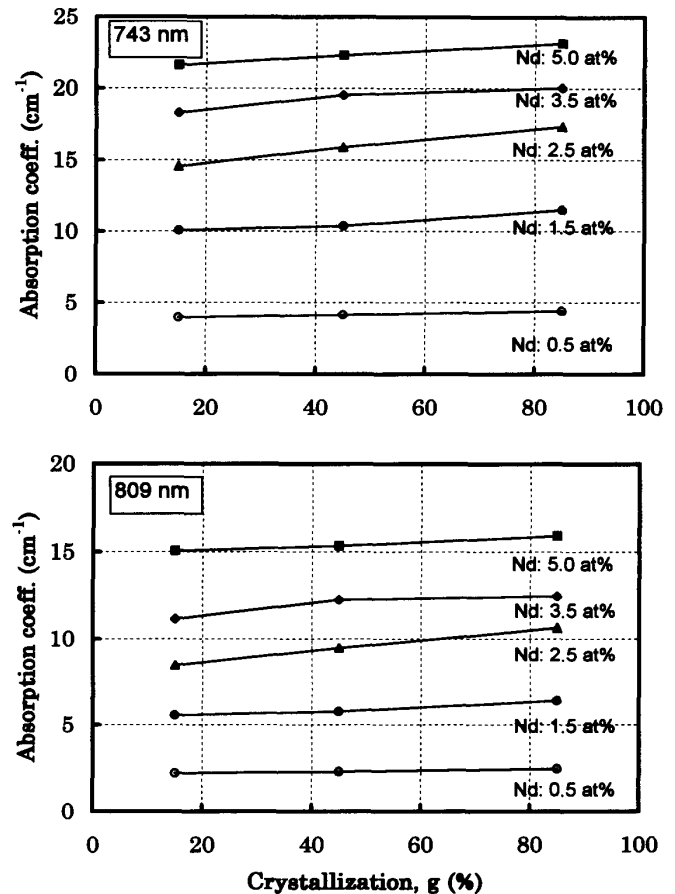

Fig. 4. Variation of absorption coefficient, α with amount of crystallization, g for the crystals grown with different Nd concentration (sample thickness: 3.5 mm).
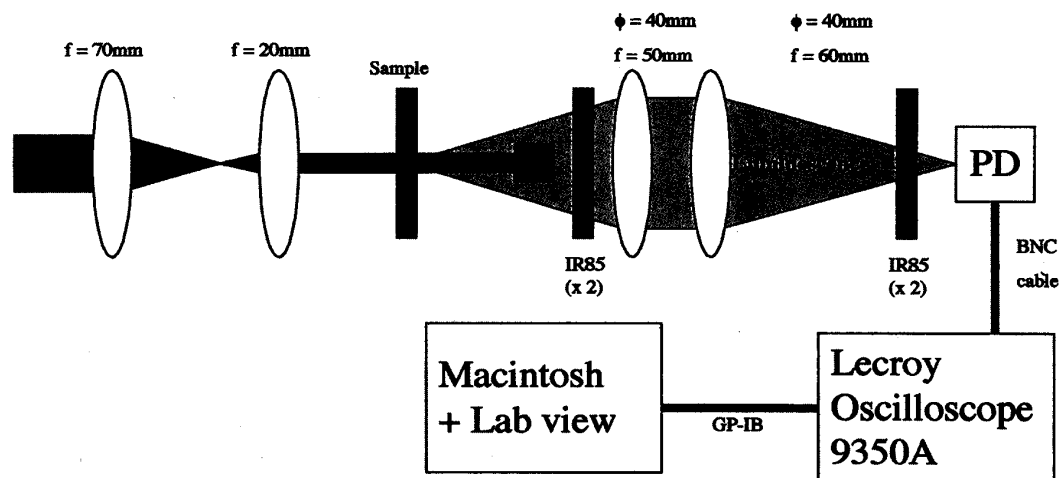
to the larger sample thickness (3.5 mm) used for the measurement. This figure shows an increase in absorption coefficient with increase in crystallization indicating higher impurity concentration at the end of the crystallization. Since the distribution coefficient of Nd has been found to be greater than one (k=1.1) the increased absorption at the end of crystallization in Fig. 4 might be due to other impurities in the crystal with

— 33 —

Fig. 5. Schematic of experimental setup for lifetime measurement.

the segregation coefficient less than unity.

3.3 Fluorescence lifetime

Fluorescence lifetime was determined by the measurement of the time dependence of the fluorescence intensity, which decayed exponentially. We used a pump source an output from an optical parametric oscillator (Lambda Physik SCANMATE OPPO) pumped by a frequency-tripled Q-switched Nd:YAG laser (Coherent Infinity 40–100) as shown in Fig. 5. The pump wavelength and the pump pulse width were 806 nm and 10 ns, respectively. The measurement was performed for the samples with different Nd concentration (0.5, 1.5, 2.5, 3.5 and 5.0 at% Nd). The dependence of lifetime on the Nd concentration is shown in Fig. 6. The solid curve is the fit to the data using the following equation

$$\tau = \frac{\tau_0}{1+(C_{Nd}/C_0)^2} \qquad (2)$$

where C_{Nd} is the Nd concentration, τ_0 is the lifetime at $C_{Nd}=0$ and C_0 is the quenching parameter.[9] From this calculation, the fluorescence lifetime τ_0 was found to be 267.7 μs which is longer than that of Nd:YAG and Nd:YVO$_4$ crystals (see Table 1).

3.4 Emission characteristics

The measurement of emission spectra of 0.5 at% Nd doped BSO was accomplished with a high resolution fluorescence spectrometer (Fluolog-2, SPEX Inc.). The measured spectrum in the range of 1000 nm is shown in Fig. 7. Fluorescence peak at 1064 nm has emission
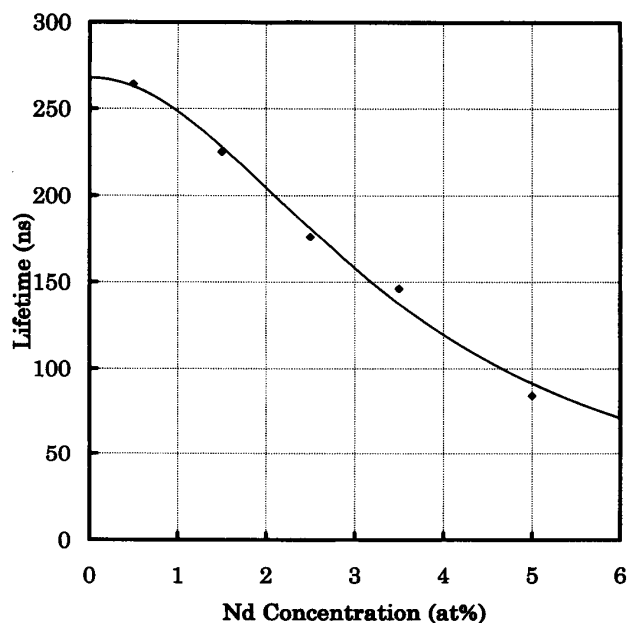

Fig. 6. Fluorescence lifetime as a function of Nd concentration. The solid curve is the fitting with equation (2).

bandwidth of 3.3 nm which is the gain line width for laser oscillation. The fluorescence in the range of 900 nm is reduced by self-absorption.

3.5 Thermal conductivity

Thermal conductivity studies were carried out on samples of 3 mm in thickness and 10×10 mm^2 in area. Measurements were made on samples of BSO doped with 1.5, 2.5, 3.5 and 5.0 at% Nd using a laser flash thermal constant measuring apparatus (Shinkurico

Crystal Growth and Characterization of New Laser Crystal $Bi_4Si_3O_{12}$:Nd (N. Senguttuvan et al.)

Co.) at NGK Insulators, Ltd. The results are given in Table 3 along with specific heat and thermal diffucibility. As can be seen from the table the samples do not show any change in the thermal conductivity values with different Nd concentrations. The value of around 3.5 W/(m·K) for Nd:BSO is of the same order to those of Nd:YAG and Nd:YVO_4 crystals with the thermal conductivity values of around 10 and 5 W/(m·K), respectively.

4. Conclusions

A series of Nd doped BSO single crystals have been grown by the vertical Bridgman method. The grown crystals have been found to possess good optical quality. Crystals with Nd concentration as high as 5.0 at% could be grown without much difficulty. The Nd concentration in the grown crystals were determined by

ICP mass spectroscopy analysis and the distribution coefficient, k, was found to be 1.1. The absorption coefficient, α, was calculated and it was found to increase steadily with the Nd concentration. For 5.0 at% Nd concentration, α is about 34 and 19 cm^{-1} at the peak absorption wavelengths of 743 and 809 nm, respectively. The fluorescence lifetime was measured and the value of τ_0 was calculated to be 267.7 μs. Thermal conductivity measurement was also carried out on samples with different Nd concentration and it was found that it has no dependence on Nd concentration.

Acknowledgements

References

1) P. Gavrilovic, M. S. O'Neill, J. H. Zarrabi, S. Singh, J. E. Williams, W. H. Grodkiewicz, A. Bruce, *Appl. Phys. Lett.*, **65**, 1620, 1994.
2) X. Meng, L. Zhu, H. Zhang, C. Wang, Y. T. Chow, M. Lu, *J. Crystal Growth*, **200**, 199, 1999.
3) M. Kobayashi, M. Ishii, K. Harada, I. Yamaga, *Nucl. Instr. & Meth. A*, **372**, 45, 1996.
4) M. Ishii, K. Harada, N. Senguttuvan, M. Kobayashi, I. Yamaga, *J. Crystal Growth*, **205**, 191, 1999.
5) M. Kobayashi, K. Harada, Y. Hirose, M. Ishii, I. Yamaga, *Nucl. Instr. & Meth. A*, **400**, 392, 1997.
6) X. Q. Feng, G. Q. Hu, Z. W. Yin, Y. P. Huang, S. Kapphan, C. Fisher, F. Z. Zhou, Y. Yang, D. Y. Fan, *Mater. Sci. Enging.*, **B23**, 83, 1994.
7) N. Senguttuvan, N. Kidokoro, K. Ootsuka, M. Ishii, M. Kobayashi, T. Taira, Y. Sato, S. Kurimura, *J. Crystal Growth* (accepted).
8) K. Harada, M. Ishii, N. Senguttuvan, M. Kobayashi, I. Yamaga, S. Fan, Y. Fei (to be communicated).
9) I. Shoji, S. Kurimura, Y. Sato, T. Taira, *Appl. Phys. Lett.* (accepted for publication).
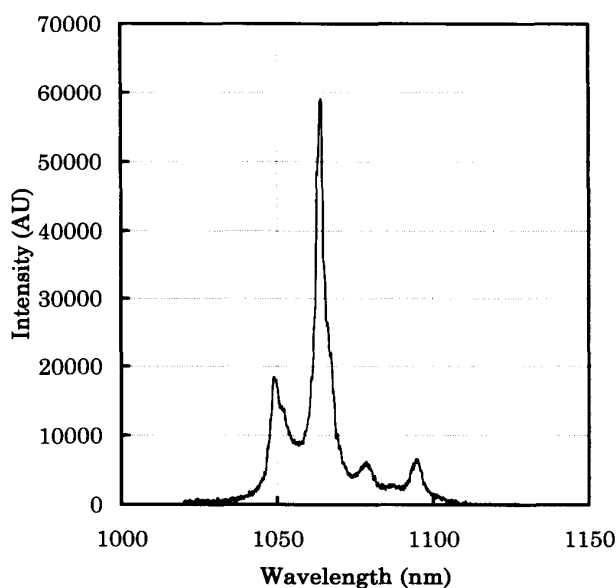
Fig. 7. Emission spectrum of 0.5 at% Nd doped BSO in the 1000 nm region.

Table 3. Thermal conductivity measurements on BSO crystals doped with various Nd concentration.

Nd concentration in the melt (at%)	Specific heat J/(kg·K)	Thermal diffusibility ×10^{-6} m²/s	Thermal conductivity W/(m·K)
1.5	375	1.3	3.42
2.5	347	1.4	3.26
3.5	439	1.2	3.61
5.0	422	1.2	3.30