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Temperature dependence of $Bi_4Ge_3O_{12}$ photoluminescence spectra

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$Bi_4Ge_3O_{12}$ single crystals were obtained using Czochralski growth method. Photoluminescence spectra were analyzed versus temperature from 12 to 295 K. Besides the previously observed emission bands at 610 and 820 nm, the new emission band at 475 nm was found by a careful temperature dependence measurement in the present study. The influence of basic and defect structure on the shape and position of the spectra versus temperature was discussed.

Keywords: *bismuth ortho-germanate; single crystal; Czochralski growth; photoluminescence*

1. Introduction

Bismuth ortho-germanate single crystals (cubic, eulytine type, space group $I\bar{4}3d$), $Bi_4Ge_3O_{l2}$ (called BGO, hereafter), are widely used as laser host crystal and scintillator detector [1, 2]. The elementary cell of BGO contains four formula units per unit cell. Each Ge^{4+} ion is located in the environment of four oxygen ions, situated at the apices of a regular tetrahedron, while each Bi^{3+} ion is located in the environment of a distorted octahedron of six oxygen atoms. The BGO is characterized by high radiation hardness and absence of afterglow, good light output, energy resolution, and scintillation decay time [3–5], being often commonly used as a kind of a reference pattern at determining the yield of other scintillators. Due to the above features it has been applied for, e.g., medical positron emission tomography (PET) scanners [6–8], HEP electromagnetic calorimeters [9], and complex detectors for astrophysics [10, 11]. The intrinsic 300 ns luminescence of Bi^{3+} ions ($^3P_1$–$^1S_0$) at

~480 nm is regarded as an advantage over well known NaI:Tl scintillator, since it eliminates the problems with non-uniform distribution of luminescence centers, prevalent in doped crystals.

Although many studies have been performed on BGO, the spectroscopic properties of BGO have not been clarified yet, especially the assignment of the photoluminescence (PL) band and relaxation processes. Doping with rare-earth and transition metal ions significantly changes absorption and emission spectra of BGO single crystals [12–14]. Some models were recently developed to assign charge transfer between Bi^{3+} and cations having configuration d^0 or d^{10} for any their coordination [15]. Additionally, it was suggested that the triplet state of a self-trapped exciton (STE) is responsible for the luminescence from BGO host, which consists of a pair of closely spaced sublevels with separation energy of 5.7 meV [16].

In the present paper we report the temperature dependence of the emission bands at 295 – 12 K in detail, which was not performed previously. This information helps in choosing the temperature to obtain high luminescence intensity. We also try to

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find new information for understanding the nature of BGO luminescence.

2.   Experimental

The $Bi_4Ge_3O_{12}$ single crystals have been grown in the Institute of Physics, West Pomeranian University of Technology in Szczecin, from the melt by the Czochralski method using a Malvern MSR4 puller with automatic diameter control based on weighing the crucible [8]. The crystals were grown in air, from an inductively heated platinum crucible and a passive afterheater placed on a ceramic distance plate above but very close to the crucible of 52 mm in diameter. A mixture of oxides Bi_2O_3 and GeO_2 of 4N5 purity was used as a starting material. It was dried at 300 °C for 4 h before weighing. The powders were mixed together and then pressed into cylinder tablets under a high pressure before melting in the crucible. At the crystal growth temperature Bi_2O_3 oxide is more volatile than GeO_2. This was compensated with application of 1 mol% excess of Bi_2O_3 in the starting composition. Single crystals were grown on an $\langle 111 \rangle$ oriented seed with a pulling rate of 3 mm/h and a speed of rotation 10 rpm. Transparent and colorless crystals with 25 mm of the diameter and 95 mm in length and with a convex crystal melt interface were obtained.

The samples used for optical measurements were ~1 mm in thickness, with both sides polished. Transmission measurements were made at room temperature using Lambda-900 of Perkin-Elmer and FTIR-3025 spectrophotometers in the range of 190 – 6000 nm. Absorption was calculated using thickness of the sample and its refraction coefficient. Additional absorption induced by gamma irradiation with a dose of 10^5 Gy was assumed to be:

$$\Delta K = d^{-1}\ln(T_1/T_2) \qquad (1)$$

where d is the thickness of the sample and T_1, T_2 are the transmissions of the sample before and after the process of irradiation.

Photoluminescence (PL) and PL excitation (PLE) spectra were measured with a Spex Fluorolog-3 spectrophotometer. A 450 W Xe-lamp was used as an excitation source.

3.   Results and discussion

Room temperature absorption spectrum of BGO single crystal is presented in Fig. 1. The crystal is transparent in a wide range of 400 – 5700 nm. The fundamental absorption edge (FAE) is observed at 295 nm (4.20 eV). To check the presence of defects in the crystal, we irradiated γ-rays from ^{60}Co source, up to dose of 10^5 Gy (see inset in Fig. 1).
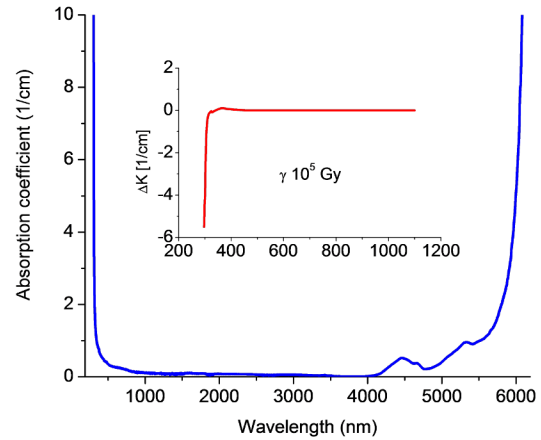

Fig. 1.   RT absorption spectrum of BGO single crystal. In the inset additional absorption after gamma irradiation with a dose of 10^5 Gy is plotted versus wavelength.

Only in a range of FAE one can see negative value of $\Delta K \sim -6$ cm^{-1}. Negative additional absorption indicates on curing effect of point defects, such as, e.g., oxygen vacancies. The presence of oxygen vacancies may be a reason of changes in a shape of PL spectra of the crystal as reported by Bordun [17].

Rogemond et al. [18] and Moncorge et al. [19] suggested that (1) two centers give rise to the absorption of BGO single crystal: $(BiO_6)^{9-}$ and $(GeO_4)^{4-}$ molecule ions, where the central metal ion is octahedrally and tetrahedrally coordinated by the oxygen ions, respectively, and (2) especially the 6s and 6p bismuth orbitals, 2p oxygen orbital, and 4s orbital of germanium in these molecules are responsible for the absorption.
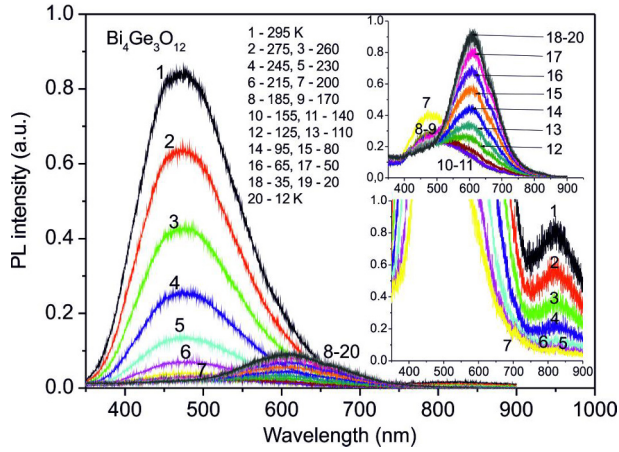
Fig. 2. PL spectra of BGO single crystals for several temperatures.

Fig. 3. Temperature evolution of the intensity of three emission bands at 475 nm (1), 610 nm (2), and 820 nm (3).

In Fig. 2 temperature evolution of PL spectra of BGO single crystal is shown. Intense emission bands are observed at about 475 nm (2.61 eV), together with a weak band at about 610 nm (2.03 eV) and a very weak band at 820 nm (1.51 eV). Besides the previously observed emission bands at 610 and 820 nm [18], the new emission band at 475 nm was found by a careful temperature dependence measurement in the present study. It was clarified from the detailed examination of temperature dependence of the emission bands that the 475 and 820 nm emission bands have the same temperature dependence: their intensities decrease with decreasing temperature from room temperature (295 K) to about 180 K, and they become very weak (nearly disappear) below about 180 K (Fig. 3). Unlike the 475 and 820 nm emission bands the 610 nm emission band has never appeared at temperatures ranging from room temperature to about 180 K. The 610 nm emission intensity increases with decreasing temperature below 180 K. These results indicate that the 475 and 820 nm emission bands arise from the origins or conformations which are quite similar to each other, while the 610 nm emission band arises from another conformation which is thermally converted from the conformation of the 475 nm emission.

Fig. 4 shows the PLE spectra for 480 and 680 nm at 12 K, to investigate the absorption spectra for the 475 and 610 nm emission bands, respec-
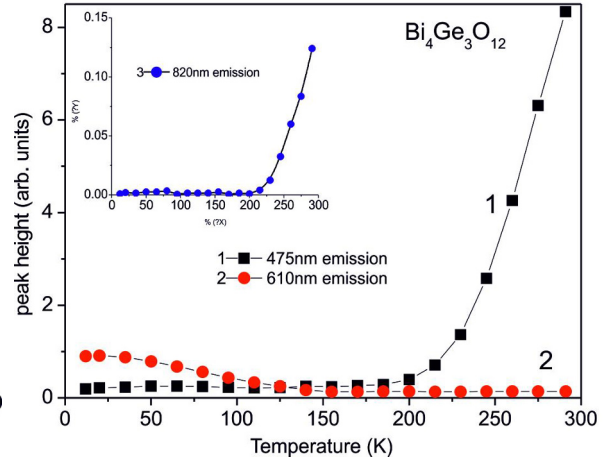
tively. Both the 475 and 610 nm emission bands have the same broad absorption band at 280 – 250 nm, indicating that they arise from the same origin. This is consistent with the temperature dependence of the PL spectra. The edge at 280 nm of the 280 – 250 nm absorption is in agreement with the FAE observed in Fig. 1. It is noted that a sharp absorption is observed at 279 nm in the PLE spectrum for 680 nm emission. The 610 nm emission band is found to have an additional absorption band at about 290 nm and two weak absorption bands at about 560 and 380 nm (the enlarged spectrum in Fig. 4). From the broadening of the all PLE bands except the 279 nm sharp line, it is suggested that they are characteristic of charge transfer bands with a contribution of defect centers like oxygen vacancies. The sharp line at 279 nm indicates an exciton contribution.

Rogemond et al. [18] have suggested that the absorption band at 280 – 250 nm at 10 K is attributable to the electron transition from the 2p orbital of O^{2-} to the 4s orbital of Ge^{4+} for the low energy absorption and transition from the 6s orbital of Bi^{3+} to the 6p orbital ($^3P_1$) of Bi^{3+} for the high energy absorption [18]. They have attributed the 475 nm emission band to the electronic transition in Bi^{3+} ions, i.e., it is due to the transition from the $^3P_0$ ($^1A_{1u}$) metastable state to the ground state $^1S_0$ ($^1A_{1g}$) at very low temperature and the
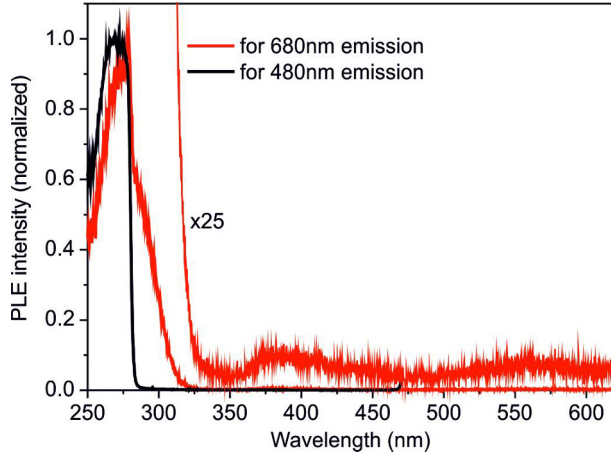
Fig. 4. PL excitation (PLE) spectra of BGO single crystal for 480 and 680 nm emissions at 12 K. The PLE spectrum for 680 nm emission enlarged by 25 times is also shown.

transition from the $^3P_1$ ($^3T_{1u}$) state to the ground state $^1S_0$ ($^1A_{1g}$) at higher temperatures. We observed that the green emission becomes very weak below 180 K. Our result supports the Rogemond et al. attribution because the $^3P_0 \rightarrow {}^1S_0$ transition is dipole-forbidden.

Rogemond et al. [18] have also observed a weak emission band at about 640 nm which appears below 150 K. They have considered that this emission is possible to arise from the unwanted impurity Pb^{2+} ions. Our 610 nm emission band is not located at the same position as the 640 nm emission band. Therefore we cannot attribute the 610 nm emission to Pb^{2+}. The temperature behavior and spectroscopic characteristics, however, are quite similar to the 640 nm emission band. The 610 nm emission has the absorption bands at about 290, 380, and 560 nm at the low-energy side of the BGO absorption band. Therefore the 610 nm emission is suggested to be due to unwanted impurity ions that are located close to Bi^{3+} ions. Such a suggestion is reasonable because the impurity ion is expected to have the emitting excited state at lower energy than the $^3P_1$ state of Bi^{3+}, leading to energy transfer from the $^3P_1$ state to the impurity, followed by the 610 nm emission from the impurity. The identification of the impurity will be made in near future by chemical and physical analysis.

Regarding the 820 nm emission band and taking into account the same temperature dependence of the 820 nm and 475 nm emission bands we suggest that the 820 nm emission arises from the center strongly related with Bi^{3+} ions. The luminescence of BGO is caused by Bi^{3+} with and without trap [19]. The emission from the trap is expected to have a lower energy than the emission from Bi^{3+} without trap. Therefore it is suggested that 820 nm emission arises from the trap.

4. Conclusions

Good optical quality $Bi_4Ge_3O_{12}$ single crystals were obtained using Czochralski growth method. Room temperature absorption and temperature evolution of PL spectra from 12 to 195 K were recorded and analyzed. Besides the previously observed emission bands at 610 and 820 nm, a new emission band at 475 nm was found in BGO crystal in the present study. The temperature dependence has been clarified in detail for the first time on these three emission bands. The 475 and 820 nm emission bands have the same temperature dependence and they become very weak below about 180 K. The former one is assigned to Bi^{3+} ions while the latter to the traps, originating from centers strongly related to Bi^{3+} ion. The 610 nm emission is suggested to be due to unwanted impurity ions that are located close to Bi^{3+} ions.

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