Radiation Measurements 63 (2014) 26–31

Contents lists available at ScienceDirect

Radiation Measurements

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

Studies on shallow traps in $Li_2B_4O_7$:Eu,Mn

Winicjusz Drozdowski [a,*], Kamil Brylew [a], Sławomir M. Kaczmarek [b], Danuta Piwowarska [b], Yosuke Nakai [c], Taiju Tsuboi [d], Wei Huang [d]

[a] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland
[b] Institute of Physics, Faculty of Mechanical Engineering and Mechatronics, West Pomeranian University of Technology in Szczecin, Al. Piastow 17, 70-310 Szczecin, Poland
[c] Faculty of Engineering, Kyoto Sangyo University, Kyoto 603-8555, Japan
[d] Institute of Advanced Materials, Nanjing Tech University, Nanjing 210009, China

HIGHLIGHTS

- Radioluminescence spectra of LTB:Eu,Mn have been measured at various temperatures.
- Glow curves of LTB:Eu,Mn have been recorded between 10 and 300 K.
- Thermoluminescence studies have been extended with the $T_{max} - T_{stop}$ method.
- Trap parameters related to particular glow peaks have been derived.
- Besides discrete traps a quasi-continuous distribution has been found.

ARTICLE INFO

Article history:
Received 9 December 2013
Received in revised form
29 January 2014
Accepted 20 February 2014

Keywords:
LTB
Manganese
Europium
Low temperature thermoluminescence
$T_{max} - T_{stop}$ method
Trap distribution

ABSTRACT

$Li_2B_4O_7$ (LTB) single crystals doped with 0.5 mol% Mn and 0.005 mol% Eu have been grown by the Czochralski method. The presence of Eu^{3+} has been confirmed by photoluminescence spectra of non-irradiated crystals, whereas the presence of Mn^{2+} by absorption spectra of gamma-irradiated ones, as well as by EPR measurements. Unlike in most thermoluminescence studies on pure and doped LTB, performed usually above 300 K, glow curves have been recorded between 10 and 300 K in order to focus the attention on shallow traps. A broad, intense glow peak is observed around 80 K, with three weaker peaks at 205, 255, and 280 K. Based on supplementary $T_{max} - T_{stop}$ experiments, the trap parameters have been derived assuming that the glow curve is in fact formed by a superposition of a double Gaussian band related to a quasi-continuous distribution of trapping levels, and several glow peaks produced by discrete traps. The nature of the traps is also discussed.

1. Introduction

Lithium tetraborate, $Li_2B_4O_7$ (LTB), has found widespread applications in various fields. Inter alia, due to its piezoelectric properties (with parameters exceeding those of quartz) it has been used as a substrate for surface acoustic wave devices in TV and signal processing techniques (Wiatmore et al., 1981). Since it contains lithium, it has been considered as a neutron scintillator (Katagiri et al., 2004). Mn-doped LTB is a commercial thermoluminescence dosimeter, denoted as TLD-800 (Horowitz, 1981). The utility of LTB for nonlinear integrated optics and as superionic conductors is also worth mentioning. All these applications necessitate a scientific interest in physical properties of this material. In particular, charge trapping processes have attracted a lot of attention so far.

Thermoluminescence (TL) of pure and doped LTB has been studied by several groups. Although the first records on this topic are more than a quarter of century old (Jones and Bjarngar, 1968; Lakshmaran and Ayyangar, 1976), the most extensive research has been carried out in recent years (Martini et al., 1995; Watanabe et al., 1996; Dubovik et al., 2000; Grinyov et al., 2000; Holovey et al., 2006, 2008; Kitis et al., 2006; Thanh et al., 2008; Danikin et al., 2010; Kar et al., 2010; Singh et al., 2011; Ratas et al., 2012; Kerikmaee et al., 2013; Ekdal et al., 2014). All these investigations, however, pertain to high temperature thermoluminescence (htTL), i.e. TL measured above RT. On the contrary, only a few papers on low temperature thermoluminescence (ltTL) of $Li_2B_4O_7$ can be found in literature. To the best of our knowledge, the first results of ltTL measurements on undoped LTB have been published by

* Corresponding author. Tel.: +48 56 6113319; fax: +48 56 6225397.
E-mail addresses: wind@fizyka.umk.pl, wind@wind.lap.pl (W. Drozdowski).

http://dx.doi.org/10.1016/j.radmeas.2014.02.017
1350-4487/

Antonyak et al. (1986). In their paper a glow curve taken between 90 and 310 K at a heating rate of 0.5 K/s is displayed, yielding three distinct peaks at about 110, 190, and 270 K, with some weaker ones close to 150, 165, 200, 215, and 225 K. Except for a rough estimation of the trap depth range, based on the historic, but not at all reliable Urbach method (Urbach, 1930), there is no data analysis. In such a case, the recent publication of Ogorodnikov and Poryvai (2012) seems to be the only trustworthy source of information on ltTL and shallow traps in undoped LTB. Although the glow curve presented therein, recorded between 100 and 350 K at a heating rate of 0.3 K/s, is rather of poor quality, this imperfection is more than compensated by the proposed model and discussion. Consequently, a broad 100–150 K peak has been ascribed to two hole traps 0.24 and 0.30 eV deep, whereas two discrete peaks at 205 and 260 K to a 0.42 eV deep electron trap and a 0.58 eV deep hole trap, respectively. Concerning doped LTB crystals, ltTL has only been examined by Podgórska et al. (2004) for $Li_2B_4O_7$:Mn. A glow curve taken at a heating rate of 0.15 K/s has been resolved into four first-order glow peaks, related to traps with depths of 0.04 eV (90 K), 0.15 eV (110 K), 0.12 eV (130 K), and 0.24 eV (165 K). However, the first two traps have been regarded as responsible for the presence of a very broad and almost symmetrical peak between 50 and 120 K, which does not have to be true. Simply the use of the classic equation of Randall and Wilkins (1945) to fit wide glow peaks has always a calculated risk. Therefore, the present state of knowledge on ltTL and shallow traps in doped LTB crystals is still strongly limited and certainly deserves more attention.

In the current paper we focus on shallow traps in $Li_2B_4O_7$:Eu,Mn crystals. The presence of such traps is first postulated upon radioluminescence (RL) studies as a function of temperature, then confirmed by advanced ltTL measurements including the $T_{max} - T_{stop}$ method (McKeever, 1980). The parameters of traps are carefully derived and their significance is tentatively discussed, also against a background of the publication of Ogorodnikov and Poryvai (2012).

2. Materials and experiment

Single crystals of Mn- and Eu-doped $Li_2B_4O_7$ were grown by the Czochralski method at the West Pomeranian University of Technology. The melt was prepared by melting at first B_2O_3 of 4N purity in a platinum crucible and gradually adding Li_2CO_3 of 5N purity to reach a starting composition with 67.9 mol% of B_2O_3. The excess of B_2O_3 over the stoichiometric composition was needed because of its high vapour pressure at the crystallization temperature. The dopants in the form of fine powders of MnO_2 and Eu_2O_3 were added to the LTB charge. The crystals obtained in this way were transparent, colourless, without a core and with a thin visible inclusion line at the centre along the crystals. The crystals cross-sections were circular, approximately 20 mm in diameter, with two (110) type and two (001) type lines on the surface.

To confirm the presence of manganese and europium in the crystal, photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded with a Spex Fluorolog-3 spectrophotometer at a fixed spectral resolution of 0.5 nm. A 450 W Xe-lamp was used as an excitation source. With the same aim, electron paramagnetic resonance (EPR) spectra at various temperatures ranging from 8 to 300 K were measured with a conventional X-band Bruker ElexSys E500 CW-spectrometer operating at 9.5 GHz and equipped with a standard helium gas flow system.

A typical set-up consisting of an Inel X-ray generator (Cu-anode X-ray tube, 45 kV/10 mA), an ARC SP-150 monochromator (Hol-UV grating blazed at 300 nm, 1 mm slits, resolution 5 nm/1 mm), a Hamamatsu R928 PMT (1000 V for RL, 800 V for ltTL), and an APD Cryogenics closed-cycle helium cooler with a Lake Shore 330 temperature controller, was employed to record X-ray induced emission spectra and ltTL glow curves. The RL measurements were carried out with a step of 10 K, starting at 320 K and terminating at 10 K to avoid a possible contribution from any thermal release of charge carriers to the RL yield. Prior to the standard ltTL runs the samples were exposed to X-rays for 10 min at 10 K. The glow curves were taken between 10 and 300 K at a heating rate of 0.14 K/s.

In order to check the possible existence of radiation defects, optical absorption measurements were performed using a LAMBDA-900 Perkin–Elmer spectrophotometer in UV-VIS-IR range. Absorption spectra were examined comparatively on “as-grown” and gamma-irradiated LTB:Eu,Mn samples. The latter ones acquired a dose of 120 kGy from gamma rays delivered by a ^{60}Co source.

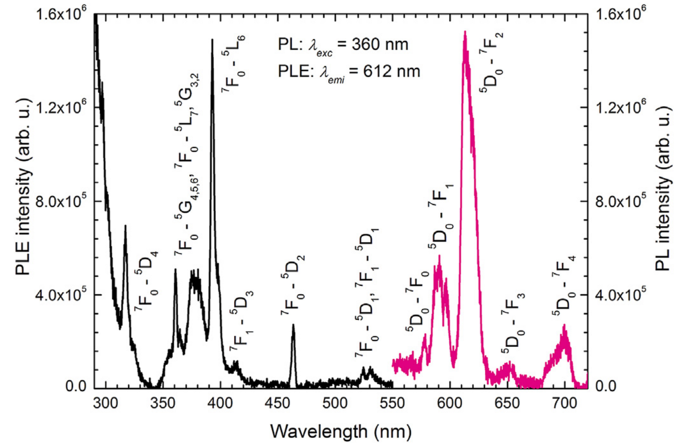

Fig. 1. PL and PLE spectra of LTB:Eu,Mn (360 nm excitation/612 nm emission).

3. Results and discussion

Fig. 1 shows room temperature PL and PLE spectra of $Li_2B_4O_7$:Eu,Mn. The spectra clearly confirm the presence of europium in the single crystal and optical transitions characteristic for Eu^{3+} ions are identified therein. Contrary to Eu^{3+}, no features characteristic for Mn^{2+} emission can be noticed. A signal from Mn^{2+} ions, however, has been detected in the EPR spectra (Fig. 2). These observations give rise to the following suggestions. Europium enters the LTB lattice as Eu^{3+} ions at Li^+ octahedral positions. The average ionic radii of Eu^{3+} and Li^+ ions in octahedral coordination are ~0.97 Å and ~0.76 Å, respectively. Some distortions of the octahedral environment should be thus associated with Eu^{3+} doping of LTB. Moreover, because Mn^{2+} ions (~0.67 Å) also substitute the same site, a kind of competition leads to the enhancement of Eu^{3+} emission intensity at the expense of Mn^{2+} emission. We note that a more extensive analysis of PL, PLE, and EPR spectra of LTB:Eu,Mn, comprising their thermal dependences, the possible existence of crystallographically nonequivalent positions of Mn^{2+} ions in the LTB lattice, and the aspect of the energy transfer from Mn^{2+} to Eu^{3+} ions, is being performed and will be published elsewhere.

To probe the incidence of radiation defects in the crystal we have measured absorption of LTB:Eu,Mn for two different crystallographic orientations (100) and (001), before and after ^{60}Co gamma irradiation delivering a dose of $1.2 \cdot 10^5$ Gy. As illustrated in Fig. 3, absorption bands related to Mn^{2+} ions are not visible in the non-irradiated crystal (curves no. 1 and 2), which seems to confirm the presence of point defects arising from Eu^{3+} substitution for Li^+ at octahedral positions. Moreover, an anisotropic characteristics can be noticed in the curves no. 1 and 2. In gamma-irradiated LTB:Eu,Mn some additional absorption bands can be recognized