Journal of Luminescence 137 (2013) 208–213

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Understanding energy transfer in Ce doped $Li_6Gd(BO_3)_3$: A study of millisecond decay kinetics in 77–300 K range

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ARTICLE INFO

Article history:
Received 13 July 2012
Received in revised form
14 December 2012
Accepted 28 December 2012
Available online 4 January 2013

Keywords:
Single crystal
Lithium–gadolinium–borate
Photoluminescence
Energy-transfer

ABSTRACT

Large size, transparent and crack-free single crystals of pure and 0.1 mol% Ce doped $Li_6Gd(BO_3)_3$ have been grown using the Czochralski technique. The photoluminescence and decay kinetics in millisecond range were investigated in the 77–300 K temperature range. In the case of Ce doped single crystals a broad emission band at 400 nm corresponding to $5d \rightarrow 4f$ transitions of Ce^{3+} centers has been observed near room temperature. This emission band splits into two peaks at 386 nm and 414 nm below 200 K. The temperature dependence of Ce^{3+} emission corresponding to excitation bands at 312 and 345 nm were studied. It was observed that for an excitation at 345 nm (corresponding to the Ce^{3+} ions alone) the emission intensity decreases with increasing temperatures while it remains constant for the excitation of Ce^{3+} at 312 nm that coincides with the Gd^{3+} energy level at the same wavelength. This suggests the participation of a temperature dependent energy transfer mechanism between Gd^{3+} and Ce^{3+} ions in the $Li_6Gd(BO_3)_3$ matrix. The mechanism has been explained by studying the temperature dependence of Gd^{3+} emission at 312 nm in the doped and undoped crystals.

1. Introduction

The doped lithium gadolinium borate $Li_6Gd(BO_3)_3$ [LGBO] single crystals are of current interest due to their potential application as scintillators for the neutron detection [1,2]. A large number of boron atoms (^{10}B isotope) per unit cell are useful to capture neutrons that yield energy of approximately 2.8 MeV per absorbed neutron through the ^{10}B (n, α) ^{7}Li reaction. In addition, Li atoms further facilitate the detection of low energy neutrons through ^{6}Li (n, α) ^{3}H reaction [3]. A large energy band gap ($E_g \sim$ 8–9 eV) of the host LGBO allows the use of several rare earth ions to tailor its luminescent properties for applications including lasers, scintillators etc [4]. Among these Ce doped LGBO (LGBO:Ce) is said to be more promising as a scintillator for the neutron detection due to its short decay time (~27 ns) and high light output yield which is approximately six fold that of ^{6}Li-glass scintillators currently used as neutron detectors [5–8].

The growth of large size doped LGBO single crystals is reported to be complicated due to difficulties in obtaining a single phase raw material of the stoichiometric composition [9]. High volatilization of Li and B components from melt, the tendency of the melt to supercool, the formation of metastable phases and cracking during the cooling makes the growth of good quality crystal much more difficult [9–13]. The other problem reported in the growth of LGBO:Ce crystals stems from an excess formation of Ce^{4+} (which is non-radiative) compared to Ce^{3+} ions when the crystal is grown in air/oxygen ambient [14]. Growth of crystals using the Bridgman techniques is also reported to address some of the growth related problems [15,16]. However the growth of high quality, large size, crack-free LGBO:Ce crystal is difficult and only possible by using the Czochralski technique. It may be noted that most of the work reported has been carried out on disc of very small size crystals [3,4].

The LGBO crystal structure as reported in literature has a monoclinic lattice with $P2_{1/C}$ space group with cell parameters; $a=7.2$ Å, $b=16.5$ Å, $c=6.7$ Å and $\beta=105.36^{\circ}$ [9–11]. Here, The Gd-polyhedra (coordinated with eight oxygen atoms) and Li-polyhedra (coordinated by 4 and 5 oxygen atoms) are coupled with each other by B–O triangles (B–O distance of 1.36–1.39 Å) to form a 3 dimensional framework. The Gd ions in the LGBO matrix form a zigzag chain aligned along the (0 0 1) direction with Gd–Gd distance of 3.8 Å which is smaller than the inter-chain distance of around 6.5 Å [11]. Thus the interaction of the Gd ions along the chain dominates over that of inter-chain ions in the LGBO crystal and expected to influence its optical and luminescence properties.

The luminescence and energy transfer mechanism of Ce doped LGBO crystals have been discussed by several authors and have indicated energy transfer between Gd^{3+} and the doped Ce^{3+} ion [17–19]. The possibility of a resonant energy transfer from Gd^{3+} to Ce^{3+} and change in decay kinetics (millisecond time range at

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http://dx.doi.org/10.1016/j.jlumin.2012.12.037

4.4–20 K and nanosecond time range at 80–500 K) have been investigated in the past. Most of the investigations have focused on the emission of Ce^{3+} at 400 nm, but the emission of Gd^{3+} at 312 nm (at which the energy transfer from Gd^{3+} to Ce^{3+} takes place) and decay kinetics in millisecond time range have not been studied in details in the 77–300 K range [4,17,20–23]. Several aspects pertaining to the energy transfer between Gd^{3+} and Ce^{3+} in LGBO:Ce and its temperature dependence are still not clear.

In this paper we report on the growth of large size single crystals of pure and 0.1 mol% doped LGBO using the Czochralski technique. Photoluminescence (PL) measurements on these crystals in the 77–300 K temperature range were carried out to study the emission from Ce^{3+} ions in the LGBO:Ce crystal as a function of temperature at different wavelengths of excitation. A direct evidence of an energy transfer occurring between Gd^{3+} and Ce^{3+} ions and its temperature dependence has been established by measuring the temperature dependence of emission intensity from Ce^{3+} and Gd^{3+} ions and their decay time in millisecond range.

2. Experimental

The LGBO:Ce single crystals were grown along (010) direction using the Czochralski technique (Cyberstar make Oxypuller). The starting charge for the growth of crystals was prepared from high pure (99.99%) constituent oxides (Li_2O_3, Gd_2O_3, CeO_2, B_2O_3) using a two step solid state reaction process. In the first step the constituent oxides were heated at 750 °C for 10 h in an alumina crucible. This material was crushed and mixed thoroughly and again sintered at 750 °C for 24 h. The two step sintering process was found necessary as a single sintering resulted into an incomplete phase formation. For the growth of single crystals, the starting material was taken in a platinum crucible and heated to 900 °C in 4 h in the air ambient. The melt was kept for 2 h at this temperature for homogenization. A pull rate of 0.7 mm/h for undoped LGBO and 0.5 mm/h for LGBO:Ce crystals were employed. The seed rotation rate was kept as 15 rpm. The phase of the sintered charge and as-grown crystal was verified using powder XRD (Rigaku make RINT-2200) and Differential Thermal Analyzer (SETRAM make DTA-TG 92). The high resolution XRD (HRXRD) was recorded using a PANALYTICAL X'Pert MRD Pro Model. Omega scan was carried out for the reflection from the (010) plane.

For optical measurements 2 mm thick samples were cut from the as-grown crystal ingots and polished to mirror finish using alumina powders down to 0.3 μm size. Transmission spectra were recorded in the wavelength range from 190 nm to 2700 nm using a UV–vis spectrophotometer JASCO (Model-V 670). PL studies were performed over a wavelength range from 250 to 600 nm in a temperature range of 77–300 K employing a fluorescence spectrometer (Edinburg Model-FLP920) having a 0.1 nm spectral resolution. A cryostat (Oxford, Optistat-DN) was used for the low-temperature measurements down to 77 K. The emission was recorded in the reflection geometry by positioning the sample at 45° with respect to the excitation beam. A steady state xenon lamp was used as an excitation source and a spectral bandwidth of 1 nm was selected for both excitation and emission arms (for high resolution measurements, a spectral bandwidth of 0.1 nm was used). The recorded luminescence spectra were corrected for the spectral sensitivity function of the instrument. A xenon flash lamp having a pulse width of 10 μs and a repetition frequency of 2 Hz was employed to record the lifetime spectrum.

3. Results and discussion

Fig. 1 shows photographs of undoped and the 0.1% Ce doped LGBO single crystals. The grown crystals were transparent and crack-free with dimensions up to 20 mm diameter and 30 mm length. The DTA pattern of an as-grown crystal, as shown in Fig. 2, shows the magnitude of supercooling (~150 K) and a very narrow freezing profile (width < 1.5 K). To overcome this problem a large axial temperature gradient of around 100 K/cm just above the melt was employed. Further, to avoid cracking of the LGBO crystal in a high temperature gradient (due to the presence of cleavage planes) small pull rates (< 0.8 mm/h) were employed in each growth run. The powder XRD pattern of the LGBO:Ce crystal given in Fig. 3 suggests the formation of a single phase material. To evaluate the crystallinity of the grown crystal an HRXRD was recorded for the (010) plane. The rocking curve shown in the inset of Fig. 3 displays a symmetric curve with a FWHM of about 175 arc-sec. The absence of any secondary peak indicates a good quality of the as-grown crystal. However, the FWHM may further be improved by using post-growth annealing.

A comparison of transmission spectra of doped and undoped crystals is shown in Fig. 4. The transmission spectrum of an undoped LGBO crystal showed sharp absorption lines below 350 nm corresponding to various transitions of Gd^{3+} ions in the LGBO matrix and can be assigned to different levels using the Dieke's energy level diagram for rare earth ions [16,24]. It is reported that in the LGBO crystals with a Ce concentration above 0.5 mol% the Gd^{3+} absorption lines above 200 nm get quenched [14]. However in the present studies Ce^{3+} concentration is 0.1%,

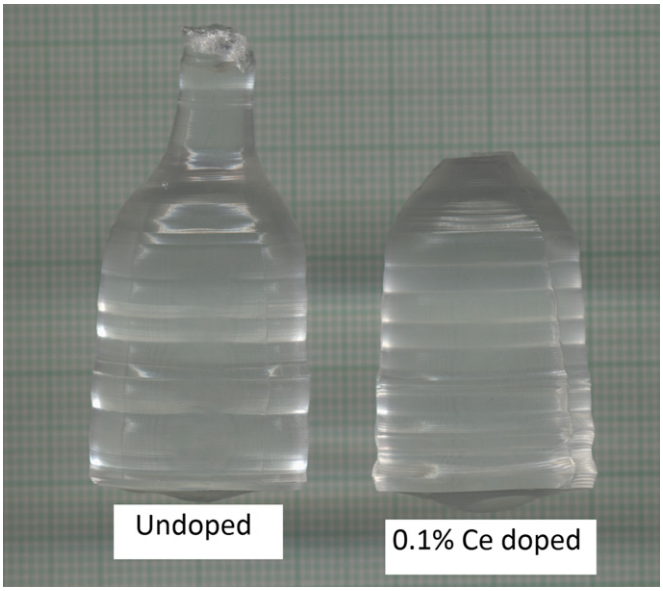

Fig. 1. Photographs of as-grown single crystal of $Li_6Gd(BO_3)_3$.

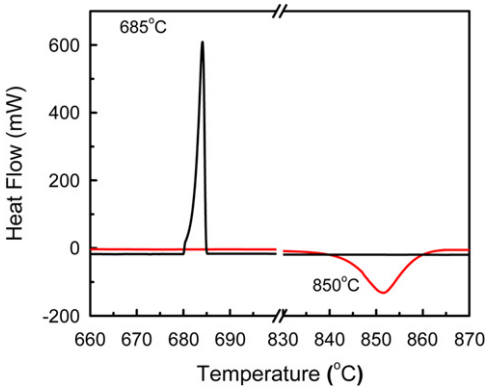

Fig. 2. Melting and freezing behavior of the $Li_6Gd(BO_3)_3$.