

# Luminescence of crystals excited by a KrCl laser and a subnanosecond electron beam

E.I. Lipatov, V.F. Tarasenko, V.M. Orlovskii, S.B. Alekseev

**Abstract.** Luminescence of crystals of natural spodumene and natural diamond of the type IIa is studied upon excitation by a laser at a wavelength of 222 nm and by a subnanosecond avalanche electron beam (SAEB) formed in air at the atmospheric pressure. The photoluminescence spectra of spodumene and diamond are shown to exhibit additional bands, which are absent upon SAEB excitation. It is demonstrated that SAEB excitation allows one to analyse various crystals under normal conditions without using any vacuum equipment.

**Keywords:** luminescence, spodumene, diamond, laser radiation, electron beam.

## 1. Introduction

Luminescence is widely used for spectral analysis of solids to study their chemical composition, the presence of defects and impurities, internal stresses, etc. [1]. There exist different methods for excitation of luminescence in solids such as excitation by electromagnetic radiation (from the visible to gamma region) and by particle beams (electrons, ions, nucleons, etc.), as well as thermal and mechanical excitation [2].

Photoluminescence excited by the UV and visible radiation sources and cathodoluminescence excited by an electron beam are most often used for spectral luminescence analysis. The study of photoluminescence allows one to obtain the most accurate spectral data, but the temperature quenching of luminescence often requires cooling of samples to low temperatures. Classical cathodoluminescence, i.e., cathodoluminescence excited by a cw electron beam requires the study of samples in vacuum and, in some cases, the discharge of the induced charge should be provided [3]. Intense pulsed excitation makes it possible to study luminescence at room temperature and normal pressure, providing rapid analysis of samples, for example, for their identification [3].

Modern pulsed lasers generate radiation covering the

entire UV and visible ranges [4]. It is preferable to excite luminescence by short-wavelength UV radiation, especially in the case of wide-gap materials, because this allows the observation of their intrinsic luminescence [5, 6].

The development of high-current electronics provided the generation of very intense electron beams [7]. Recently, a new method was realised for generating subnanosecond avalanche electron beams (SAEBs) by using gas diodes [8–11]. Gas diodes can be filled with different atomic and molecular gases and their mixtures (air, nitrogen, helium, neon, argon, krypton) up to pressures  $\sim 1$  atm and higher. The use of SAEBs to excite luminescence in non-metal solids permits the study of pulsed cathodoluminescence (PCL) of samples in natural gases without any vacuum equipment [12].

The aim of this paper is to study luminescence of natural spodumene and diamond excited by a pulsed 222-nm laser and a subnanosecond electron beam. Our experiments showed that the luminescence spectra of spodumene and diamond observed upon UV laser and SAEB excitation were substantially different. The photoluminescence spectra exhibited bands which were absent in the PCL spectra.

## 2. Experimental

Photoluminescence of samples was excited by 222-nm, 10-ns, 20-mJ pulses from a universal Foton-2 laser with a pulse repetition rate of 1 Hz [13]. The laser beam was not focused. The peak intensity of the laser pulse was  $\sim 500$  kW cm<sup>-2</sup>.

PCL was excited with a NORA modified compact X-ray source [7] in which the X-ray tube was replaced by a gas diode, whose construction is described in [10]. In experiments, the gas diode communicated with the atmosphere and was filled with air at normal pressure. Due to such a modification, this source generated SAEBs with the 0.2-ns FWHM of current pulses (Fig. 1). The pulse repetition rate was  $\sim 3$  Hz and the beam current density behind the foil on the area of diameter 15 mm was  $\sim 40$  A cm<sup>-2</sup>. The maximum of the energy distribution of electrons was located at 80 keV [12]. To reduce electromagnetic noise appearing during the electron-beam formation, the gas diode was covered with a 40- $\mu$ m thick AlBe foil.

Luminescence was excited in natural spodumene ( $\alpha$ -LiAlSi<sub>2</sub>O<sub>6</sub> doped with Mn<sup>2+</sup>) and natural diamond of the type IIa (the nitrogen concentration was lower than 10<sup>18</sup> cm<sup>-3</sup>). The 60  $\times$  20  $\times$  10-mm spodumene sample was light grey and had an irregular shape. One of its sides was polished. Natural diamond had the form of a disc of

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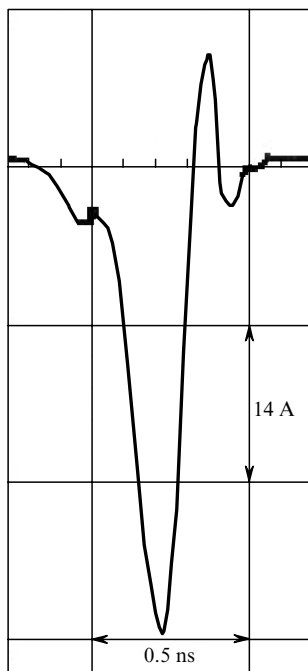
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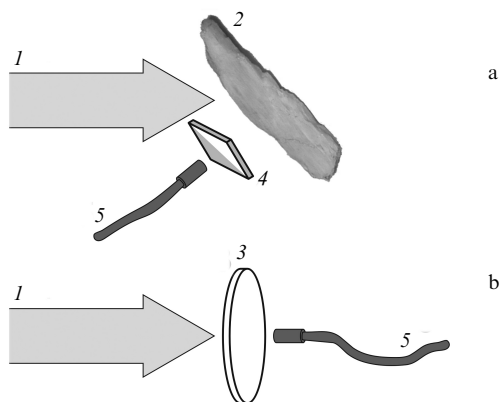
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**Figure 1.** Oscillogram of the SAEB current pulse recorded from a collector of area  $1 \text{ cm}^2$  in air at a pressure of 1 atm.

diameter 5 mm and thickness 0.25 mm with polished opposite faces.

Measurements were performed under normal conditions in the atmospheric air. Luminescence emission was coupled through a fibre into an EPP-2000C Stellar-Net Inc. diffraction spectrometer equipped with a CCD array (Fig. 2). This spectrometer allows one to record digitised emission spectra in the range from 200 to 850 nm with a spectral resolution of 1.5 nm. The luminescence spectra were recorded after 100 accumulations of pulses. The dark component was subtracted from the spectrum and the spectral sensitivity and the fibre and optical filter transmissions were taken into account. The spectra were well reproducible.



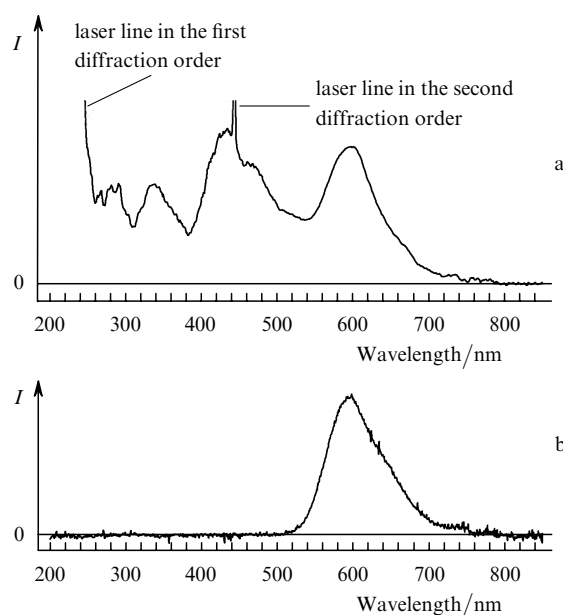
**Figure 2.** Schemes of experiments on the luminescence study of spodumene (a) and diamond (b): (1) excitation (laser radiation or an electron beam); (2) spodumene; (3) diamond; (4) optical filter (in the case of laser excitation); (5) fibre for luminescence coupling to a spectrometer.

To reduce the stray laser light upon laser excitation of spodumene, luminescence was detected at an angle of  $45^\circ$  to the incident laser beam through a BS12 optical filter, as shown in Fig. 2a. The transmission of this filter at 222 nm is 6.6%. The fibre was mounted perpendicular to the sample surface. The luminescence of diamond was excited from one plane face of a sample, while a fibre was mounted from the opposite face (Fig. 2b). Laser radiation was almost completely absorbed in a  $\sim 150\text{-}\mu\text{m}$  thick layer because the absorption coefficient of diamond at 222 nm is  $\sim 340 \text{ cm}^{-1}$  [14].

### 3. Experimental results and discussion

#### 3.1 Luminescence of spodumene

The photoluminescence spectrum of spodumene consists of several broad bands covering the entire wavelength range recorded (Fig. 3a). The spectrum also shows the laser line recorded in the first and second diffraction orders. Visually, the photoluminescence of spodumene had nearly white colour with violet and red tints, whereas the PCL of spodumene was orange. The PCL spectrum of spodumene (Fig. 3b) exhibited only one broad band in the 520–760-nm range with a maximum at 600–608 nm and the FWHM equal to  $\sim 80$  nm. This band corresponds to the  ${}^4T_1 \rightarrow {}^6A_1$  transition in impurity  $\text{Mn}^{2+}$  ions [3]. The luminescence band of manganese is also present in the photoluminescence spectrum of spodumene (Fig. 3a). However, unlike the PCL spectrum, the photoluminescence spectrum also contains broad bands at 336 and 434 nm. The luminescence spectrum of spodumene excited by an argon laser [15] exhibited only the orange band. We can assume that these broad luminescence bands are related to the  $\text{Mn}^{2+}$  ions excited by short-wavelength radiation used in our experiments or can be caused by some intrinsic defects of the spodumene crystal.

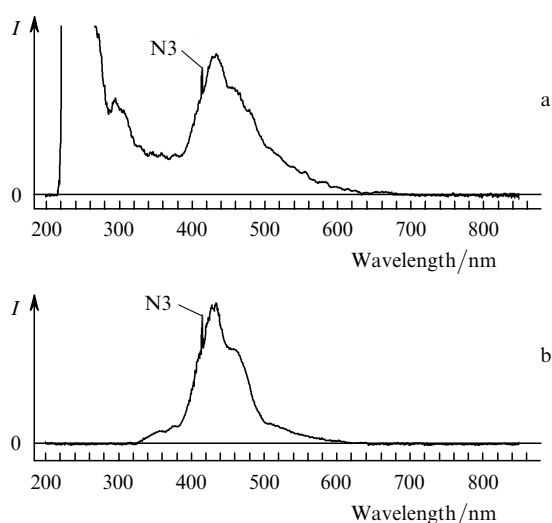


**Figure 3.** Laser-induced luminescence (a) and pulsed cathodoluminescence (b) spectra of natural spodumene.

### 3.2 Luminescence of diamond

The luminescence spectra of diamond of the type IIa observed upon laser and SAEB excitation differ from each other, as in the case of spodumene. In both cases, luminescence had violet colour.

Figure 4 shows that the spectra exhibit a broad band at 434 nm with the FWHM equal to 80–90 nm. In this region, the vibronic structure of the N3 defect with the zero-phonon line at 415.2 nm is observed. According to the generally accepted model, the N3 defect consists of three nitrogen substituents located in the (111) plane of the diamond lattice, which are related to the vacancy [16]. In addition, the A band (300–700 nm), which probably belongs to dislocations, is observed in this region [17]. The A band was observed in the luminescence spectra of natural diamonds [17–21] and synthetic diamonds without nitrogen [22, 23].

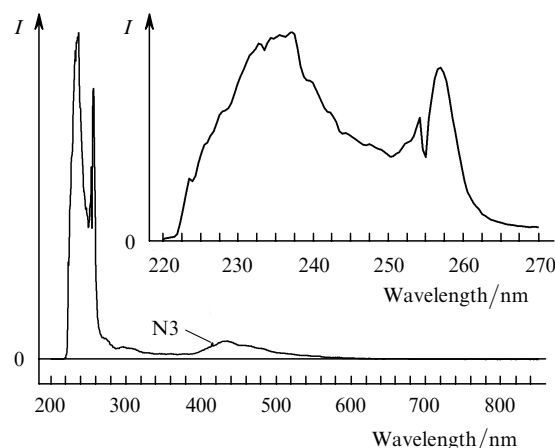


**Figure 4.** Laser-induced luminescence (a) and pulsed cathodoluminescence (b) spectra of natural diamond of the type IIa. N3 is the zero-phonon line of the N3 defect.

The luminescence spectrum of diamond excited in the UV region [24] exhibits two intense bands (Fig. 5), which are absent upon electron-beam excitation. It seems that these bands are weak in the PCL spectrum upon SAEB excitation and are indistinguishable against the dark background. The band located in the 225–250-nm region is more intense, while a slightly weaker band located in the 250–270-nm region has a hole at 255 nm.

It is known from the literature [5, 6, 25] that the luminescence of diamond near the fundamental absorption edge is caused by exciton recombination. Free excitons recombining in diamond generate phonons. The most intense is the 235-nm recombination line of free excitons involving transverse optical phonons.

In addition, the recombination of excitons localised on defects can be observed in the UV region. These defects can be substituent boron [26] (according to [21], all natural diamonds contain this element), dislocations [25, 27], and nitrogen complexes [27]. The recombination of excitons localised on boron gives rise to a few lines in the region from 230 to 245 nm, the 237.5-nm line being dominant. In [25, 27], a few new lines were observed in the 250–260-nm region, which were assigned to exciton luminescence involv-



**Figure 5.** Laser-induced luminescence spectrum of natural diamond of the type IIa. The inset shows the UV luminescence bands on an enlarged scale.

ing dislocations. The known N9 centre observed in natural diamonds in the 230–265-nm region [28] was assigned to the recombination of excitons localised on nitrogen complexes. The zero-phonon line related to this centre is located at 236.5 nm.

The exciton recombination lines described above have the FWHM of a few nanometres. However, the FWHM of the 235–237-nm band observed in our experiments was  $\sim 20$  nm. It is possible that the luminescence band will narrow down upon cooling of a sample to liquid nitrogen temperature. To reliably identify the UV luminescence bands, additional experiments are required.

### 4. Conclusions

We have studied the integrated pulsed photo- and cathodoluminescence spectra of crystals of spodumene and diamond of the type IIa.

It is shown that subnanosecond electron beams can excite the intense luminescence of non-metal solids. Unlike excitation of luminescence by high-current nanosecond electron beams, SAEB excitation allows investigations in different gases without using vacuum diodes, in particular, in air at the atmospheric pressure. This circumstance and a comparatively simple construction of accelerators can provide the application of SAEBs for a rapid luminescent analysis of samples in natural gases, for example, in the diamond mining industry or for investigations of minerals on other planets.

However, the PCL spectra of spodumene and diamond of the type IIa exhibit only bands typical for these minerals: the 600-nm orange band with the FWHM  $\sim 80$  nm and the 434-nm blue band with the FWHM 80–90 nm.

At the same time, the luminescence spectra of the spodumene and diamond crystals observed upon UV laser excitation at 222 nm exhibit additional more intense short-wavelengths bands.

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