LUMINESCENCE SPECTRA AND KINETICS OF NATURAL DIAMOND TYPE IIa UNDER OPTICAL INTERBAND EXCITATION

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Research motivation: Photoluminescence or X-ray luminescence?

Studies of the luminescence of diamonds of our team have long been largely motivated by applications in the field of **technologies for luminescent separation of diamond-bearing ores**. Diamond crystals contain numerous luminescence centers of various natures, which can be excited by optical radiation in the region of intracenter transitions, when photoluminescence occurs. It would seem that it would be more convenient and cheaper to use photoluminescence rather than X-ray luminescence in luminescent separators of diamond ores. However, studies have shown that the luminescence of various diamond samples arising upon photoexcitation is characterized by a very wide variety of properties. The photoluminescence characteristics of diamonds are not repeated from sample to sample. Therefore, based on photoluminescence, it is difficult to automatically reliably separate diamonds from accompanying luminescent minerals in order to ensure sufficient selectivity of diamond extraction from the rock. Already the first comparative studies of the properties of X-ray luminescence and photoluminescence, carried out in the last century, showed that the properties of X-ray luminescence of different samples of natural diamonds are much less diverse. The emission spectra of most natural diamonds contain mainly one, the so-called A-band of X-ray luminescence, which is visually perceived as a blue glow. Thus, the significantly higher uniformity of the X-ray luminescence characteristics of various diamond samples determined the possibility of using precisely X-ray luminescence, rather than photoluminescence, in technologies for the separation of diamond-bearing ores.

X-ray luminescence separation

is the main production process in beneficiation technology

X-ray luminescence separation is well developed and widely used at diamond recovery factories in Russia and foreign countries. Modern X-ray luminescent separators, along with a stationary mode of excitation and registration of luminescence, also provide a mode of non-stationary pulsed excitation of diamond-bearing rock in combination with time analysis and time selection of response luminescent signals from diamonds and related minerals. Under certain conditions, this can significantly increase the selectivity of diamond extraction.

X-ray luminescence methods extract about 95% of diamonds of class 1 - 6 mm and 100% of diamonds of class +6 mm.

V.V. Novikov. The history of the creation of luminescent separation (Honored Inventor of the USSR)

Novikov Vladlen Vasilievich,
Semyanov Alexander Ivanovich

Для повышения селективности сепараторов институт избрал путь исследования кинетических характеристик алмазов и сопутствующих минералов. Этот путь был впервые предложен в одном из совместных с Григорием Осиповичем Гомоном изобретений в 1962 г. Практическое использование этих свойств производилось начиная с 1962 г. в сепараторах с постоянным излучением рентгеновских трубок, но научное объяснение началось с 1970 г. после подключения к исследованиям научно-исследовательского института прикладной физики (НИИ ПФ) Иркутского госуниверситета. По моей просьбе создатель этого института И.А. Парфианович подключил к нашим работам молодых специалистов Е.Ф. Мартыновича (в настоящее время он профессор, директор НИИ ПФ), Ю.С. Мухачева, Л.В. Моражникову и студентов-выпускников, в том числе С.В. Терещенко (в настоящее время он про-

В этом сепараторе мы впервые использовали импульсный режим работы рентгеновских трубок, двухстороннее облучение и контроль потока материала, увеличили скорость перемещения потока материала в контрольной зоне, а также селективность сепарации за счет нового способа возбуждения и обнаружения люминесценции алмазов. Все это позволило повысить почти в три раза производительность сепараторов без увеличения количества использованных в них рентгеновских трубок и фотоприемников. В разработке способа сепарации принимали участие В.С. Вьюнник и Е.Ф. Мартынович, в разработке и изготовлении сепаратора — А.Н. Чирков, Ю.В. Ляхов, в технологических испытаниях — Ф.А. Пацианский, Г.А. Трусевич, И.Б. Сидорова, Ю.А. Лаврентьев.

Испытания экспериментального образца сепаратора показали правильность выбранных

Diamond Book of Russia. T. 2. Moscow, Gornaya Kniga Publishing House, 2015

By order of the Institute "Yakutniproalmaz" to substantiate the modern X-ray luminescent pulsed enrichment technology, the following research works were carried out at the Research Institute of Applied Physics at Irkutsk State University:

1. "Study of the physical properties of diamonds and minerals from deposits in Yakutia." NIIPF at Irkutsk State University. Irkutsk, 1971, theme 2.40 p. (report).
2. "Investigation of the physical properties of diamonds and related minerals of the deposits of Yakutia." NIIPF at Irkutsk State University. Irkutsk, 1972, topic 77-11. 48 p. (report).
3. "Investigation of the physical properties of diamonds and related minerals of the deposits of Yakutia." - Irkutsk: NIIPF at ISU, 1974.85 p. (report).
4. "Investigation of the physical properties of low-luminescent diamonds from deposits in Yakutia." Irkutsk: NIIPF at ISU, 1974.78 p. (report).
5. "Investigation of the physical properties of diamonds and related minerals from deposits in Yakutia." Irkutsk: NIIPF at ISU, 1975. (report).
6. Study of the nature of the kinetics of X-ray luminescence of diamonds and its relationship with the known physical properties. NIIPF at Irkutsk State University. Irkutsk, 1976 .-- 69 p. (report).

Inventions made:

1. Patent No. 387540, H 05g 1/24. **X-ray pulse generator**. E.F. Martynovich, B.B. Pologrudov. No. 1345723 / 25-26 app. 07.07.69.
2. Patent No. 519889, B 03 B 13/06. Method for separating minerals and device for its implementation. V.S.Vyunnik, V.V. Novikov, E.F. Martynovich. No. 2085566/01 App. 08.12.74.
3. Patent No. 544195, B 03 B 13/6. Luminescent separator. V.V. Novikov, V.S. Vyunnik, E.F. Martynovich. No. 2132619/03 App. 05/13/75.
4. Patent No. 127556. EF Martynovich, VS Tatarinov, YS Mukhachev, LV Morozhnikova, SA Filyuk, VV Novikov, AM Volkov, V. F. Potapov. No. 2211636, app. 11/22/76.

Articles published:

1. Martynovich EF, Morozhnikova L.B., Parfianovich I.A. Spectral and kinetic characteristics of X-ray luminescence centers in diamond. Solid state physics. 1973, T. 15, No. 3. S. 927-929.
2. Martynovich EF, Morozhnikova L.B., Novikov V.V. X-ray luminescence of diamonds. In the book: "Luminescence and Spectral Analysis", Irkutsk State University, Irkutsk, 1974, p. 146-155.
3. Martynovich EF, Klyuev Yu.A., Plotnikova S.P. X-ray luminescence of different types of natural diamonds. In the book: Questions of theory and practice of diamond processing. M. NIIMASH, 1977, p. 28-38.

Diamond extraction technology is a complex, multi-stage process,

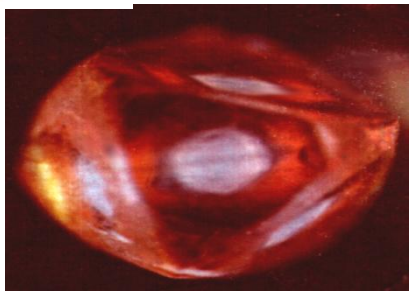
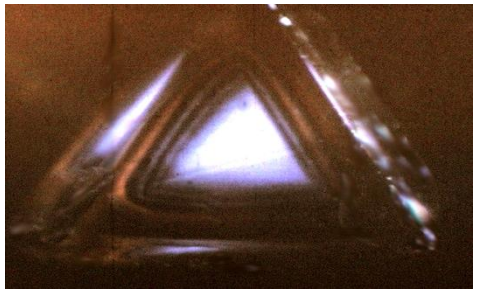
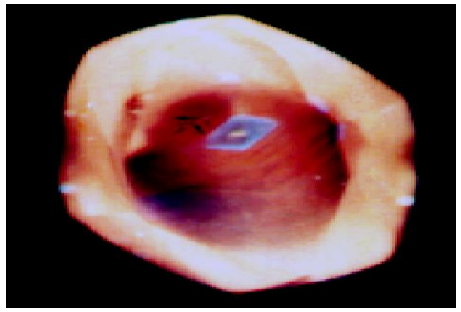
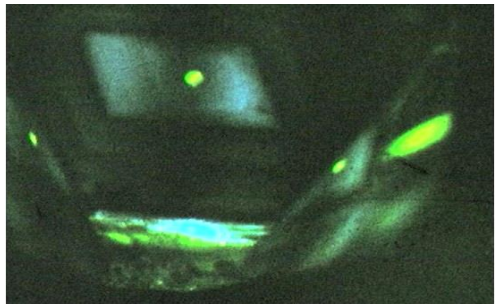
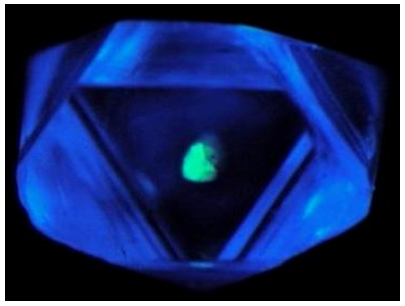
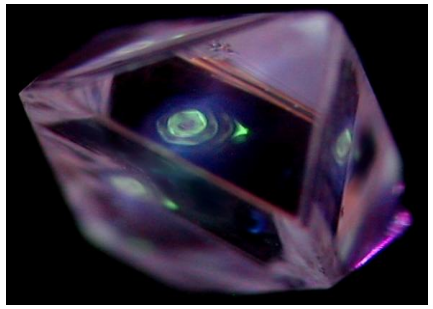
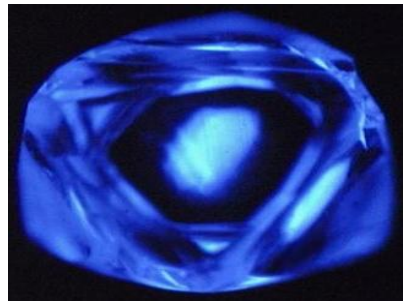
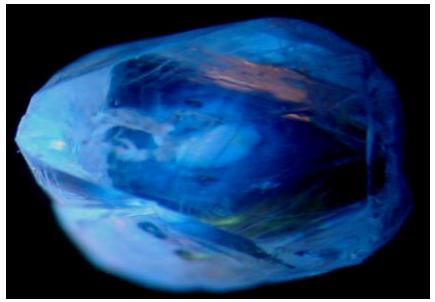
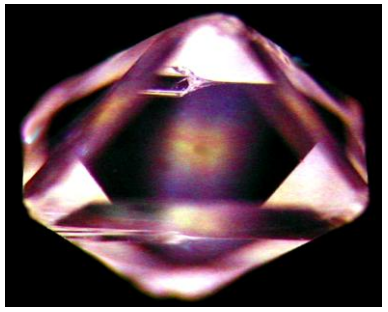
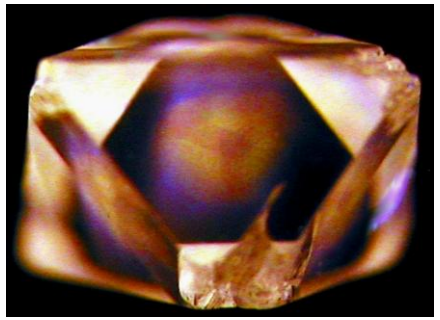
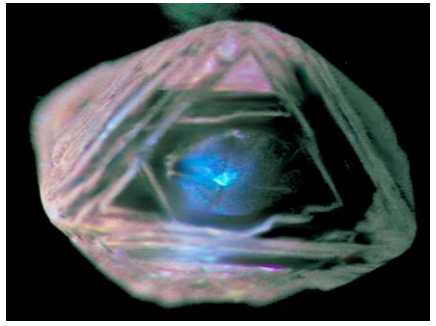
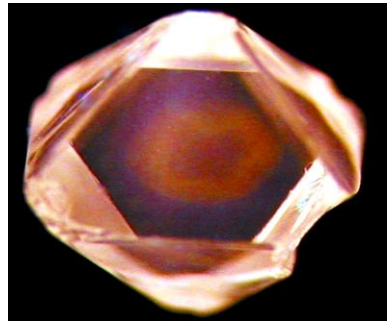
conditionally subdivided into enrichment (separators of LS-type) and stages of concentrate refinement: preliminary (separators of LS-D type) and final (separators of LS-OD type). Depending on the purpose, the design of the separators is significantly different.

The characteristics of some separators are given in the article: Avdeev et al: Rentenoluminescent separators of NPP "Burevestnik" - the hardware basis of the Russian technology for enrichment of diamond-containing raw materials. // Mining journal. - 2005. - №7. – С.105 – 107.

Separator LS-20-04-3N for enrichment of wet ore or fine-tuning of concentrate with grain size -20 + 10 and -10 + 5 mm. Productivity is up to 20 t / h when working with class -20 + 10 mm and up to 10 t / h when working with class -10 + 5 mm. Two X-ray tubes are used in pulsed mode. The number of registration channels is 4, the number of pneumatic cutters is 4, the passport extraction of diamonds is 98%.

Separator LS-OD-4-04N for finishing concentrate with size -5 +2, -2 +1 and -1 +0.5 mm. Productivity, t / h, up to: 0.1 (-5 + 2 mm); 0.025 (-2 + 1 mm); 0.004 (-1 + 0.5 mm). One X-ray tube is used in continuous radiation mode, material is fed through 8 channels, each of which has its own registration and cut-off system. Extraction,% by class, not less: 98 (-5 + 2 mm); 96 (-2 + 1 mm); 90 (-1 + 0.5mm).

Luminescence is a working phenomenon, the main production process in the technology for the separation of diamond ores

Научная задача, которую мы решали
Scientific problem that we solved

Решаемая задача, состояла в том, чтобы найти ответ на вопрос:

«Можно ли в кристаллах алмаза любых типов реализовать оптическое возбуждение в алмазах тех же самых центров люминесценции, которые возбуждаются в них под действием рентгеновского излучения?»

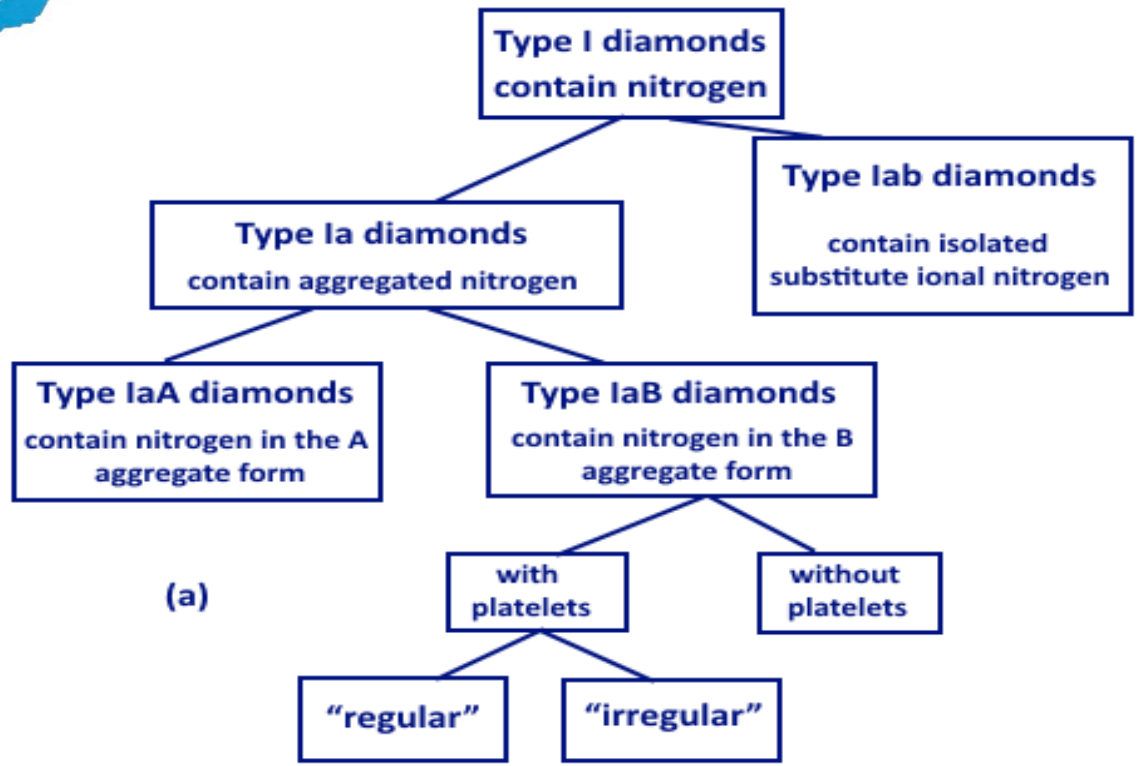
Решение этой задачи позволит в некоторых классах люминесцентных сепараторов заменить рентгеновское возбуждающее излучение на оптическое.

The problem to be solved was to find the answer to the question:

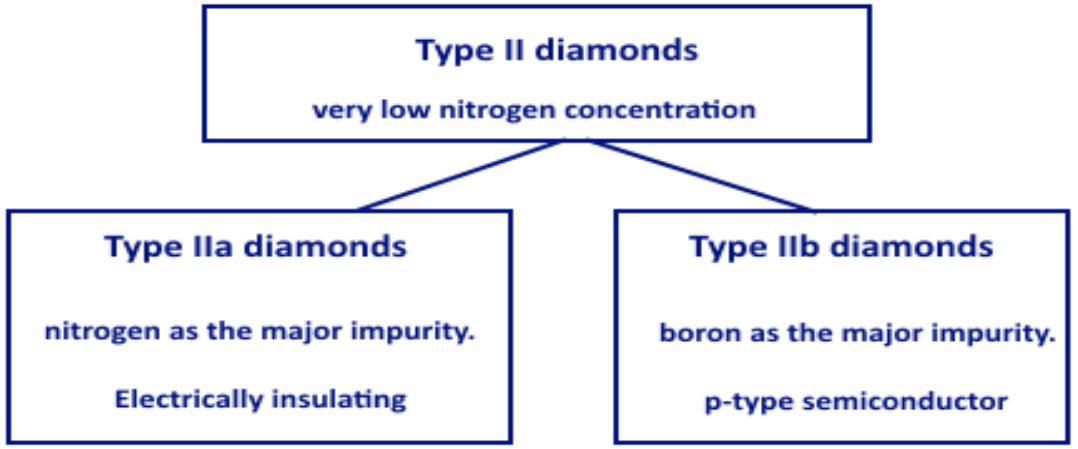
"Is it possible in diamond crystals of any type to realize optical excitation in diamonds of the same luminescence centers that are excited in them under the action of X-rays?"

The solution of this problem will make it possible, in some classes of luminescent separators, to replace exciting X-ray radiation with optical radiation.

Diamond type classification table



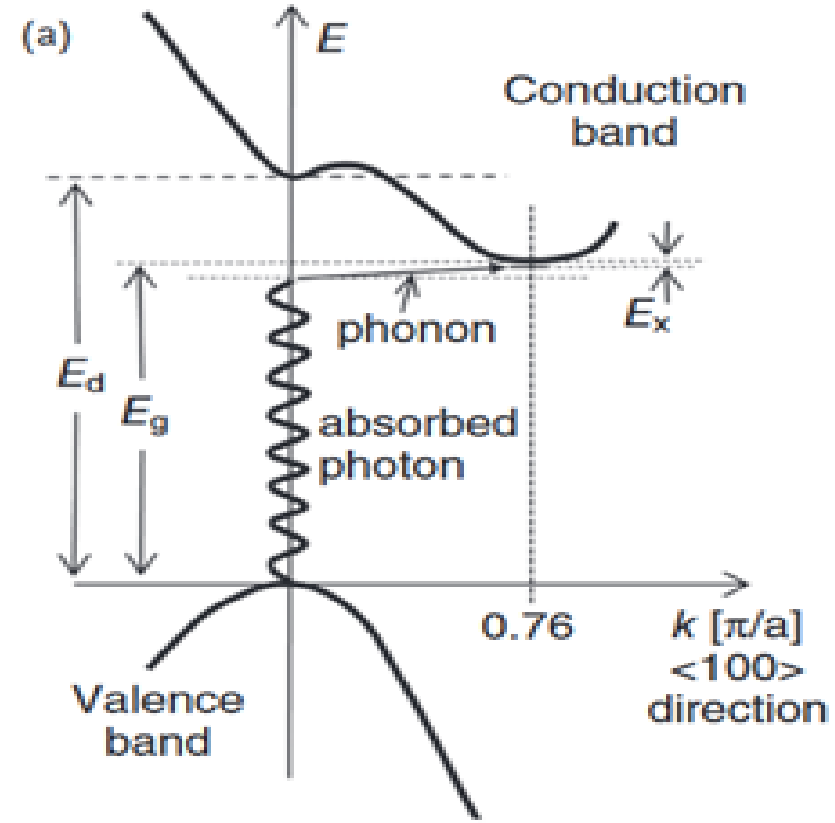
(a)

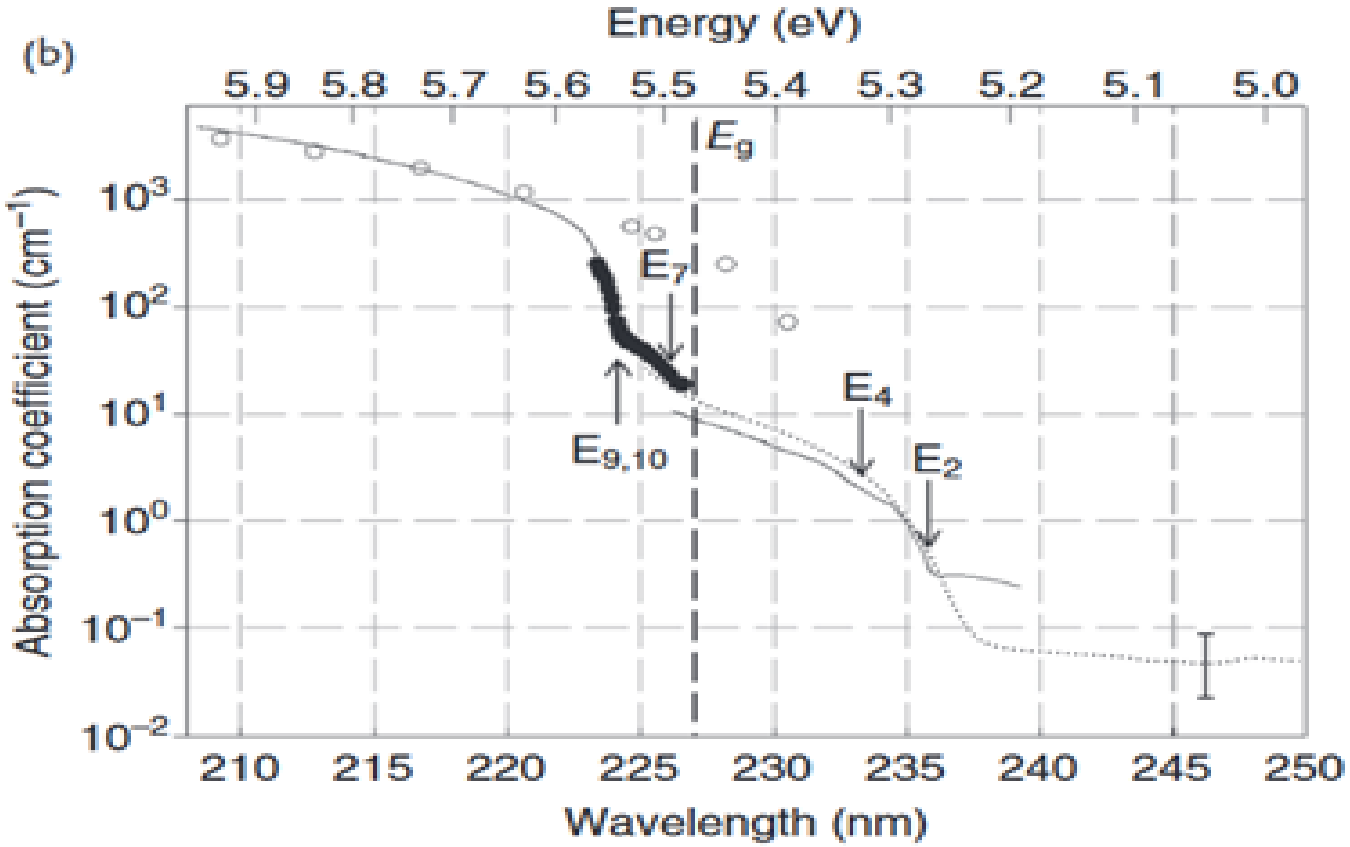


(b)

A. Collins. Physica B 185 (1993) 284-296

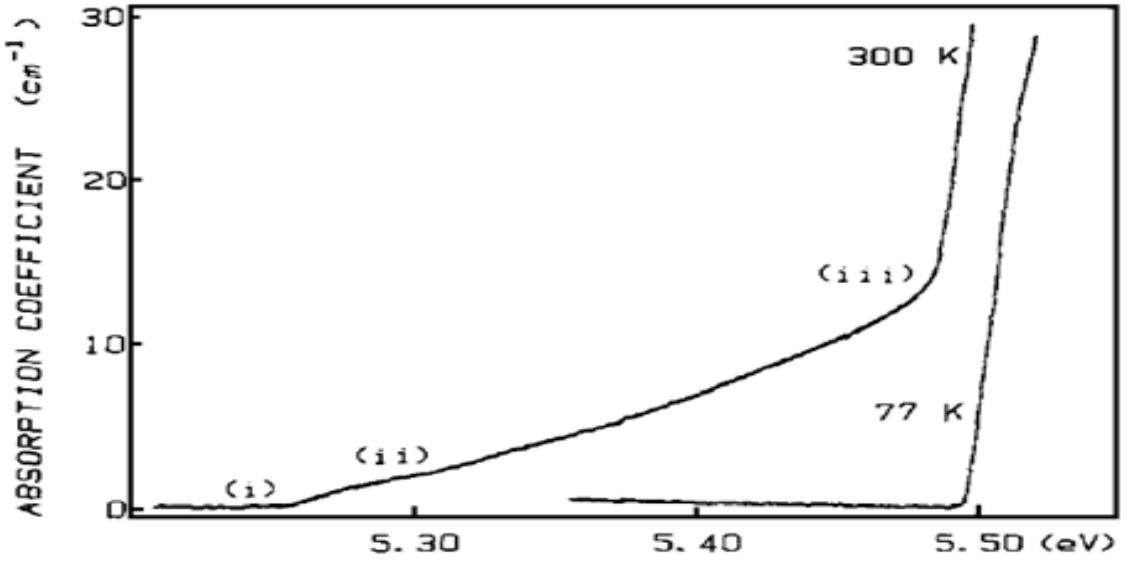
Interband optical transitions in diamond

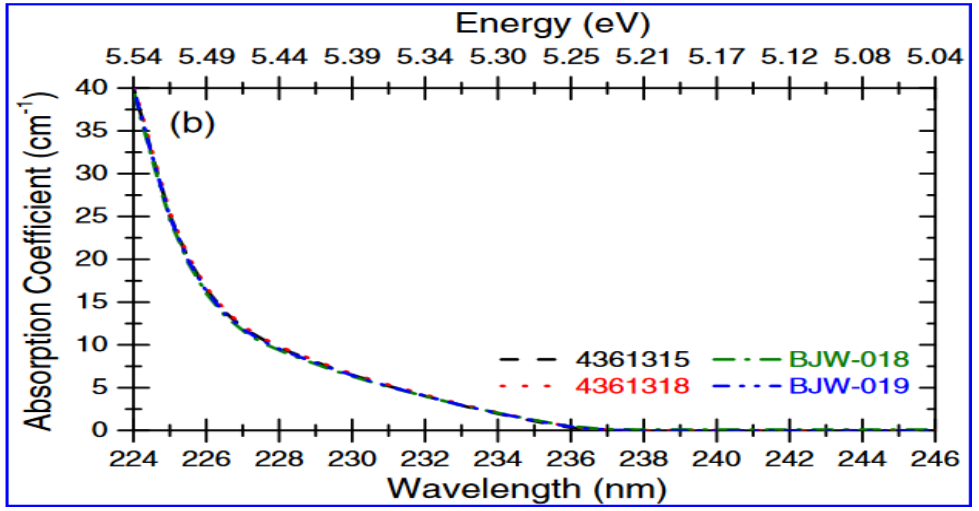




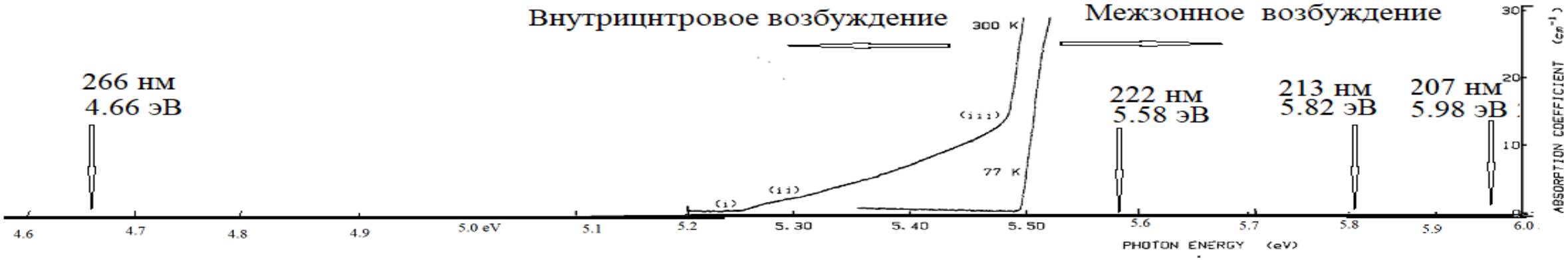
Richard P. Mildren. Intrinsic Optical Properties of Diamond. 2013

Spectrum of intrinsic absorption of light by diamond and wavelengths of optical radiation corresponding to interband transitions

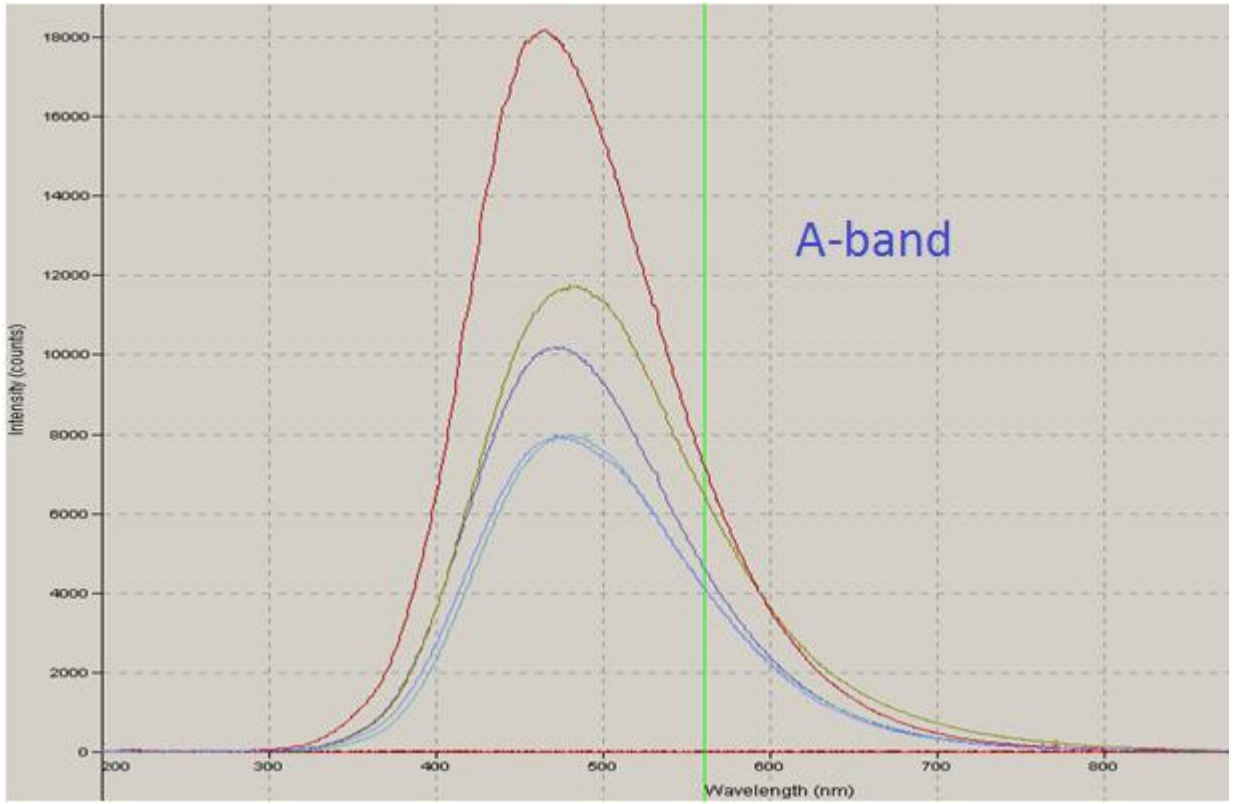




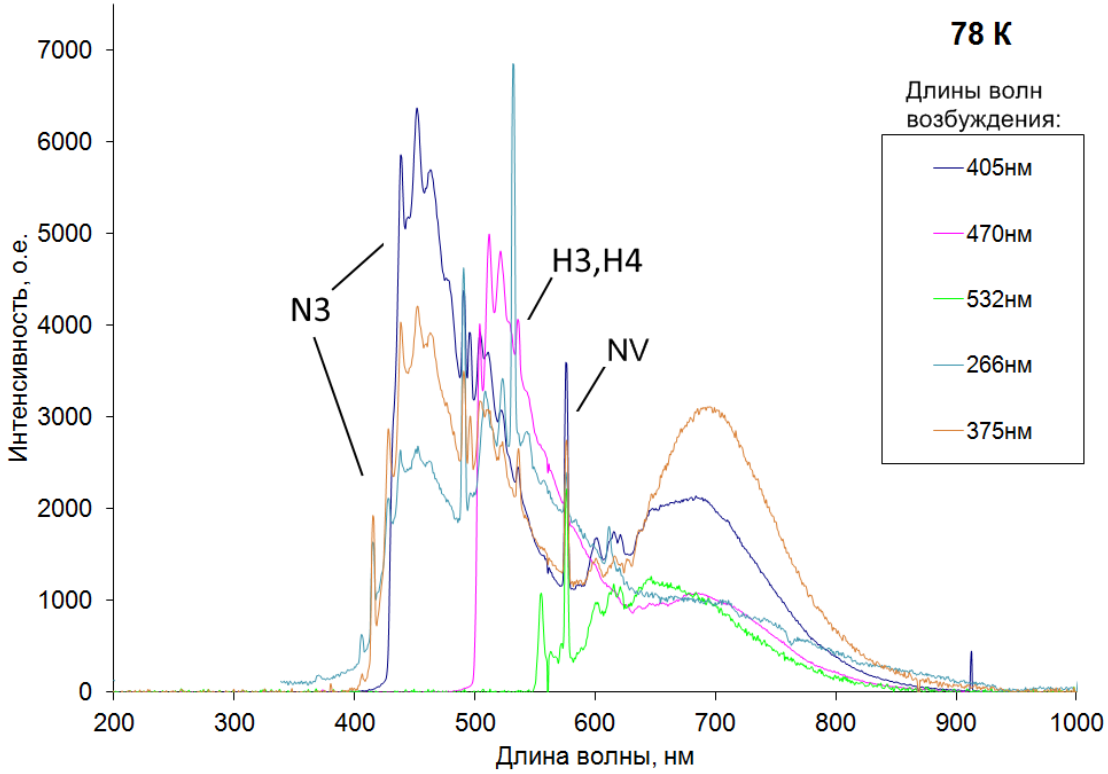
Webster et al., Vol. 32, No. 3, 2015, J. Opt. Soc. Am. B 479]



Photoluminescence spectra with interband optical excitation and with intracenter excitation

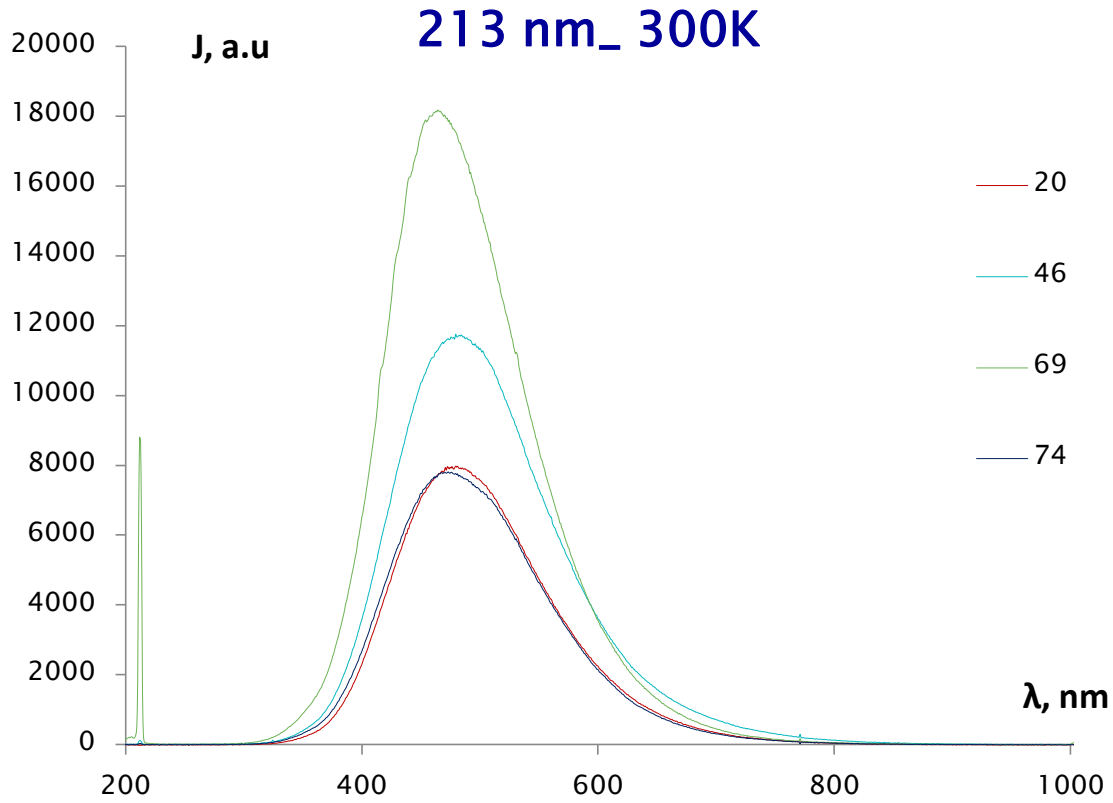


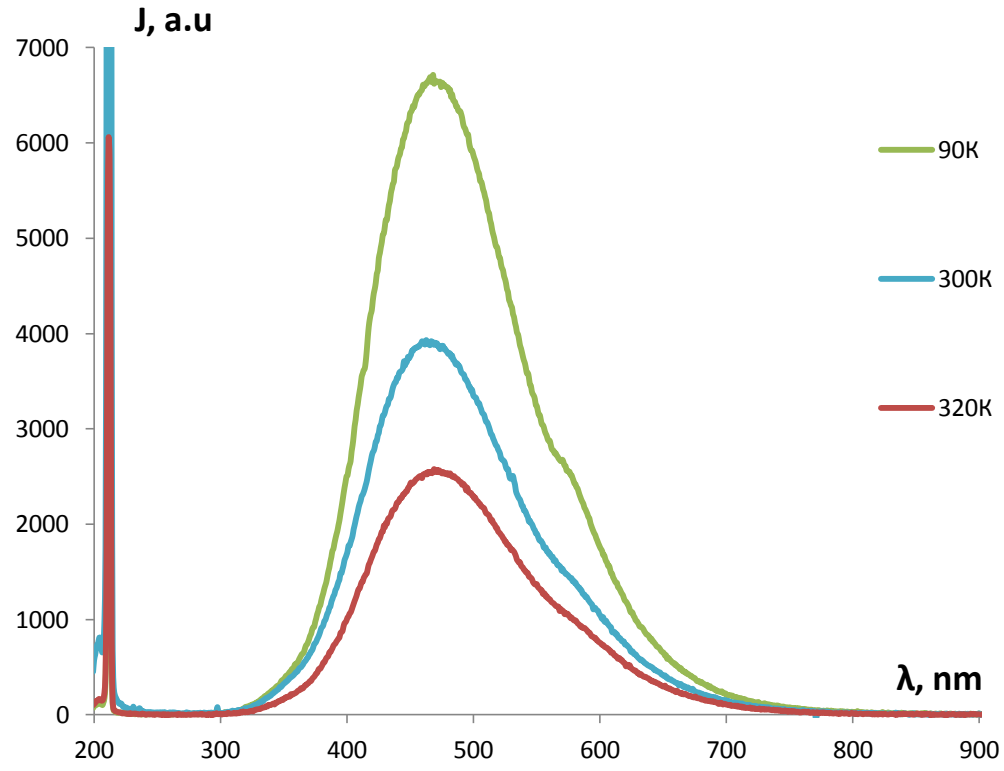
Luminescence spectra of diamond samples from deposits in Yakutia and Brazil with excitation at 213 nm. The spectra are the same as under X-ray



The photoluminescence spectra under intracenter excitation do not contain the A band

Luminescence spectra under interband excitation at different temperatures

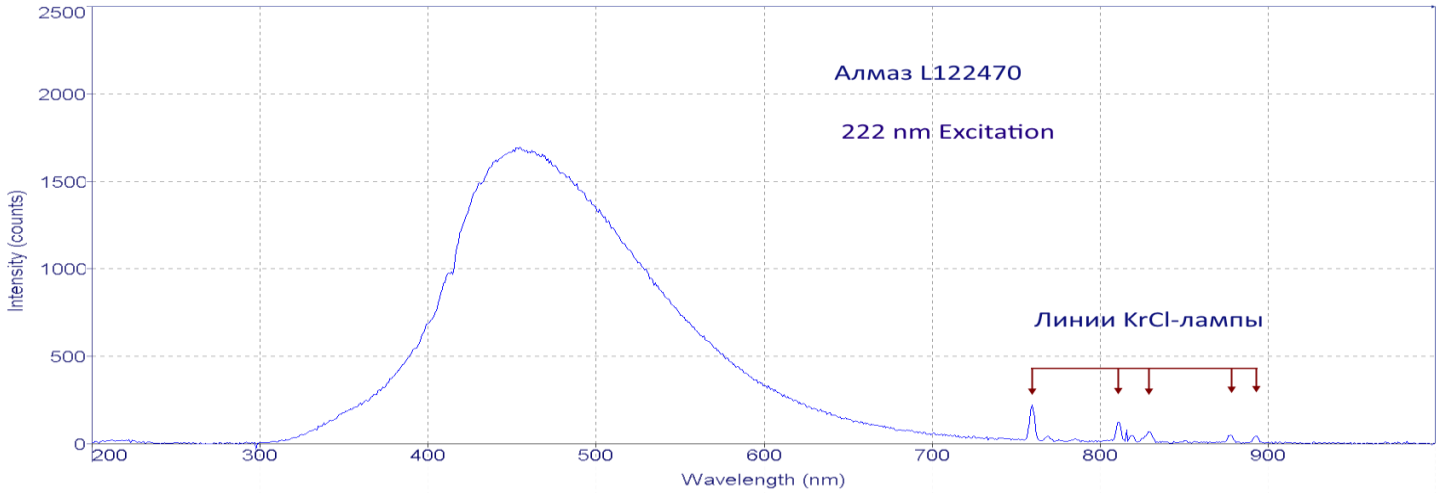


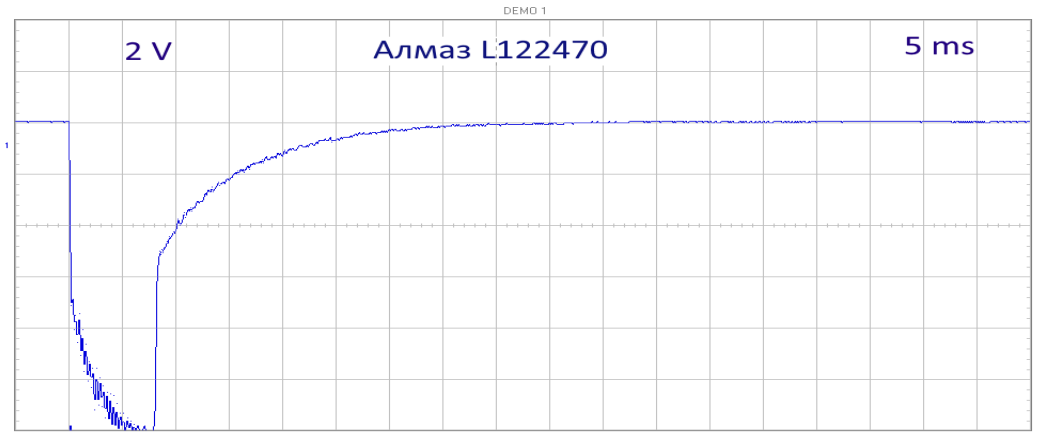


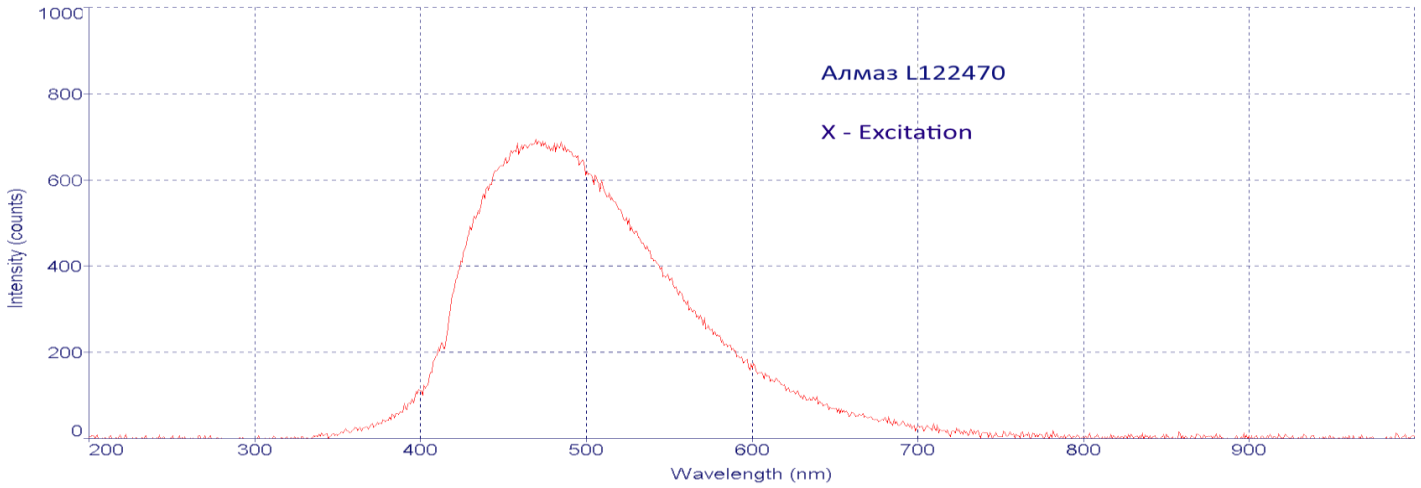
In most crystals, one broad spectral luminescence band is recorded, stretching from ~ 350 to 700 nm with a maximum in the region of 470-480 nm (A-band)

Diamond L122470.

PL spectrum and kinetics upon excitation at 222 nm and XRL spectrum

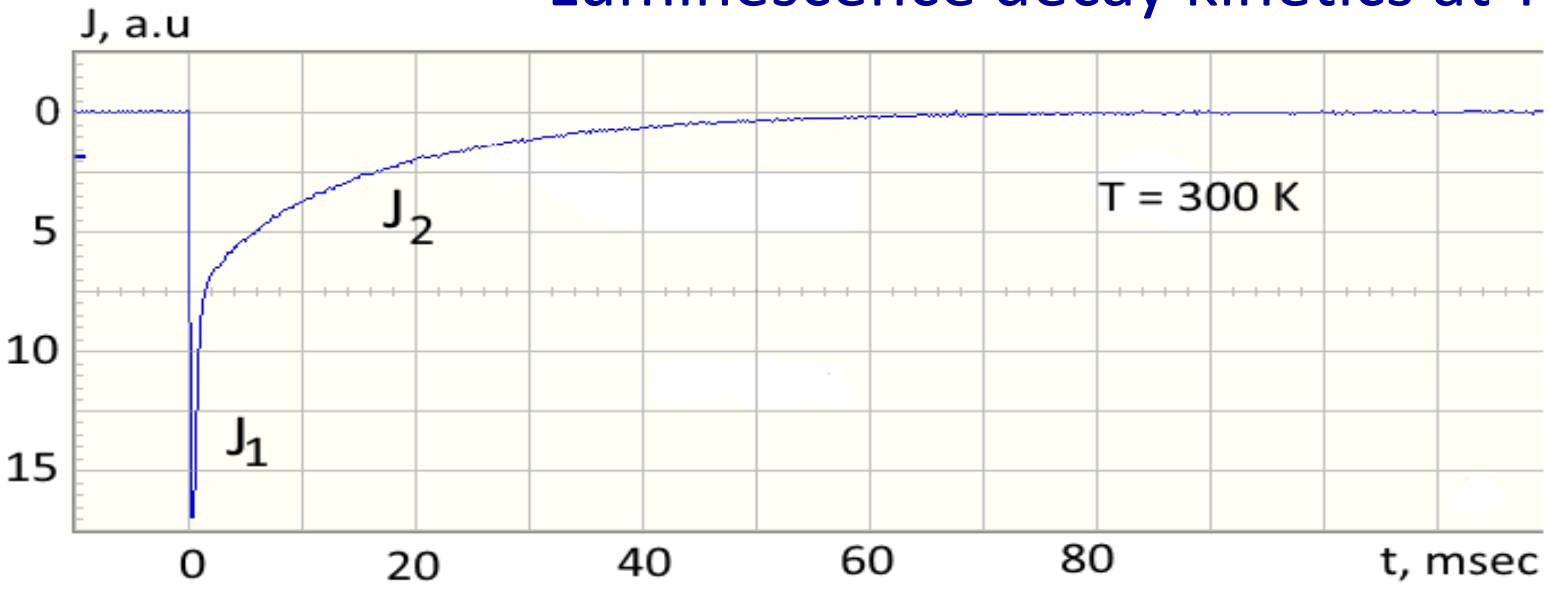


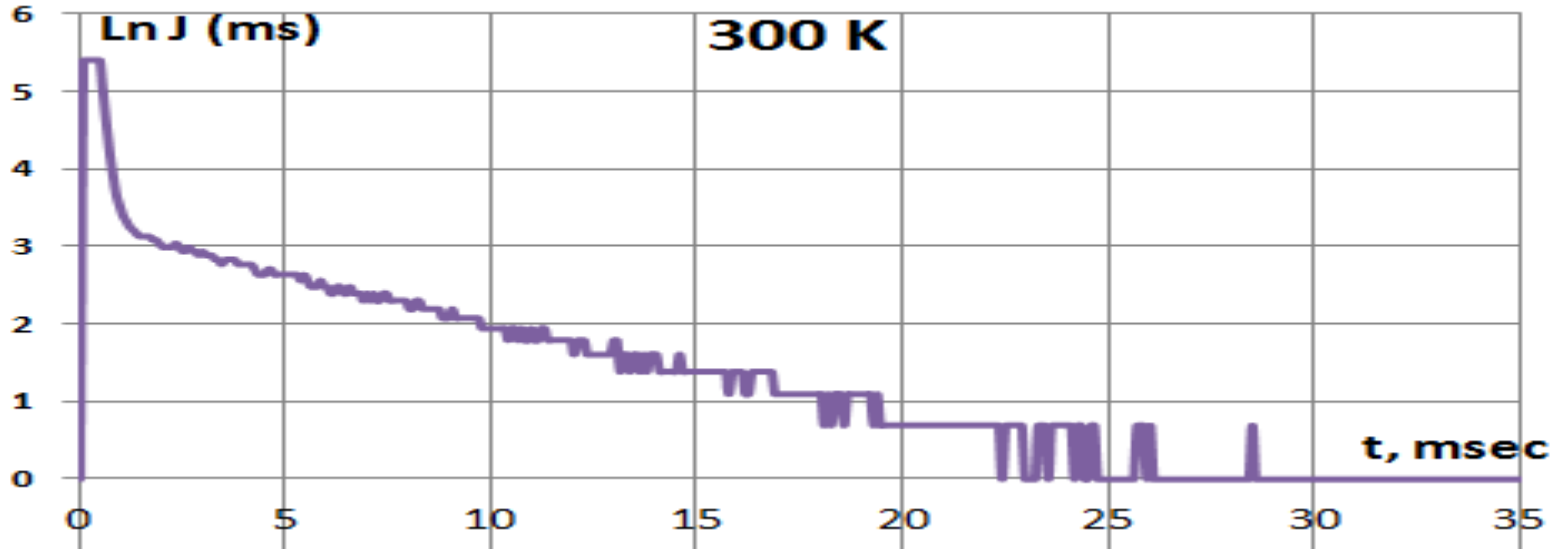




Typical A-band of XRL and PL
with characteristic kinetics

Luminescence decay kinetics at T = 300K





At room temperature, two time components are recorded: short-term J1 and long-term J2, with the long-term component making up the bulk of the light sum.

τ2 = 8,1 msec

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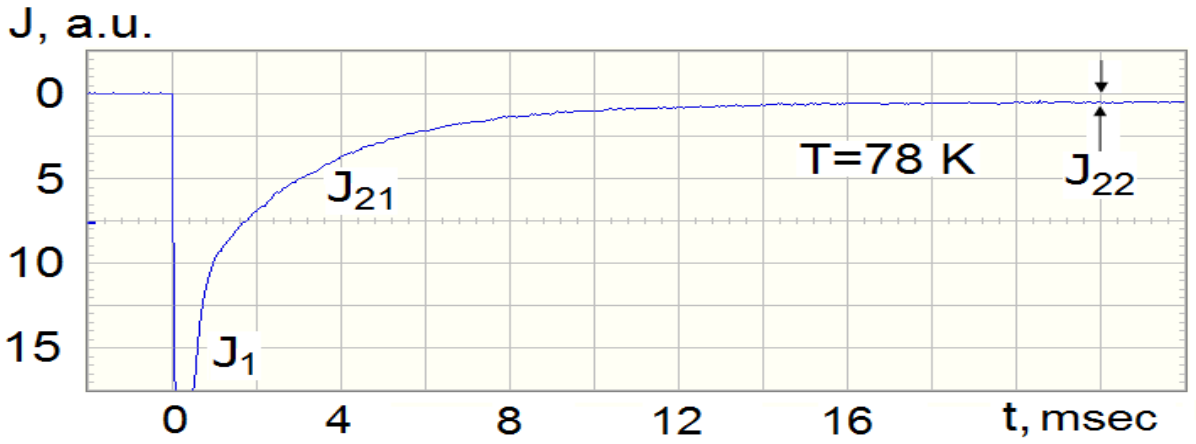
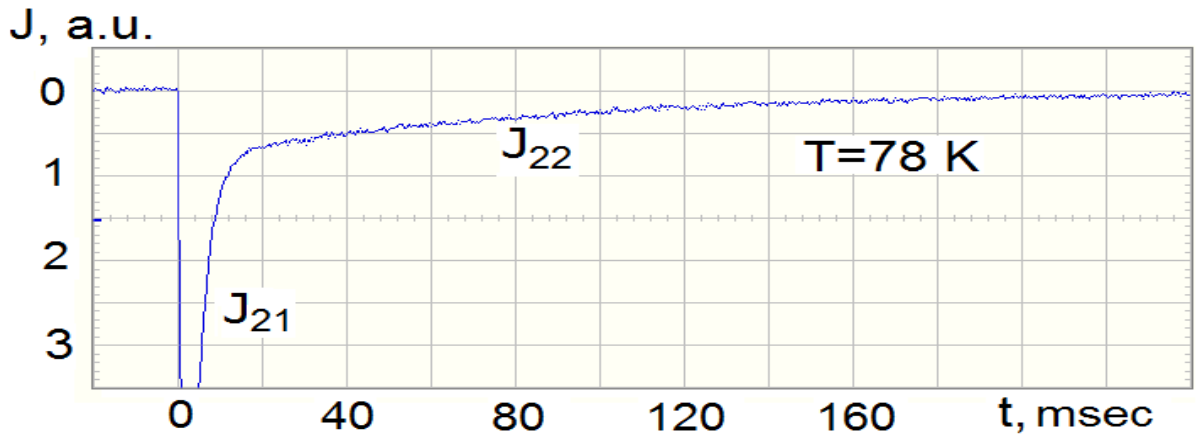
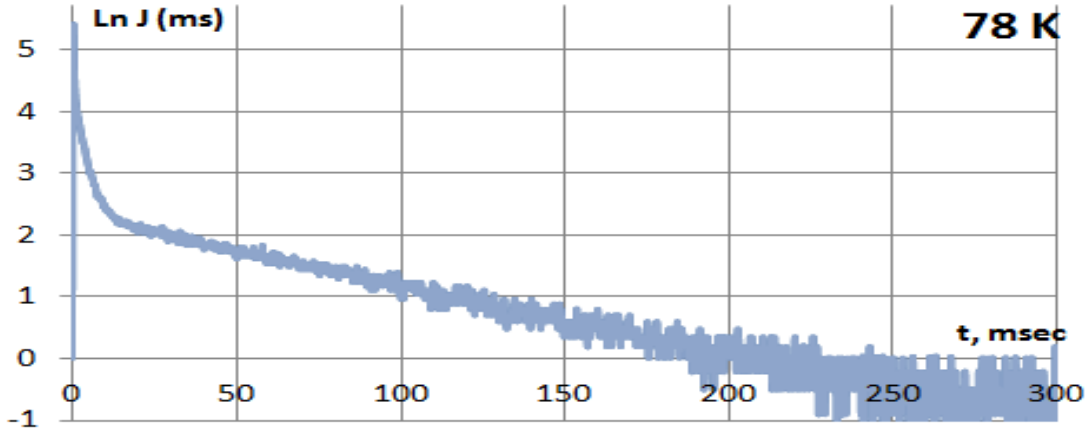
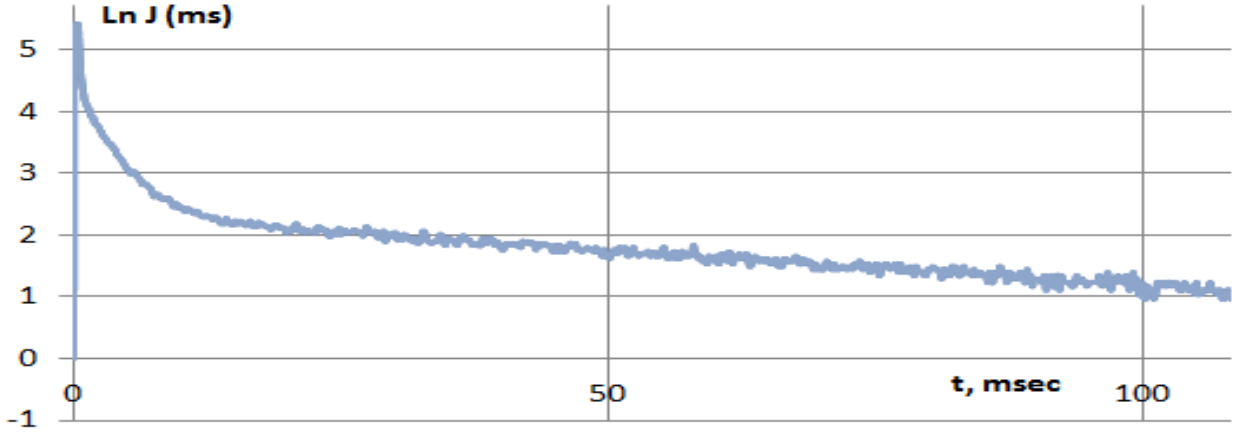
ИФ ИЛФ

Luminescence decay kinetics at T = 78K









At temperatures below ~ 200 K, the long-term component J2 decomposes into two other components J21 and J2

τ_{21} = 3,1 msec

τ_{22} = 90 msec

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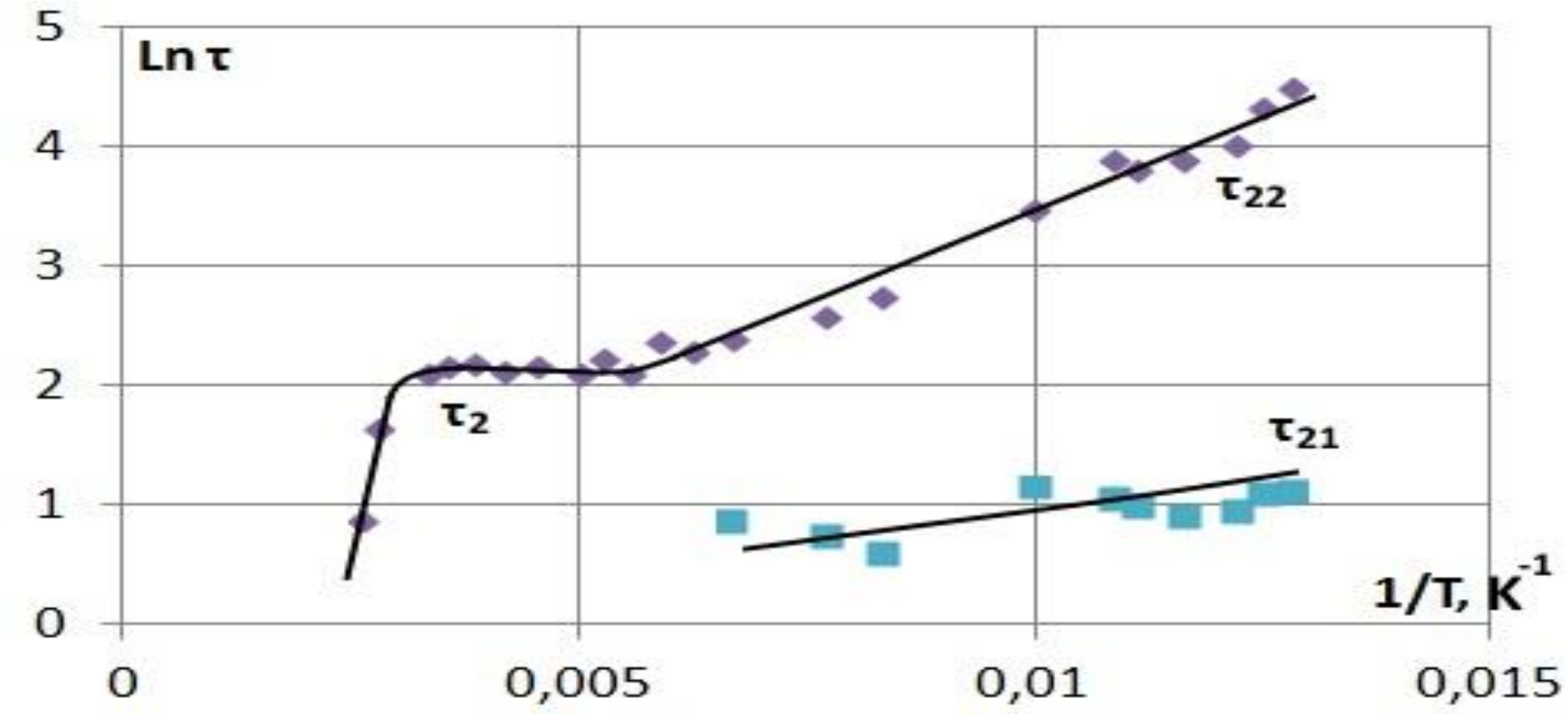
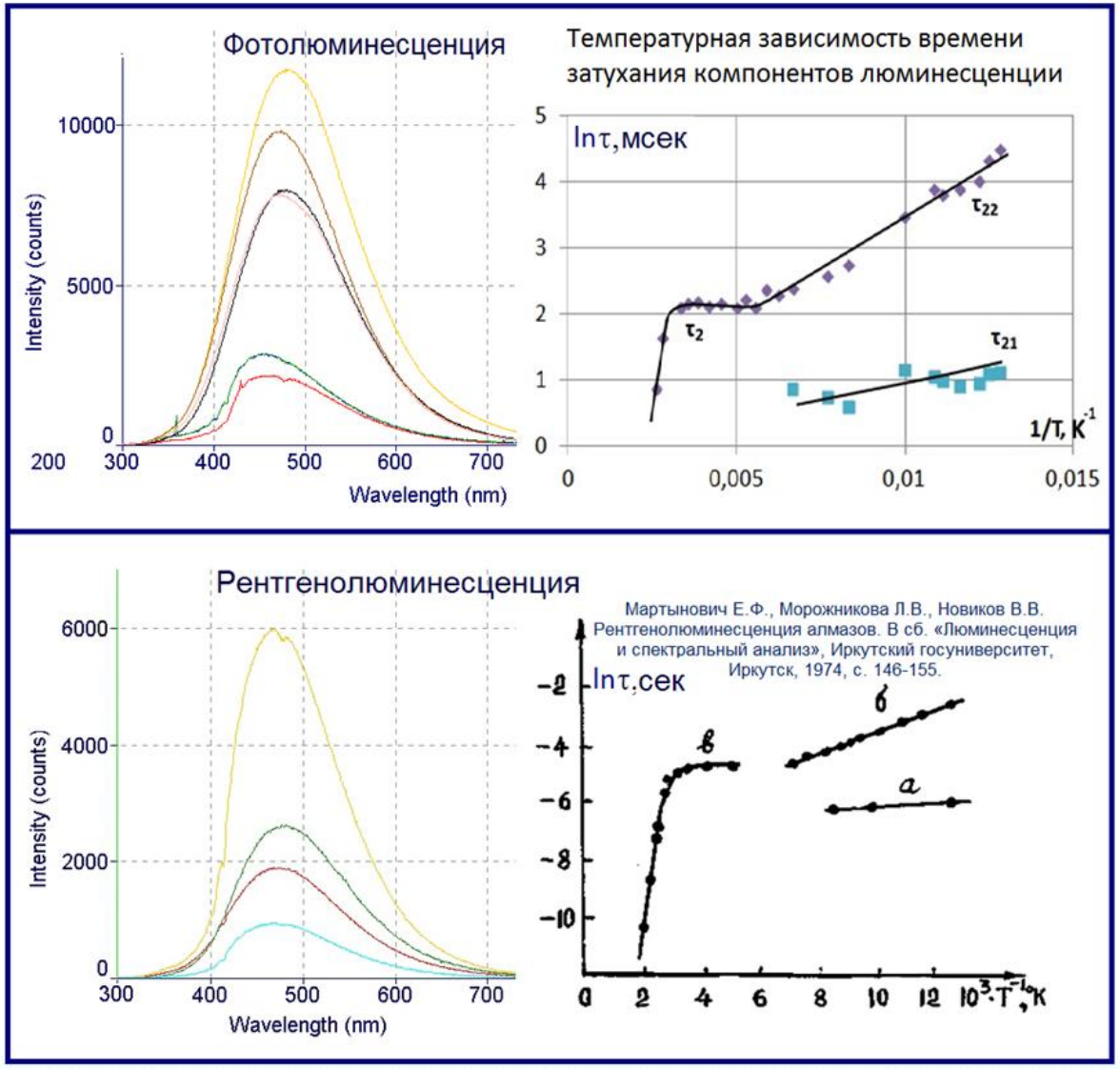
Temperature dependence of the decay time of luminescence components excited by laser radiation



Comparison of the spectral, temporal, and temperature characteristics of photoluminescence under interband excitation and X-ray luminescence of the priority luminescence center responsible for the A-band



Thus, the priority luminescence center responsible for the X-ray luminescence (namely, the center emitting the A-luminescence band) is effectively excited by optical radiation.

The question remains: will other luminescence centers that exist in diamond crystals that do not have an A-luminescence band be also effectively excited?

Spectral-temperature-time passport of the priority centers responsible for the A-luminescence band

The set of temperature dependences of the decay time constants of individual X-ray time components can be considered as the spectral-temperature-time passport of the priority centers responsible for the A-band of recombination luminescence. A characteristic feature of these dependences is the transformation at ~ 140 K of the long time XRL component (~ 8 msec at near room temperatures) into two other components with their own characteristic temperature dependences. This result is very important for identifying the centers responsible for the A-band of recombination luminescence, since it is very difficult to identify them only by the shape, width, and position of the maximum of this band, due to the variability of these characteristics for different diamond samples. Therefore, the spectral-temperature-time passport of the A-luminescence band of diamond presented in this review is a reliable indicator of the priority centers of recombination luminescence of natural diamond.

Это не A-полоса !
This is not an A-band!

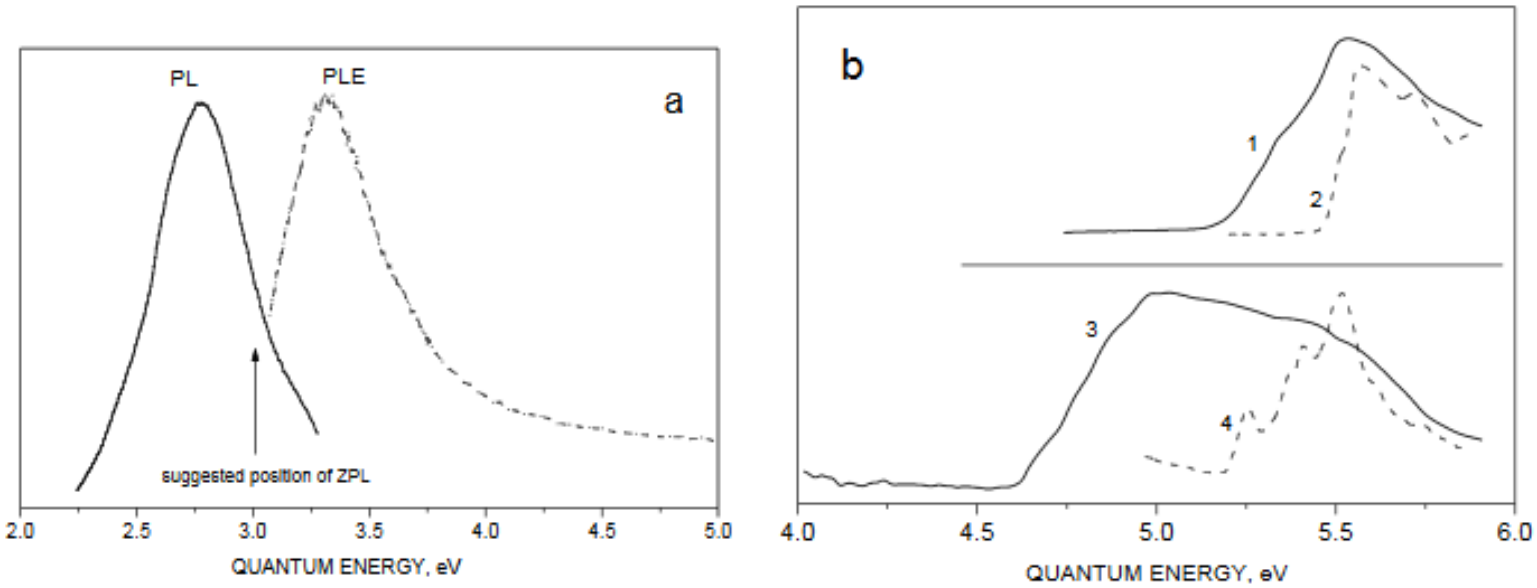


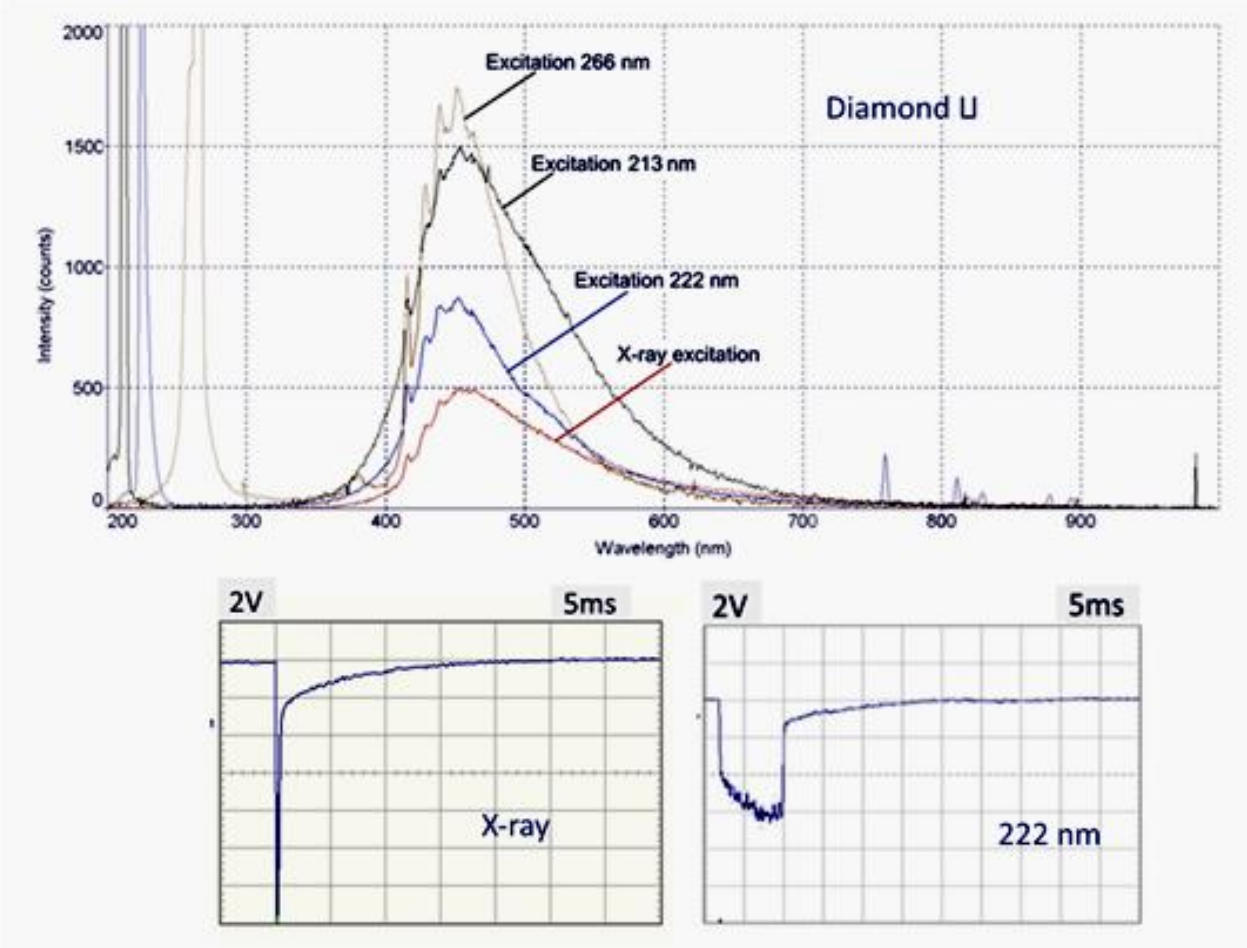
Fig. 5.135. PL and PLE spectra of the dislocation-related A-band observed in CVD diamond films, natural type Ia and IIb diamonds, and type Ib synthetic diamonds. (**a**) PL and PLE spectra taken at LNT. The PLE spectrum is identical for emission energies from 2.5 to 3 eV. (**b**) UV PLE spectra measured in type IIb diamond at RT (1) and LNT (2), in type Ib synthetic diamond at RT and LNT (3) and in type Ia diamond at RT (4) (Iakoubovskii and Adriaenssens 1999a)

Zaitsev A.M. Optical Properties of Diamond

A-band and the mechanism of donor-acceptor pairs

In the mid-sixties, the concept of the donor-acceptor mechanism of emission of the A-luminescence band of diamonds was widely discussed in the scientific literature. We did not accept these ideas on the basis of a detailed study of the kinetics of X-ray luminescence and its other properties in a publication back in 1974. The kinetics of luminescence of donor-acceptor pairs is determined by the probability of electron tunneling between the components of these pairs. In this case, the decay time of luminescence cannot decrease upon cooling. It can only increase. However, in diamonds below ~ 140 K, the glow becomes shorter. These data are fundamentally inconsistent with the donor-acceptor luminescence mechanism. They correspond to the concept of ordinary isolated luminescence centers with thermally stimulated transitions between the excited states of these centers. The duration of the observed luminescence is determined by the probabilities of radiative and nonradiative transitions in these centers. The energy transfer time from the basic diamond substance to the luminescence centers is much shorter than the recorded values of the luminescence decay time.

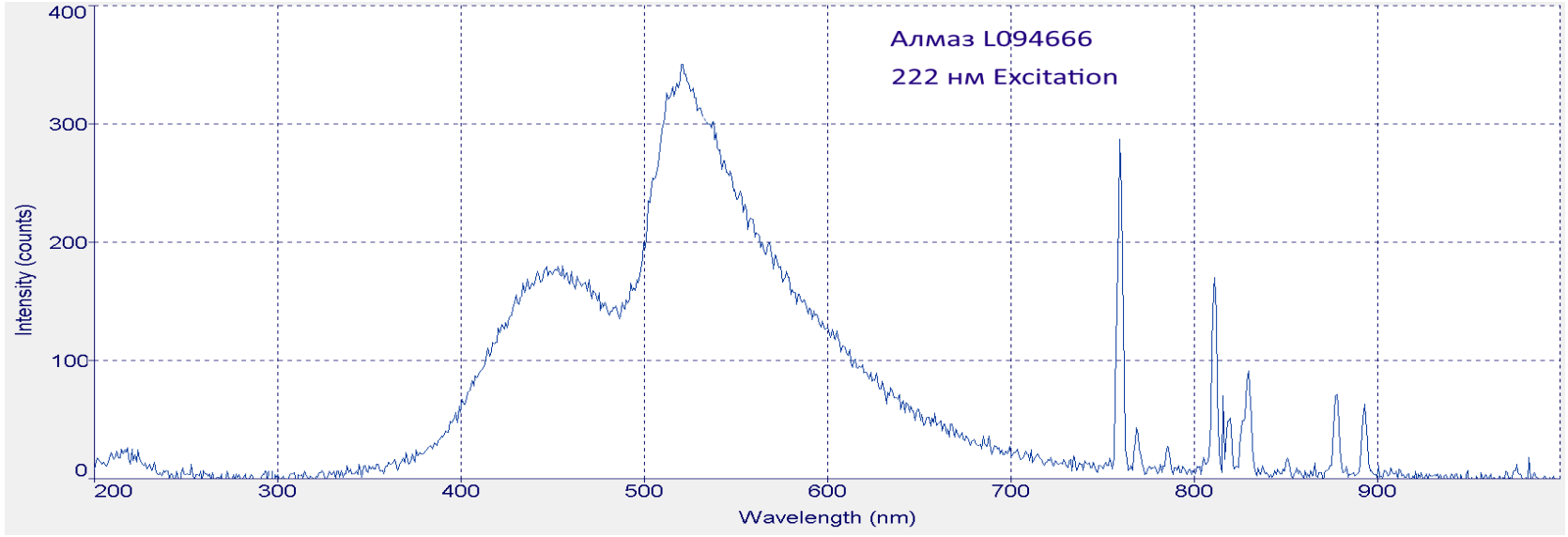
Ionization and excitation

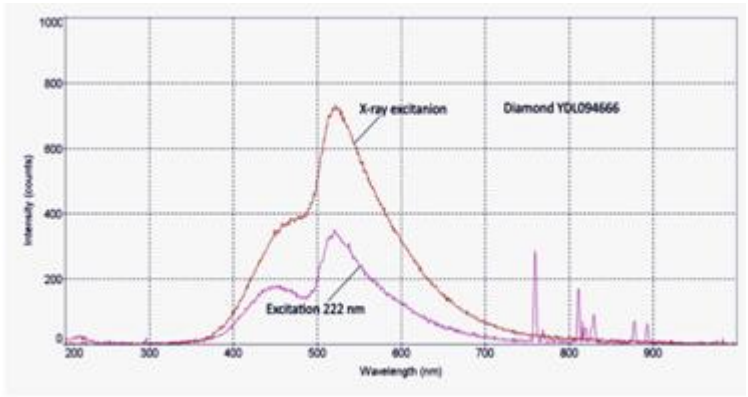


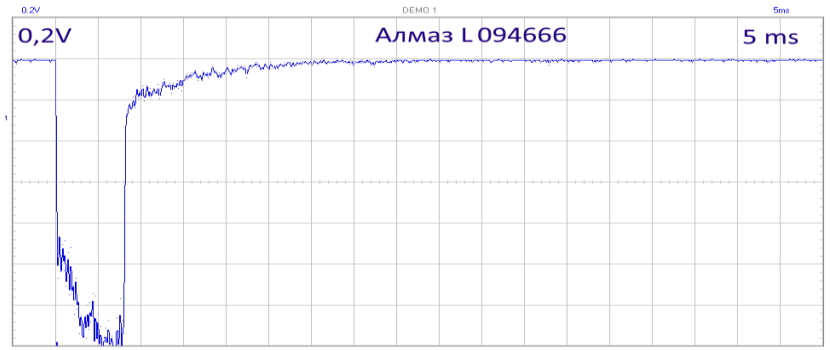
Radiation with wavelengths of 213 and 222 nm excites the A-luminescence band and N3 centers, as does X-ray radiation.

Radiation with a wavelength of 266 nm excites only the N3 centers and does not excite the A-band. This is due to the fact that electrons and holes are needed to excite the A-band, and the 266 nm radiation is not capable of ionizing diamond.

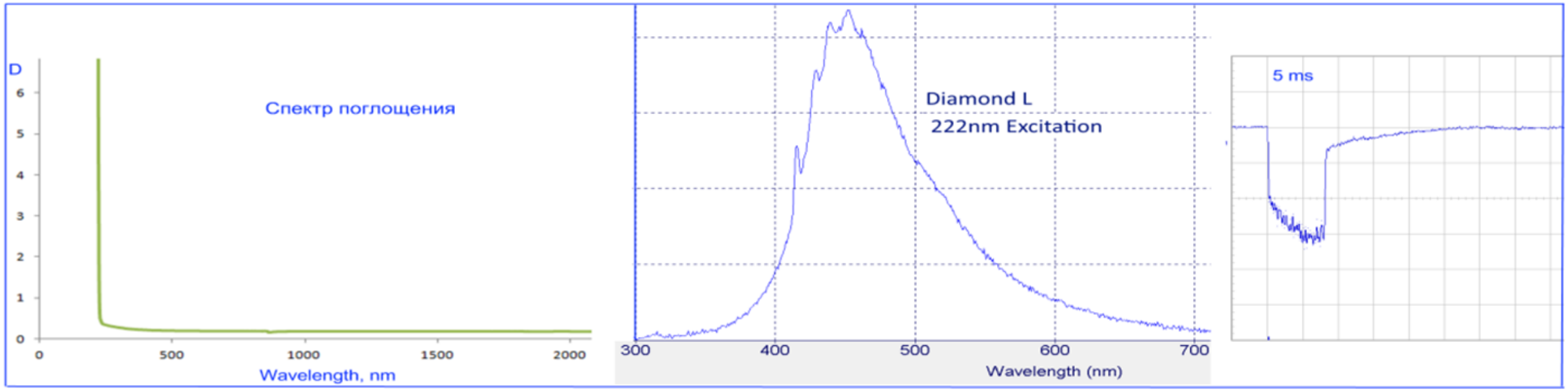
Spectra and kinetics of a sample containing H3 centers and centers responsible for the A-band





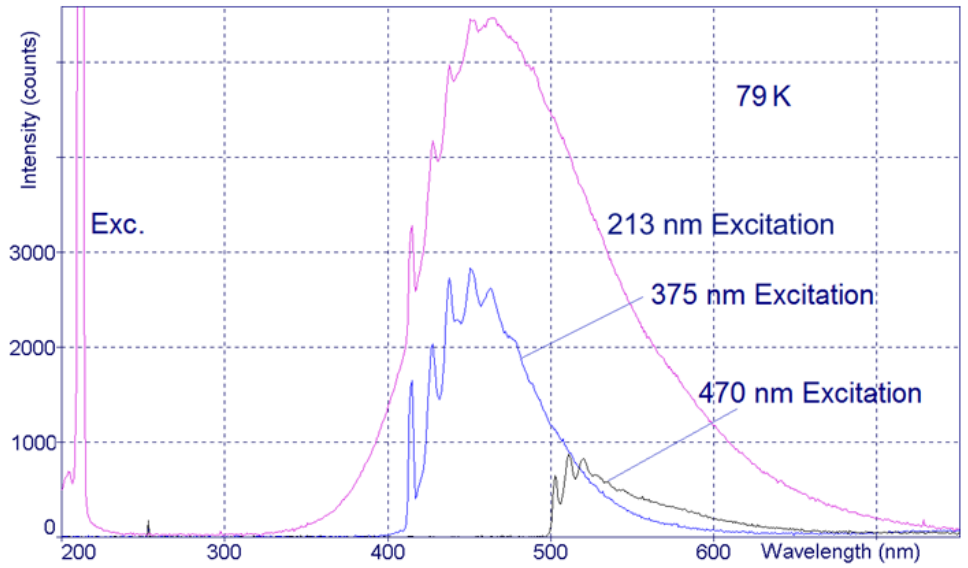


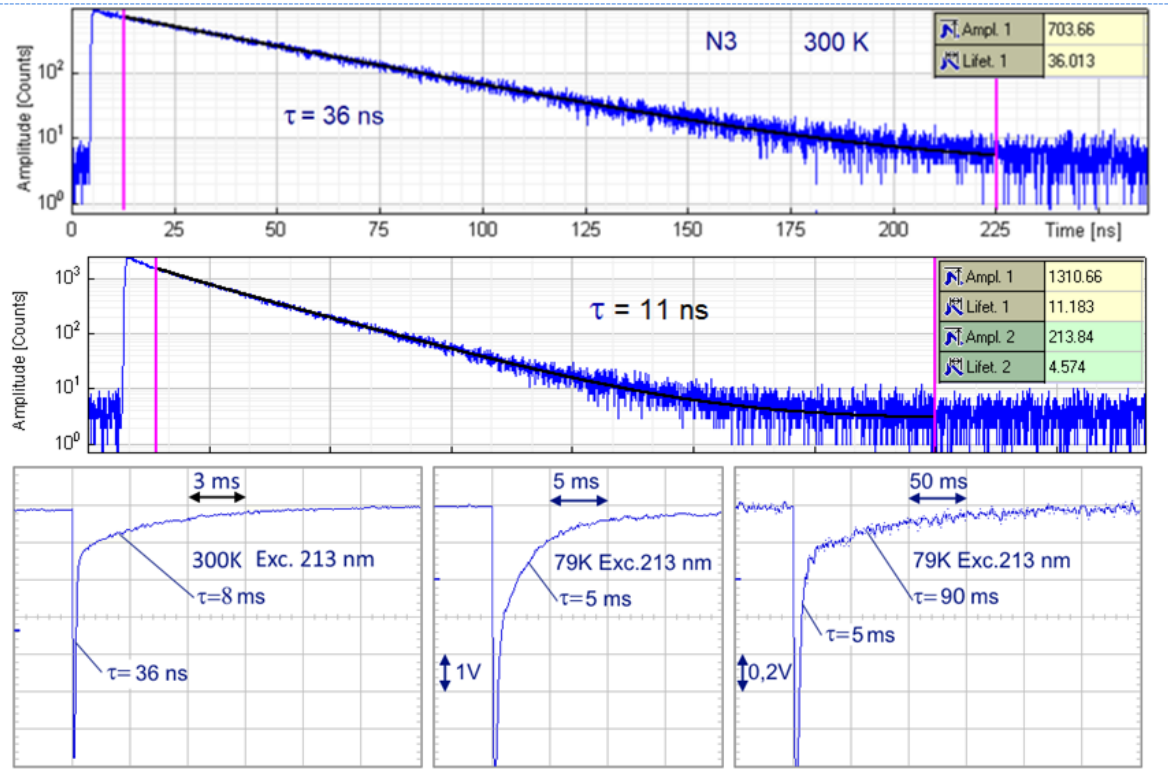
Спектральные и кинетические характеристики образца алмаза типа IIa
Spectral and kinetic characteristics of a type IIa diamond sample



The absorption spectrum has no spectral bands associated with any diamond centers. Nevertheless, they are in the crystal, but their concentration is low. In the luminescence spectrum under interband excitation at 222 nm, lines of N3 centers are visible. The long-term luminescence component of 8 ms indicates the presence of centers emitting the A-luminescence band.

Спектральные и кинетические характеристики образца алмаза типа IIa
Spectral and kinetic characteristics of a type IIa diamond sample

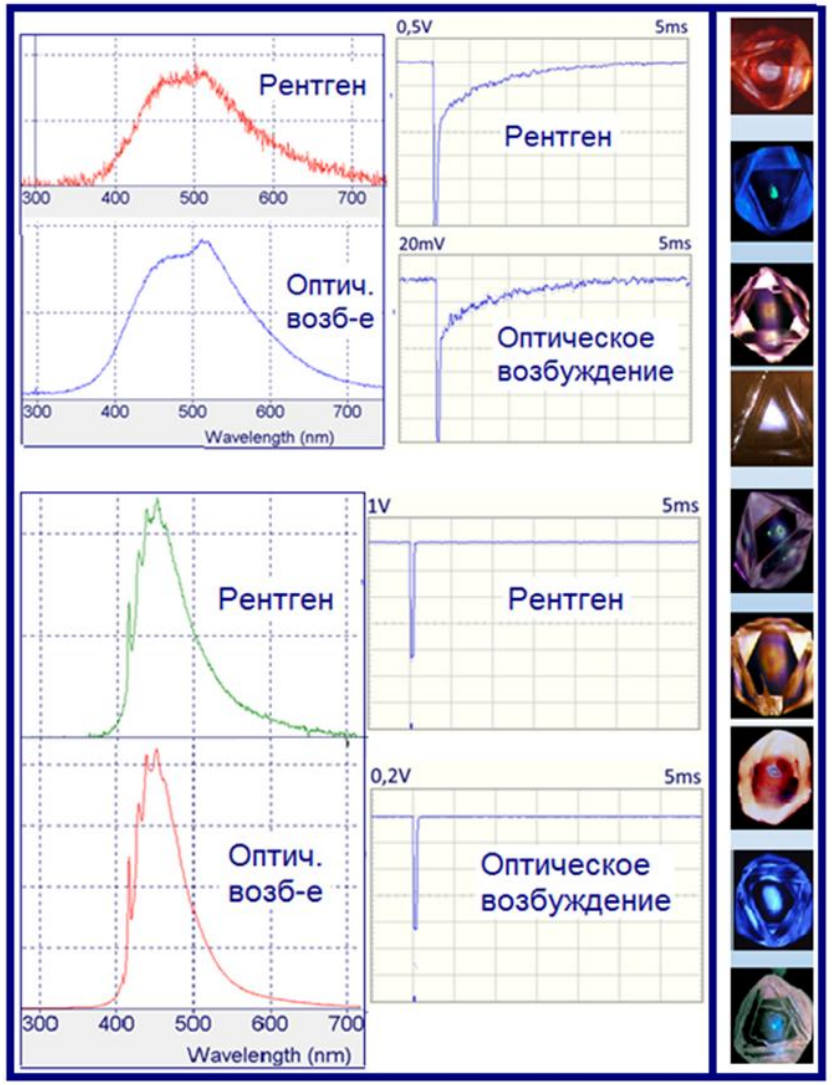




Luminescence spectra under optical interband and intracenter excitation at 79 K

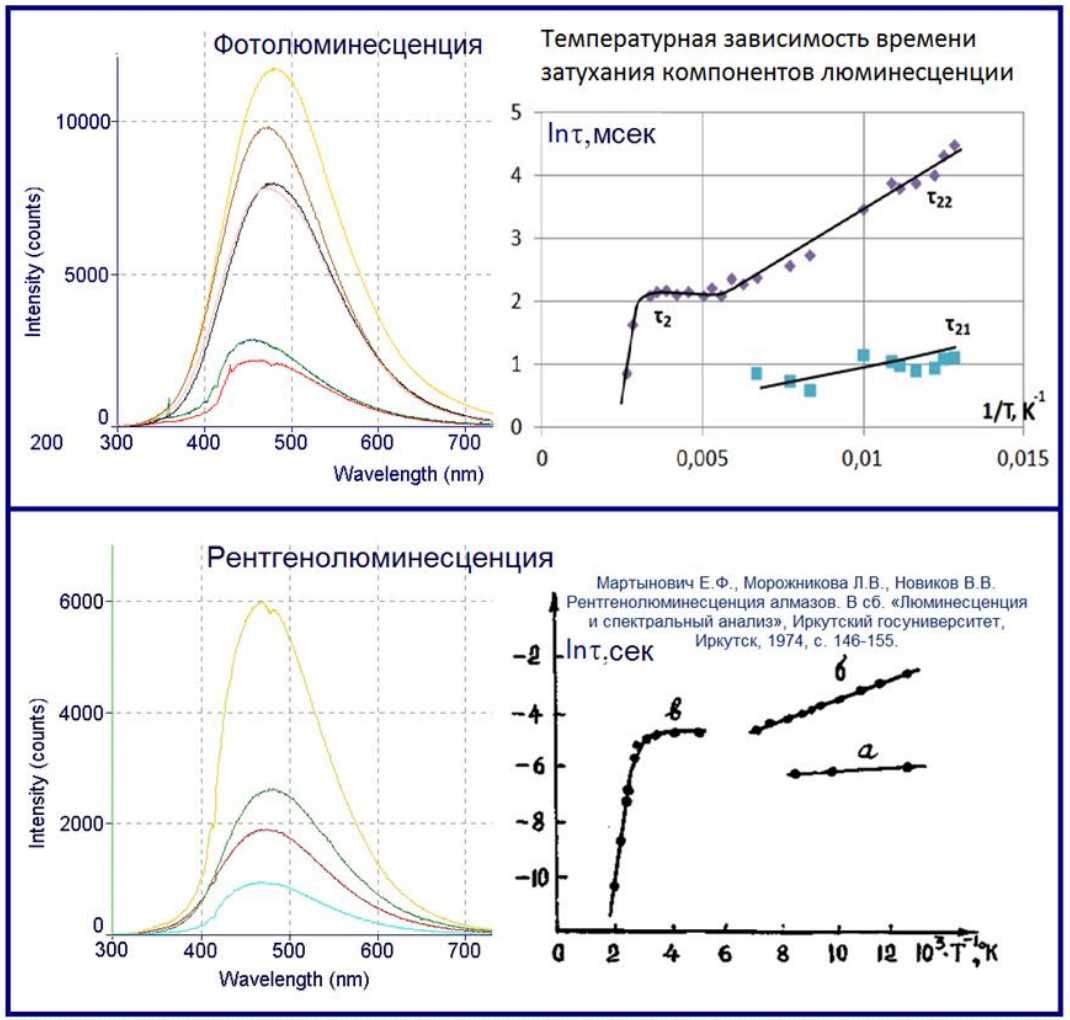
Kinetics of luminescence with interband and intracenter excitation at 300 and 79 K

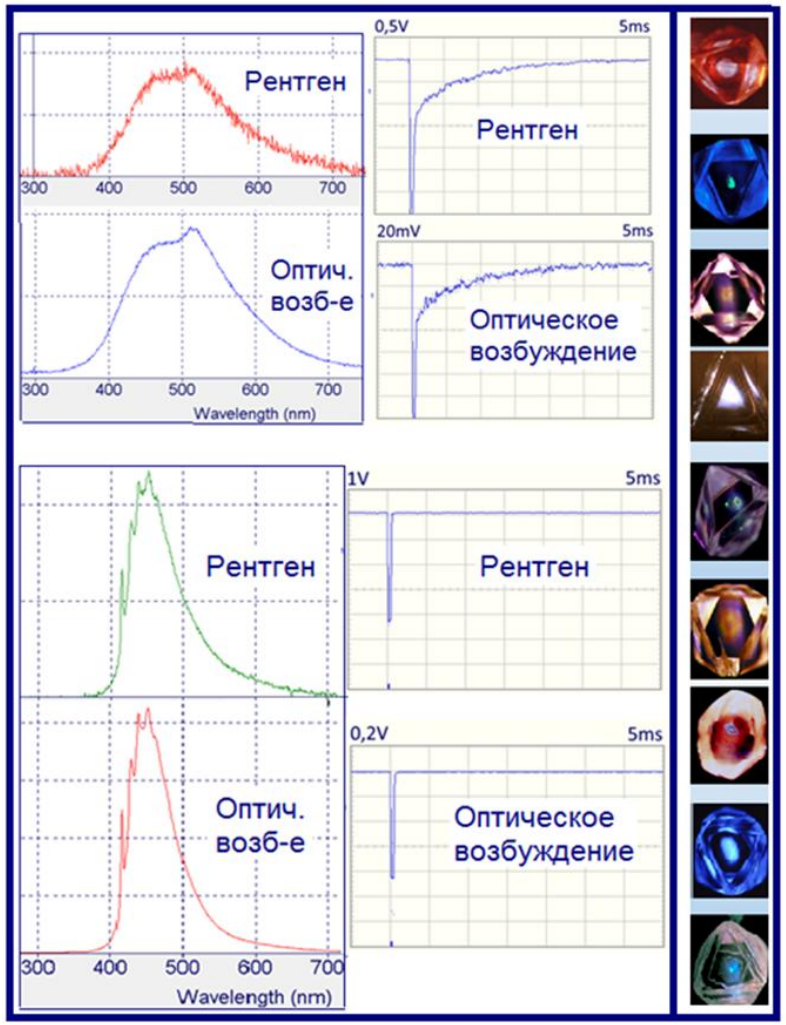
The spectra and kinetics of X-ray luminescence are identical to the spectra and kinetics of photoluminescence of the same crystal upon interband excitation



Conclusion:

1. A spectral-temperature-time passport of the priority centers responsible for the A-luminescence band has been created;
2. A method has been found for optical excitation in diamonds of the same luminescence centers that are excited in them by the action of X-rays.





СО РАН
ИФ ИЛФ

MicroTime 200

Спасибо за внимание!

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