Available online at www.sciencedirect.com
ScienceDirect
Journal of Luminescence 126 (2007) 817–821
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Comparison of luminescence spectra of natural spodumene under KrCl laser and e-beam excitation

E.I. Lipatov[a,*], V.M. Orlovskii[a], V.F. Tarasenko[a], V.I. Solomonov[b]

[a]High Current Electronics Institute SB RAS, 2/3, Akademichesky Avenue, Tomsk 634055, Russian Federation
[b]Institute of Electrophysics UB RAS, 106, Amundsen Street, Ekaterinburg, Russian Federation

Received in revised form 9 October 2006; accepted 1 December 2006
Available online 17 January 2007

Abstract

Spectral characteristics of pulsed photoluminescence (PL) and pulsed cathodoluminescence (PCL) of a natural spodumene were investigated. PL was excited by laser radiation at 222 nm with pulse duration of 10 ns at FWHM. PCL was excited by electron beams with pulse duration from 0.1 up to 4 ns and with current densities of 40–200 A/cm^2. There was a dominant broad band at 600 nm due to the manganese impurity in PCL spectra. But in PL spectra, the orange band had the intensity comparable with intensities of intrinsic defect bands. At sample cooling by liquid nitrogen, the intensity of orange band in the PCL spectrum increased by two times and the short-wave shoulder of the band reduced.

PACS: 78.90.+t; 41.75.Fr; 42.55.−f

Keywords: Luminescence; Pulsed cathodoluminescence; Electron beam; Laser; Spodumene

1. Introduction

It is a well-known fact that luminescent parameters of crystals depend on power and type of an external action due to certain features of excitation processes [1]. It is necessary to take into account this dependence to interpret luminescent spectra and kinetics properly. The most obvious features of an excitation process become apparent by comparison of luminescent parameters excited in one crystal but in different ways. Such comparative experiments occur to be important especially for pulsed cathodoluminescence (PCL)—a very attractive instrument for luminescent analysis of different materials [2].

During a few last years, a new type of subnanosecond avalanche electron beam (SAEB) accelerators based on gas diodes (nitrogen, helium, neon, argon, krypton and air up to atmospheric pressure) was developed [3–5]. Picosecond duration of SAEB (~100–200 ps) makes it attractive for PCL excitation due to low intensities of thermal and electric charge effects in the samples under study. Such SAEB application availability was shown in Ref. [6].

In this paper, we report about comparative experiments of natural spodumene luminescence. The choice of material was stimulated by the well-known luminescent properties of spodumene [2,7]. Besides, the PCL of natural spodumene differs significantly from its PL and X-ray luminescence due to Mn^{2+} impurity. Excitation of samples was performed by laser radiation and by e-beams of various durations (0.2–4 ns). Some peculiarities of luminescent spectra were observed.

2. Experimental

We have investigated the natural spodumene crystal ($LiAlSi_2O_6$) of lamellar modification, which was mined from Baikal's deposit (Russian Federation). The sample had a light gray color and irregular shape of $60 \times 20 \times 10\,mm^3$. It contained about 1 mass% of Mn^{2+} impurities. We did not analyze the contents of other impurities. We chose the natural spodumene due to it adequately studied properties of luminescence [2,7,14]. The natural spodumene

*Corresponding author. Tel.: +7 3822 492 392
E-mail address: lipatov@loi.hcei.tsc.ru (E.I. Lipatov).

0022-2313/$ - see front matter
doi:10.1016/j.jlumin.2006.12.007

contains two forms of sufficiently different luminescent centers: (1) extrinsic 3d-ions Mn^{2+} and (2) distorted tetrahedrons SiO_4^{4-}-intrinsic defects, which are characterized by strong dependence of luminescence efficiency on the type of excitation. Besides, spodumenes are very convenient for research of radiation defects produced by electrons, because it contains a light element—lithium. For lithium atoms, a probability of impact displacement is very high.

The excitation of sample luminescence was carried out in air in the normal conditions in a vacuum chamber under the residual pressure $\sim 10^{-2}$ Torr. In vacuum, the sample was at room temperature or cooled down through a copper heat sink by liquid nitrogen.

The PL was excited by UV laser radiation of a KrCl-laser (“FOTON” series [8]) at 222 nm. Laser pulse duration at FWHM was ~10 ns, energy per pulse—~20 mJ, pulse repetition rate—1 Hz, intensity on the sample without focusing—~500 kW/cm^2. In order to attenuate scattered laser radiation, the PL was measured through the BS12 and BS14 light filters. These light filters have transmission at 222 nm of 6.6 and ~0%, correspondingly (Fig. 1, the curves 3, 4). The PL was measured through an optical fiber normally located to sample face. The laser radiation was directed at the sample on the angle of 45°. The PL radiation was measured by a spectrometer.

The PCL measurements were carried out using a RADAN-220 accelerator [9], a PCL KLAVI-1 spectrograph equipped with an accelerator RADAN-EXPERT [10] and a lab-made accelerator based on a modified X-ray device NORA [11] equipped with an e-beam gas diode [12,13]. The accelerators RADAN-220 and RADAN-EXPERT were equipped with sealed-off vacuum tubes IMA3-150E. The main characteristics of accelerators are shown in Table 1, where E_m is maximum in electron energy distribution, t is e-beam pulse duration at FWHM, j is e-beam current density on the sample, and E is energy density on the sample.

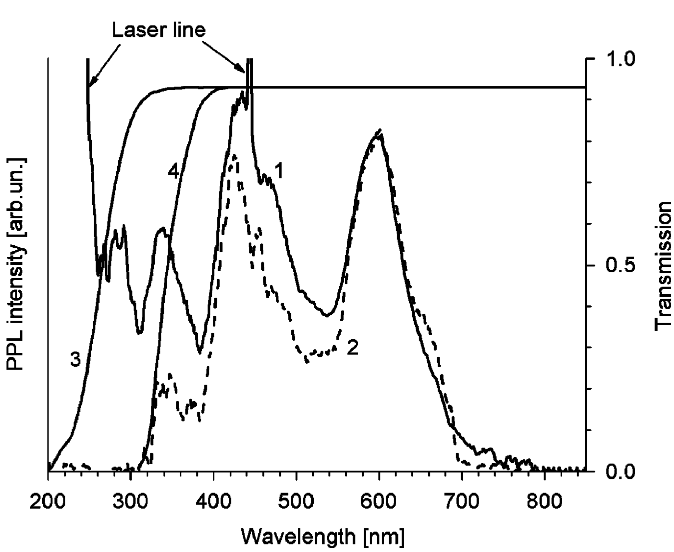

Fig. 1. The PL spectra of natural spodumene at room temperature under KrCl-laser irradiation (222 nm) through the light filters BS12 (1) and BS14 (2). Transmission spectra of the light filters BS12 (3) and BS14 (4).

Table 1

Accelerator	E_m (keV)	t (ns)	j (A/cm^2)	E (mJ/cm^2)
NORA (gas diode)	80 [6]	0.2	40 [13]	1.5
RADAN-EXPERT (KLAVI-1)	100	1.5	100	20
RADAN-220	180	2	200	60
NORA (vacuum in a gas diode)	200	4	200	120

The gas diode of NORA device was filled in with air. In order to reduce an electromagnetic noise and to shield the discharge optical radiation (discharge forms a SAEB), the gas diode was screened with 40 μm AlBe-foil. In condition of forevacuum pumping, the same gas diode formed a 4 ns e-beam with the higher parameters (“vacuum in a gas diode” in Table 1).

Moreover, for comparison we tried to measure a pulsed X-ray luminescence of the sample. In this case, an electronic tube IMA3-150E of accelerator RADAN-220 was replaced by an X-ray tube IMA5-320D.

In case of the accelerators NORA and RADAN-220, the sample was placed into a vacuum chamber on a copper heat sink (“cold finger”). The distance between the sample and output windows of accelerators was ~15 mm. PCL spectra were measured by EPP-2000C (Stellar-Net Inc.) in the spectral range of 200–850 nm. The spectrometer equipped with a CCD array has the spectral resolution of 0.4 nm. The PL and PCL radiation was transferred to the spectrometer through an optical fiber. Depending on intensity, the meter spectra were accumulated during about 100 shots. Saved spectra were corrected taking into account the spectral response of the spectrometer and optical fiber and light filters transmission.

The PCL spectrograph KLAVI-1 has its own chamber for samples, allowing measurements of emission spectra in the spectral range of 350–750 nm. Such spectra were accumulated during 16 shots. In all cases, the meter spectra were reproduced stably.

3. Results

Visually, the PL of natural spodumene had a close to white color with violet and red tints. The PL spectrum of spodumene measured without light filters demonstrated a dominant laser line and its second-order diffraction replica. We used the light filters in order to reduce a strong distortion of PL spectrum due to laser line.

The PL spectrum of spodumene contains several wide bands at 300–700 nm (Fig. 1). There were wide bands with maxima at 596 nm (FWHM 80 nm), 425 nm (90–100 nm), and 335–345 nm (70–80 nm). In case of the light filter BS12, the laser line and its secondary diffraction still appeared