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Thermally stimulated luminescence process in copper and silver co-doped lithium tetraborate single crystals and its implication to dosimetry

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ABSTRACT

Single crystals of $Li_2B_4O_7$ (LTB) doped with Cu and Ag and Cu, Ag co-doped have been grown using the Czochralski technique. Luminescence studies revealed a sensitizer role of Ag in the LTB:Cu,Ag crystal. It is found that, despite an energy transfer from Ag^+ to Cu^+ centers, emission from both the centers participate in the thermally stimulated luminescence (TSL) of co-doped. We propose that the LTB:Cu,Ag crystal will be a better and efficient material for dosimeters [TSL as well as optically stimulated luminescence (OSL)] compared to singly doped LTB crystals in a photo-readout system having a maximum response in the 200 nm to 600 nm range.

1. Introduction

Lithium tetraborate ($Li_2B_4O_7$), (LTB) has attracted much attention of the science community as a radiation proof material for optical devices and personal dosimetry [1–5]. An effective atomic number (Z_{eff}=7.3) equivalent to human tissues makes it suitable for the personal dosimetry. It is also a promising scintillator for the neutron detection due to large thermal neutron capture cross-sections of ^{6}Li and ^{10}B and to its high gamma transparency [6]. The large band gap (E_g~9 eV) of this crystal provides a wide transparent energy window range to dopants and hence the luminescent spectra have the signs of atomic or ionic emission from the relevant dopant atoms [7]. Though its sensitivity to ionizing radiation is more or less independent of dopants, the scintillation yield can be increased significantly depending on the choice of the dopant. Luminescence studies on LTB doped with different dopants (Ce, In, Ni, Cu and Ti ions) have been reported by many researchers in polycrystalline and glassy samples [8–12]. However, single crystals could be more advantageous due to the uniform crystal-field and absence of grain boundaries making them highly transparent to visible light and very effective to collect the emitted light from the bulk of the samples. In addition, the resistance to humidity due to its stoichiometric composition, small surface area, simple annealing process, simplicity of glow curves, high sensitivity and easy handling compared with powder samples make the LTB single crystals a potential candidate for applications in the TLD [4]. Though doping of the LTB crystal is difficult due to its compact structure, small amounts of Cu (a few hundreds of ppm) incorporated in the crystal could make a scintillator suited for the neutron detection and dosimetry with outstanding sensitivities exceeding that of the well-known LiF:Mg,Ti (TLD-100) phosphor [13,14]. The efficiency and sensitivity of LTB:Cu can be further increased through an effective energy transfer by co-doping with elements like Ag, In and P [15]. For the effective energy transfer it is necessary that the emission of a dopant atom should lie in the excitation range of the other. It has been observed that in the LTB crystals, Cu and Ag impurities are incorporated as Cu^+ and Ag^+ by substituting Li^+ wherein the emission of Ag^+ lies in the excitation region of Cu^+ states and it may increase the overall light yield through an energy transfer mechanism [16]. It is further reported that co-doping with Ag makes it sensitive to optical stimulation of traps making it an efficient optically stimulated luminescence (OSL) material [17]. Though there are reports on the luminescence properties of Cu, Ag co-doped LTB, a detailed and satisfactory explanation about energy transfer mechanism and its role in thermally stimulated luminescence (TSL) and OSL properties have not been elaborated earlier which may be helpful in developing it as an effective TSL or OSL material.

In this communication, we present photoluminescence (PL) and TSL studies on single crystals of LTB:Cu, LTB:Ag and LTB:Cu,Ag grown from melts using the Czochralski technique. These crystals were exposed to the ionizing radiation at room temperatures to study their TSL properties. The energy transfer mechanism in the

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Cu and Ag co-doped LTB single crystals are studied and explained, and a suitable readout for the co-doped LTB is proposed which will be helpful to realize its full potential in the dosimetric application.

2. Experimental

LTB single crystals doped with Cu, Ag, and co-doped with Cu and Ag, were grown using the Czochralski technique. The details for undoped and doped crystals are explained in our recent communications [2,16]. Single crystal growth of pure and doped LTB were carried out in the air ambient. Commercially available high purity (99.99+%) polycrystalline powders of LTB, Cu_2O and Ag_2O were taken as a starting charge for the growth. Clear, transparent and crack-free single crystals (20 mm diameter, 25 mm length) have been grown in all the experiments. The doping concentration in the melt was 0.5 mol% for Cu and Ag when doped individually, while it was 0.25 mol% for each in the co-doped crystals.

For optical measurements 2 mm thick slices were cut perpendicular to the growth direction from the crystal ingots and polished with different grades of alumina powders down to 0.3 μm. Optical absorption/transmission measurements were carried out in the range from 200 nm to 1100 nm with 1 nm resolution on a Chemito 2500 spectrophotometer. Photoluminescence (PL) studies were performed over a wavelength range from 200 nm to 800 nm by employing an Edinburg fluorescence spectrometer (Model FLP920). The emission was recorded in the reflection geometry by positioning the samples at 45° with respect to the excitation beam. For measurements in the spectral domain, a continuous Xe lamp was used as the excitation source and a spectral bandwidth of 0.5 nm was selected for both excitation and emission monochromators. All the recorded luminescence spectra were corrected for the spectral sensitivity function of the instrument.

Samples of identical size were cut from the single crystal ingots in a size ($3 \times 200D71\ mm^3$) to study the TSL properties. These samples were irradiated using a calibrated ^{60}Co gamma source at two different dose rates of 0.57 centi-Gy/min (for small doses) and 2 Gy/min (for large doses). The LTB:Cu, LTB:Ag and LTB:Cu,Ag single crystals were studied for their TSL response in the absorbed dose range from 10 mGy to 250 Gy. The LTB crystals were given an annealing treatment at 300 °C for 30 min to erase the irradiation history of the sample prior to its reuse. It has been found that an annealing at 300 °C for 30 min is adequate to erase the residual TSL signal and restore the original TSL sensitivity of the TSL dosimeters. The TSL glow curves were recorded at a constant heating rate of 1 K/s. The TSL emission was read using a photomultiplier tube (Hamamatsu R3896) having a spectral response in the range from 180 nm to 900 nm. A Pico-ammeter was used to read the output of the PMT in the current mode. All the data were recorded with a computer-based data acquisition system.

To record TSL emission spectra, a compact Horiba scientific (H-20UV) monochromator in a low light loss configuration was mounted at an optimized focal distance from the sample. The emitted photons were focused on the monochromator and an output slit corresponding to a window of 10 nm wavelength range. To study the glow curve at a particular wavelength, the monochromator was fixed at that wavelength and corresponding TSL glow curves were recorded.

3. Results and discussions

All the grown crystals showed over 80% transmission in the visible range, as shown in Fig. 1, indicating a good optical quality of the grown crystals. In case of Cu doping the absorption edge was observed with an onset at about 200 nm and absorption band

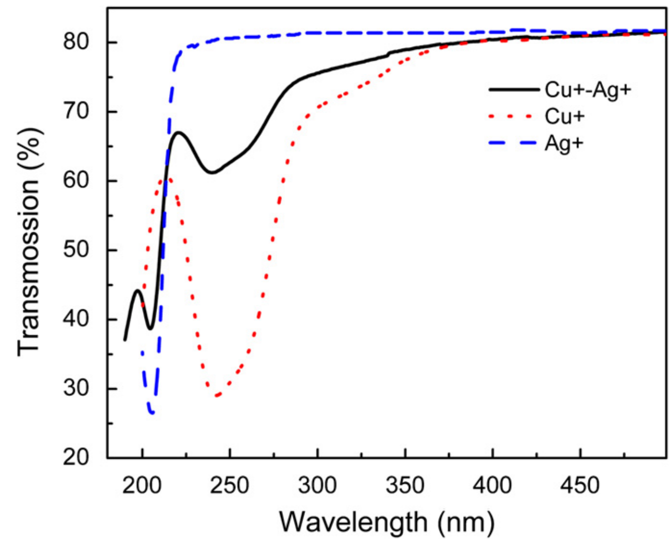

Fig. 1. Transmission spectra of $Li_2B_4O_7$:Cu,Ag co-doped (solid black), Cu doped (dotted red) and Ag doped (dashed blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

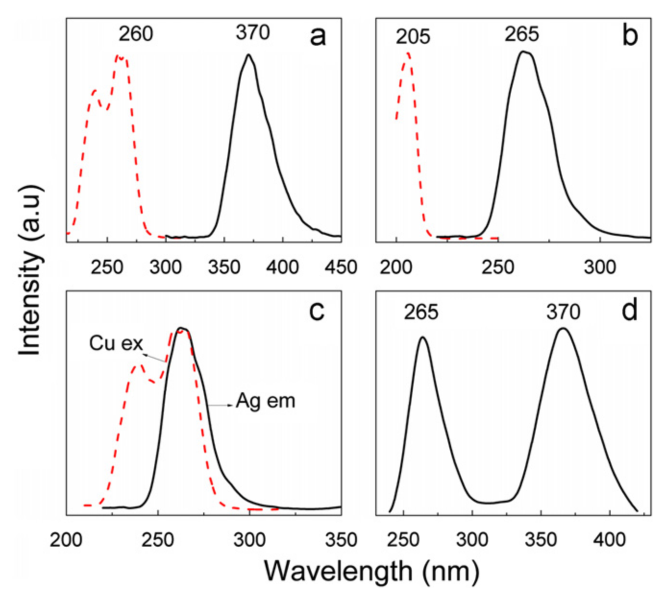

Fig. 2. Photoluminescence spectra of (a) $Li_2B_4O_7$:Cu, (b) $Li_2B_4O_7$:Ag (c) overlapping of Ag emission and Cu excitation and (d) emission of $Li_2B_4O_7$:Cu,Ag for excitation at 205 nm (excitation—dashed red, emission—solid black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

peaking at 240 nm. The absorption at 240 nm of LTB:Cu crystals is due to the $3d^{10} \rightarrow 3d^94s$ transition of Cu^+ centers [18]. For Ag doped crystals the absorption band is around 205 nm corresponding to the $4d^{10} \rightarrow 4d^95s$ transition of Ag^+ centers [19]. The transmission of co-doped LTB crystals has two main absorption bands around 205 and 240 nm, corresponding to Ag^+ and Cu^+ centers, respectively. This suggests that Cu^+ and Ag^+ ions in the co-doped LTB lattice occupy the same position as they do when doped individually in the LTB crystal.

The emission and excitation spectra for the LTB:Cu crystals as presented in Fig. 2(a) exhibit a strong emission band peaking at 370 nm as reported earlier by many research groups [4,10,16]. The excitation spectrum of Cu^+ consists of mainly two bands centered at 240 nm and 260 nm; accordingly its $3d^94s \rightarrow 3d^{10}$