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$Bi_4Ge_3O_{12}$:Nd^{3+} and $Bi_{12}SiO_{20}$:Nd^{3+} A comparative spectroscopic study

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Abstract

A systematic and comparative study of luminescence and optical absorption properties of the trivalent rare earth neodymium ion in the $Bi_4Ge_3O_{12}$ and $Bi_{12}SiO_{20}$ crystal lattices is presented. The incorporation of Nd^{3+} ions into these crystals is more easily achieved in the first one than in the latter. In both matrices their intrinsic emission gives rise to a radiative energy transfer between the host and the impurity ion. On the other hand most of the Stark energy levels have been identified for both matrices. A calculation of the Ω_2, Ω_4 and Ω_6 Judd–Ofelt parameters is given for each crystal.

Keywords: Bismuth germanates and silicates; Neodymium spectra; Judd–Ofelt parameters

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1. Introduction

Bismuth germanates and silicates have become the subjects of study using a great variety of techniques due to their technological applications. In particular, $Bi_{12}SiO_{20}$ (BSO) has found application in optoelectronics as an efficient photorefractive material [1]. On the other hand, $Bi_4Ge_3O_{12}$ (BGO) is used as a good X-ray, γ-ray and high-energy particle detector [2–4]. Of course, both types of materials can be used alternatively for these purposes, although each one presents better characteristics in the role already described.

Besides, these materials doped with rare earths may be considered as good candidates as laser crystals. The Nd^{3+} ion possesses a set of characteristics that makes it a good candidate for this latter application. However, it is necessary to perform a complete comparative study in order to establish this possibility.

The crystalline structures of BGO and BSO are cubic; the former corresponds to the space group *143d* [5] (Td^6), while the latter corresponds to the space group *23* [6] (T). In the cubic cell of these materials the Ge/Si ions are surrounded by oxygen tetrahedra, while the Bi^{3+} ions are located in the middle of a trigonally distorted oxygen octahedra. It has been found that trivalent impurity ions enter substitutionally in the bismuth sites [7,8]. Thus, it is expected that the trigonal crystal field acting on the RE^{3+} impurity ions splits the electronic energy levels into several Stark levels.

In this work, the results on the comparison of the Stark neodymium energy levels in BGO and BSO are presented. Results on radiative energy transfer between the host lattice and the impurity ion are discussed. Also the values of the Judd–Ofelt Ω_2, Ω_4 and Ω_6 parameters are given allowing a comparison of the possible laser efficiency for both type of crystals.

2. Experimental

$Bi_4Ge_3O_{12}$ and $Bi_{12}SiO_{20}$ crystals doped with 0.1% at. of Nd_2 O_3 were grown from the melt by the Czochralski technique using platinum crucibles. The optical absorption spectra were recorded on a Perkin Elmer spectrophotometer model 330. The photoluminescence spectra were acquired by exciting with different sources: a CW Ti:sapphire laser (Coherent); an Spectra-Physics YAG:Nd pulsed

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laser; an Argon 2020 Spectra-Physics laser; a Xe 150 W lamp with a 22.5 cm Spex monochromator. Light emission from the samples was dispersed by a 50 cm Spex monochromator and the detection was made using appropriate photon counting and amplification techniques. The emission spectra were corrected for the spectral sensitivity of the detector.

3. Results and discussion

The absorption spectra of BSO and BGO are the characteristic ones for these materials, with the absorption edge at 500 nm and 300 nm respectively. Excitation with light lying near these edges produces an intrinsic emission [9] due to an internal transition of the Bi^{3+} ions. Fig. 1 shows the absorption spectrum of neodymium doped BGO in the 350 nm to 650 nm range. There are several groups of lines that correspond to transitions from the $^4I_{9/2}$ Nd^{3+} ground state manifold to $^{2,4}L_J$ (L = P, D, G) excited states of the $4f^3$ electronic configuration and that are located in this wavelength interval. $BSO:Nd^{3+}$ absorption spectrum is quite similar, being the line groups around the same wavelength positions as in the former case. The main difference between both cases is due to the absorption edge that is around 500 nm for BSO as mentioned above. This fact does not allow a clear observation of the transitions to the $^4G_{7/2}$, $^4G_{9/2}$, $^2D_{3/2}$, $^2G_{9/2}$ and $^2P_{1/2}$ manifolds in $BSO:Nd^{3+}$. On the other hand, it was found that the neodymium ions do not incorporate in BSO as well as they do in BGO.

The emission band corresponding to BSO is centered around 600 nm, while for BGO is located around 480 nm. This Stoke's shift is dependent on the local structure surrounding the Bi^{3+} ion responsible for the observed emission [9]. On the other hand, as mentioned before the $BSO:Nd^{3+}$ absorption spectrum is very weak, but nevertheless the different absorption peaks can be perfectly identified, and as it will be discussed later the peak positions are close to those of $BGO:Nd^{3+}$. In Fig. 1 the emission spectra of both crystals are presented and superimposed on the $BGO:Nd^{3+}$ absorption spectrum in order to make some worthy observations.

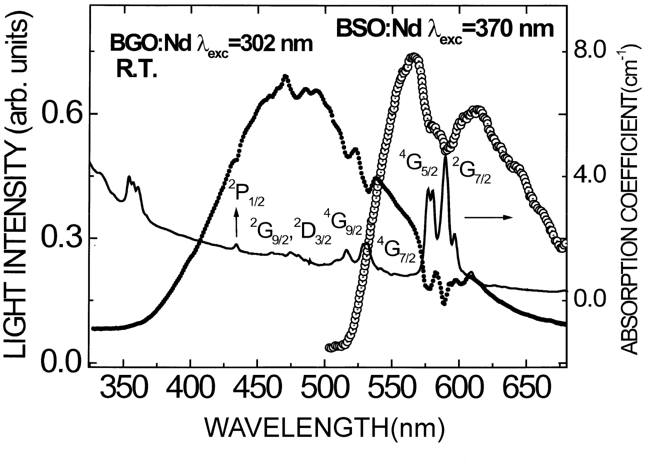

Fig. 1. Absorption and emission spectra of $BGO:Nd^{3+}$ in the UV-visible region. The emission spectrum of $BSO:Nd^{3+}$ is shown for the sake of comparison in the same figure.

As can be seen in Fig. 1, a number of valleys superimposed on the BSO and BGO emission bands are perfectly noticeable. There is a one-to-one correspondence between the wavelength position of these dips and the absorption peaks for a given Nd^{3+} electronic transition from the $^4I_{9/2}$ to $^{2S+1}L_J$ Stark manifolds. For BGO the $^4G_{5/2}$ and $^2G_{7/2}$ manifolds in the region of 600 nm, and between 425 nm to 550 nm the $^2P_{1/2}$, $^2G_{9/2}$, $^2D_{3/2}$, $^4G_{9/2}$ and $^4G_{7/2}$ absorption peaks there are valleys in the BGO emission band. There is a light re-absorption process in the $BGO:Nd^{3+}$ system. From a microscopic point of view, this process can be seen as a radiative energy transfer process [10] among resonant energy levels of the host crystal and the Nd^{3+} ion, as mentioned before. A similar process is observed for neodymium doped BSO crystal (with $^4G_{5/2}$ and $^2G_{7/2}$ manifolds).

Fig. 2 shows some selected bands of the absorption spectra of Nd^{3+} doped BGO and BSO crystals. They are presented in order to compare the crystal field effects on the $^{2S+1}L_J$ electronic levels. They consist of several groups of lines corresponding to transitions between the $^4I_{9/2}$ ground state and the higher energy states of the $4f^3$ electronic configuration of the Nd^{3+} ion. The center of gravity of these manifolds can be found summarized in Table 1, and are in good agreement with previous measurements. As can be clearly seen, there is a larger splitting of the $^{2S+1}L_J$ manifolds in BSO than in BGO simply due to a larger crystal field intensity.

With this information at hand the Judd–Ofelt parameters Ω_2, Ω_4 and Ω_6 were calculated following standard procedures [11]. The results are given in Table 1. Now, using the well known spectroscopic quality factor Ω_4/Ω_6 [12], which gives information about the quality of the laser active medium, a comparison can be obtained for BGO and BSO. For BSO, the ratio Ω_4/Ω_6 has a value of 0.66, in good agreement with values previously reported [11], while for BGO the ratio has a value of 0.55. It has been reported [13] that glasses and crystals with a spectroscopic quality factor for Nd^{3+} in the range 0.3 to 0.6 are good candidates as laser devices, since in this range the fluorescence branching ratio possess desirable high values for $^4F_{3/2} \rightarrow {}^4I_J$ laser transitions. Now, a comparison of the values obtained in this work points out that both materials are good candidates as laser host, although BSO might have a poorer performance as a laser optical device than BGO.

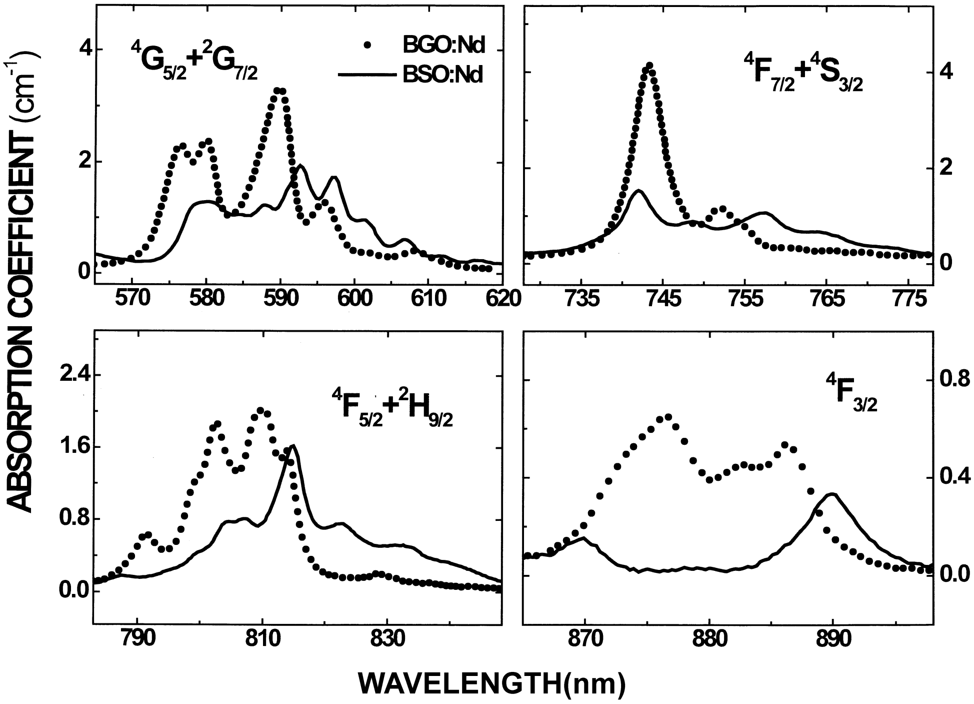

Fig. 2. Selected regions of the BGO:Nd^{3+} and BSO:Nd^{3+} absorption spectra are shown for the sake of comparison.

4. Conclusions

A comparison of the optical spectra of $Bi_4Ge_3O_{12}$:Nd^{3+} and $Bi_{12}SiO_{20}$:Nd^{3+} has been performed. It was found that there is a radiative energy transfer between the host lattice and the neodymium impurity ion. The excitation of Nd^{3+} by this channel gives rise to an emission from the $^4F_{3/2}$ excited state to the $^4I_{9/2}$ and $^4I_{11/2}$ ground Stark levels in the wavelength range 882–920 nm and 1060–1096 nm, respectively. However, the efficiency is low. The quality parameter Ω_4/Ω_6 points out that both crystals are good candidates as laser host, although BGO might have a better performance in this role.

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Table 1
Judd–Ofelt parameters and Nd^{3+} energy levels in BSO and BGO

From $^4I_{9/2}$ to	BSO (6:1)			BGO (2:3)		
	Energy (cm^{-1})	S (10^{-20} cm^2)		Energy (cm^{-1})	S (10^{-20} cm^2)	
		exp.	cal.		exp.	cal.
$^4F_{3/2}$	11 303	2.173	2.347	11 371	2.421	2.549
$^4F_{5/2}+^2H_{9/2}$	12 337	7.588	7.789	12 389	8.6317	9.202
$^4F_{7/2}+^4S_{3/2}$	13 326	8.010	7.887	13 375	9.872	9.579
$^4F_{9/2}$				14 607	0.719	0.635
$^2H_{11/2}$				15 876	0.223	0.169
$^4G_{5/2}+^2G_{7/2}$	16 915	11.867	11.902	17 122	15.767	15.798
$^4G_{7/2}+^4G_{9/2}+^2K_{13/2}$	18 796	2.850	2.202	19 203	4.707	4.190
$^2G_{9/2}+^2D_{3/2}+^2G_{11/2}+^2K_{15/2}$				21 231	2.016	0.887
$^2P_{1/2}$				23 104	0.461	0.319
	$\Omega_2=6.895$, $\Omega_4=7.494$, $\Omega_6=11.416$ rms deviation = 0.457			$\Omega_2=10.567$, $\Omega_4=7.7654$, $\Omega_6=13.949$ rms deviation = 0.0578		

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