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Visible to infrared low temperature photoluminescence of rare earth doped bismuth germanate crystals

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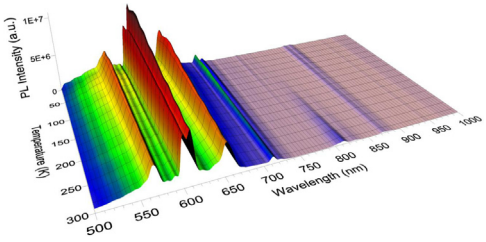
HIGHLIGHTS

- Visible to infrared low temperature photoluminescence properties have been investigated.
- Nature of several sharp and strong emission lines due to rare earth ions were discussed.
- Rare earth doped BGO can clearly affect the luminescence response of the crystal.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the influence of a series of rare earth (Eu, Tm, Nd) and Cr ion doping on the optical properties of BGO was investigated by means of photoluminescence (PL) from visible to IR region in the 10–300 K temperature range using different types of detectors, namely, photomultiplier tube (PMT), InGaAs (IGA), and Si. Several samples were investigated having dopants concentrations of 0.3 wt%Nd, 0.4 wt%Tm, 0.06 wt% Cr and 3 ppm Eu. The PL spectra of the samples showed different luminescence behaviour which is assigned to the 4f intra shell transition from rare earth ions. The temperature dependence of the PL from rare earth doped BGO crystals is also examined.

1. Introduction

The bismuth germanate or bismuth germanate oxide, also called BGO is a well-known high density scintillator material with a chemical composition ($Bi_4Ge_3O_{12}$) and radiation detector based on its main intrinsic luminescence response. It is extensively utilized in high energy physics (e.g. scintillators for electromagnetic calorimeters and detecting assemblies of accelerators), tomography systems for medicine such as positron tomography and in check-light source for TL systems (Blasse et al., 1995; Nagpal et al., 1999). It has also become an essential part of applications in electro-optical, electro-mechanic and nonlinear optical devices (Ganeev et al., 2004). Recently, there is of great interest in studying the defect structure of the materials for all these applications. Recent efforts appeared to find appropriate dopants which reduce damage and instabilities BGO crystal structures (Classe et al., 2005; Auffray et al., 2002). The BGO crystal has a large energy gap, which appears to be a suitable matrix for extrinsic impurities, such as transition metals and/or rare earth ions. In addition, several studies was indicated that the radiation resistance of BGO crystal was improved by Eu doping and such a crystal has shown faster induced absorption recovery than undoped BGO crystal under the

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same irradiation conditions (Wei et al.,1990; Shim et al., 2003a). The trivalent cationic dopants in doped BGO host lattice are expected to occupy the Bi^{3+} ion (Bi^{3+} = 103 pm) (Jazmati and Townsend, 2000; Santana et al. 2007). BGO single crystals doped with rare earth ions were employed in order to increase of the light output, and in some cases these additives are also used to reduce the radiation damage (Kibar et al., 2009; Shim et al., 2003a, 2003b).

Although some new scintillators have been developed during recent years, ultimately they are likely to replace BGO in those applications. There is still a scientific interest in this material as either undoped or doped (Gironnet et al., 2008; Lalic and Souza, 2008; Mazaev et al., 2009; Yu et al., 2013; Kaczmarek et al. 2014). Additionally, BGO is commonly used as a kind of a reference pattern at determining the yield of other scintillators, i.e. the yield of an examined crystal is compared to the yield of a well-characterized BGO sample and then expressed as "*x*% of BGO".

There is no reported work in the literature on rare earth doped BGO crystals at low temperature and this has thus motivated us to perform present work. The main purpose of the research is to analyse photoluminescence characteristics of BGO scintillators doped with Cr ions and the rare earth ions (Nd, Eu and Tm) in the temperature range 10–300 K.

2. Experimental

The undoped and rare earth doped BGO crystal samples used in this experiment were prepared at the Shanghai Institute of Ceramics in China by use of the Bridgeman-Stockbarger technique. Powders of 5N Bi_2O_3 and 6N GeO_2 were mixed in the stoichiometric ratio of 2:3 to provide a melt. The chosen method of heating depends on the materials and on the necessary growth conditions. The Bridgman furnace works with three temperature zones. The upper zone is arranged with temperatures slightly above the melting point of the BGO (i.e. 1050 °C) to be grown. The lower zone is arranged to have a temperature profile fairly below the melting point of the BGO, and an insulated adiabatic zone in between, acts as a baffle between the zones. It then cools slowly (i.e typically 5 °C/h). A certain amount of Nd_2O_3, Cr_2O_3 and Tm_2O_3 were introduced in the melt during the crystal growth process to produce Nd, Tm and Cr doped crystals. All samples were of 1 mm thickness. Temperature dependent (10–300 K) PL measurements were conducted using closed-cycle cryostat under excitation with the 473 nm line of a blue-emitting diode laser. Signals from samples were collected with Horiba Jobin-Yvon iHR550 spectrometer (focal length of 550 nm and f/6.4). The grating selected was 600 grooves/mm blazed at 2000 nm. The signal was detected using a lock-in amplifier and a dual-channel solid-state detector Si/InGaAs, which covers the optical range from 300 nm to 1700 nm. A single channel Horiba photomultiplier tube (PMT) 1911, is placed at the front exit of the spectrometer. PMT tube can only detect the light in the spectral range from 180 nm to 900 nm.

3. Results and discussions

PL spectra were recorded in the temperature range 10–300 K using different detectors for all samples in order to acquire some idea in regard to the influence of different REE ions on the BGO samples. Emission spectrum starts near 500 nm and extends to 1500 nm. As it is well known the undoped BGO shows typical emission band peaking round 500 nm (not displayed here) and the luminescence character changes dramatically as soon as rare earth ions are introduced, either intentionally, or as trace elements (Shim et al., 2003a). The broad band emission observed in undoped BGO is always suppressed and replaced by some of internal transitions within clearly identifiable energy level schemes of the rare earth ion. The suppression of the visible broad band emission suggests that the presence of the rare earth ions opens a much more effective radiative decay path. For instance, the fact that traces of Eu added at the 3 ppm level to the melt totally modifies the luminescence pattern emphasizes that PL intensity measurements based on the intrinsic broad band emission is an unreliable route to assessing the total defect concentration in BGO. Since the spectra, as well as the intensity, are drastically varied by rare earth ions it should be recognized that such sensitivity to trace elements invalidates the normal intensity comparisons which are made for many PL experiments which rely on sensitivity gained by using polychromatic light defined by broad filters. Dopant levels used in the present study are 1.1, 0.4, 0.3 wt%Nd, 0.4 wt%Tm, and 3 ppm Eu. All dopant levels exhibited different PL spectra and evidence for contributions of narrower emission bands at wavelengths which match rare earth transitions. The addition of rare-earth impurities has several effects that are immediately apparent from Figs. 1–6 for the lanthanides of Nd, Tm and Eu. The line type emissions are representative of the well-documented REE 4f transitions (Dieke and Crosswhite, 1963).

Electron configuration of Nd atom is $4f^4$. In particular, different crystal fields can affect the outer layer of electrons. The 4f shell is regarded an inner shell of the electron level configuration of the Nd atom. As a consequence of the shielding effect of the $5s^2$, $5p^6$ and $6s^2$ electrons the effect of the crystal field will significantly be weakened. Fig. 1a shows PL spectra of Nd doped BGO recorded using PMT. As can be seen from Fig. 1a, detection efficiency of PMT tube is not good in the IR region compared to UV and visible region. Three main PL bands peaking at 563–572, 600–658 and 712 nm, which can be related to the transfers of $^4G_{7/2}$, $^4H_{11/2}$ and $^4F_{9/2} \rightarrow {}^4I_{9/2}$ (Orsi Gordo et al., 2015). To investigate NIR PL properties of Nd^{3+} ions in BGO the PL emission spectra of Nd doped BGO were recorded at 300 K and 10 K by InGaAs detector which covers a spectral range from 900 to 1600 nm. As shown in Fig. 1b, upon direct excitation from ground state $^4I_{9/2}$ to the $^4F_{5/2}$ state of Nd^{3+}, two emission bands centered at 1063 and 1340 nm were observed at both temperatures, which were attributed to the radiative relaxations from $^4F_{3/2}$ to its low-lying multiplets of $^4I_{11/2}$ and $^4I_{13/2}$, respectively. The emission pattern, namely, two emission bands of Nd^{3+} ions is partially resolved crystal-field (CF) splitting. Much sharper and better resolved emission lines originating from CF levels of $^4F_{3/2}$ to that of $^4I_{11/2}$ and $^4I_{13/2}$ were observed at 10 K (Fig. 1b). Similar to the PL spectra recorded at room temperature (RT), the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition centered at 1063 nm dominated the whole spectrum, but with slightly smaller full width at half maximum (FWHM), decreasing from 11 nm at RT to 7 nm at 10 K. It is suggested that this confirms the well-ordered crystalline environment around Nd^{3+} ions in BGO lattices. The NIR PL spectra of Nd doped BGO crystals are conducted using by Si detector. As shown in the NIR PL spectra (Fig. 1c), the sample exhibits a strong emission from the $^4F_{3/2}$ level to the two terms, namely $^4I_{9/2}$ (860–970 nm) and $^4I_{11/2}$ (1030–1100 nm). Notice that FWHM values of two main emission lines are much smaller compared to one recorded using InGaAs detector. In Fig. 2a and b temperature evaluation (300–10 K) of PL spectra of BGO crystal is shown. As can be seen from Fig. 2, it was apparent that the characterisation emission lines of Nd shows different pattern as the temperature goes down. Fig. 2a and b also display there are several emission lines which have different temperature dependence. As expected, main emission lines of Nd ions increase with increasing temperature.

Fig. 3 shows the PL emission spectra of Tm^{3+} doped BGO crystals at 300 K using different detectors. The broad emission band peaked at 580 nm in the range of 510–645 nm which is