

Near-infrared luminescence of $\text{RbPb}_2\text{Cl}_5:\text{Bi}$ crystals

Andrey G. Okhrimchuk,^{1,*} Leonid N. Butvina,¹ Evgueni M. Dianov,¹ Ninel V. Lichkova,²
Vladimir N. Zagorodnev,² and Kirill N. Boldyrev³

¹Fiber Optics Research Center of Russian Academy of Sciences, 38 Vavilov Street, Moscow 119333, Russia

²Institute of Microelectronics Technology of Russian Academy of Sciences, Chernogolovka,
Moscow Region 142432, Russia

³Institute of Spectroscopy of Russian Academy of Sciences, Troitsk, Moscow Region 142190, Russia

*Corresponding author: okhrim@fo.gpi.ru

Received May 27, 2008; revised August 3, 2008; accepted August 4, 2008;
posted August 29, 2008 (Doc. ID 96721); published September 23, 2008

A wideband near-IR (NIR) luminescence centered at 1080 nm was found in a $\text{RbPb}_2\text{Cl}_5:\text{Bi}$ single crystal grown by the Bridgman technique. Absorption, luminescence, and excitation of luminescence spectra were investigated at room and cryogenic temperatures. The luminescence was proposed to be due to the $^3P_1 \rightarrow ^3P_0$ transition in Bi^+ ion. © 2008 Optical Society of America
OCIS codes: 160.4670, 300.6280.

Recent investigations of laser properties of Bi-doped silica-based fibers clearly demonstrated that a new active center with a broad gain band in the near IR (NIR) appeared in the laser family [1–3]. Meanwhile, there is no full understanding of the nature of the new active centers. There are many publications relevant to a valence state of Bi ions taking part in the oscillation. The valence state was suggested by different authors to be either +1 [4,5], +2 [3] (BiO clusters), or +5 [1,6], and the final conclusion has not been made yet.

It is well known that spectroscopy of impurity ions is much more understandable in crystals than in glasses, because there is a definite majority of sites for dopant ions in crystal, because they are determined by a rigid regular crystal lattice. Thus the investigation of Bi-doped crystals seems to be a perceptible way to understand the nature of the bismuth active center. We have discovered that RbPb_2Cl_5 crystal doped with bismuth (RPC:Bi) exhibits emission properties analogous to silica fibers doped with bismuth.

Cylindrical boules, of 60 mm length and 10 mm diameter, of the RPC crystal doped with bismuth and RPC crystals doped with Dy^{3+} , Pr^{3+} , Er^{3+} were grown by the vertical Bridgman method. The stoichiometric polycrystalline compound of RPC was synthesized by melting high-purity RbCl and a PbCl_2 mixture, and then the obtained compound was purified by the zone-refining technique. The charging material for RPC:Bi crystal growth was prepared by adding either bismuth chloride BiCl_3 or mixture of metallic bismuth with ammonium chloride to the purified RPC polycrystalline compound. The details of the preparation of the raw material are reported in [7]. All RPC:Bi crystals had a light green–gray color with a uniform intensity along the boule, and there was only a small amount of insoluble ingredients at the crystal bottom, indicating that the segregation bismuth coefficient was close to unity. The middle parts of the crystals were cut for spectroscopy investigations.

At room temperature the absorption spectrum was measured with an SF20M spectrophotometer, and at cryogenic temperatures the spectrum was measured with an IFS-125/HR FTIR spectrometer (“Bruker”).

The luminescence spectra were recorded under pumping with a He–Ne laser at 633 nm, a laser diode array at 808 nm, and a semiconductor laser at 919 nm. The excitation of luminescence spectra was recorded under excitation by a tungsten lamp light spectrally selected by a high-aperture grating monochromator and appropriate glass filters. The luminescence was detected with another grating monochromator. Spectral dependences of the detection sensitivity and excitation light intensity were not taken into account; that is, no spectral correction was made either for the luminescence spectra, or for the excitation of the luminescence spectrum.

The kinetics of the luminescence passed through the monochromator was investigated under a rectangular pulse modulation of the pump current of the 808 nm laser-diodes array. The falling edge of the modulating pulse was less than 10 μs .

At room temperature the absorption spectrum of as-grown RPC:Bi crystals has an intense band centered at 360 nm, and in visible and NIR regions the spectrum consists of low-intensity and poorly separated wide bands (Fig. 1). Most distinguishable bands are centered at 630 and 715 nm. An intense NIR luminescence was observed under laser pumping at 633 and 808 nm (Fig. 2). The luminescence spectrum was centered at 1080 nm independently upon the excitation wavelength. The excitation spectrum was recorded under detection of the lumines-

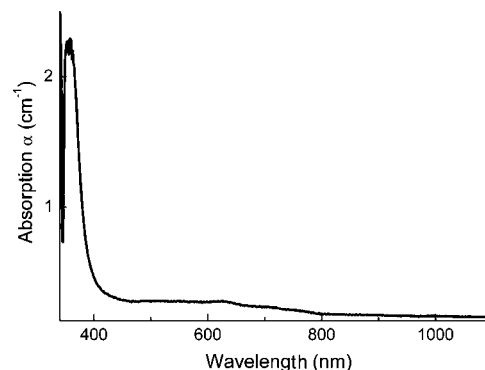


Fig. 1. Absorption spectrum of an RPC:Bi crystal. $T = 300$ K.

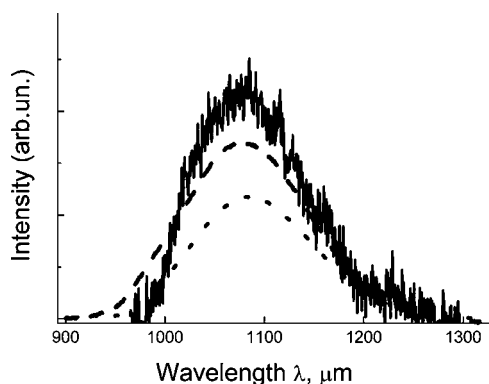


Fig. 2. Luminescence spectra of an RPC:Bi crystal under excitation at 808 (dashed curve), 633 (dotted curve), and 919 (solid curve) nm.

cence at 1080 nm, the wavelength of the luminescence band center (Fig. 3). It was found that there are four intense bands in the excitation spectrum at room temperature.

The cryogenic spectrum was obtained by subtracting background with slow spectral dependence from the initial experimental spectrum (Fig. 3). This was done because we considered that the background was due to apparatus factors and scattering (losses increased in the UV region). The three excitation bands centered at 630, 715, and 767 nm have two weak counterparts at 630 and 715 nm in the room-temperature absorption spectrum and five more pronounced counterparts at 637, 659, 701, 735, and 789 nm in an absorption spectrum taken at $T = 4.7$ K. One more band centered at 915 nm was found at cryogenic temperature. We failed to distinguish this band in the excitation spectrum because of technical difficulties. There was a parasitic residual light of the excitation lamp passed through the excitation monochromator in the wavelength regions of nearly ± 200 nm around the excitation wavelength. When the excitation monochromator was tuned on a wavelength close to the detection wavelength (that is, the excitation wavelength is more than 850 nm), the parasitic light being scattered on the sample penetrated into the detection channel and saturated the photodetection amplifier. Meanwhile, under the laser excitation at 919 nm the same luminescence spectrum as under excitation at 633 and 808 nm was de-

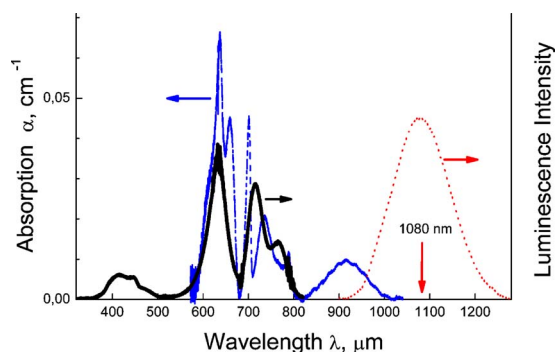


Fig. 3. (Color online) Absorption spectrum at $T=4.7$ K (dashed curve), excitation of the luminescence spectrum (solid curve), and the luminescence spectrum (dotted curve) at $T=300$ K.

tected. Only a slight difference in the spectra was observed at the short-wavelength shoulder of the spectrum, owing to different filters implemented to suppress passing of the excitation light into the detection channel.

An intense excitation band was found at 415 nm, and a corresponding absorption band could not be revealed, probably because of the superimposing of an absorption belonging to centers inactive in IR luminescence. The excitation spectrum is not corrected for the spectral shape of the excitation light. The real amplitude of the 415 nm excitation band will be about 1.5 times higher than amplitude of the 630 nm excitation band, if such correction is done. Thus an absorption coefficient at the maximum of the 415 nm band will be three times higher than an absorption coefficient at the maximum of the 630 nm band (if one takes into account the spectral dependence of the photon energy).

The kinetics of the luminescence was recorded at the wavelength of the luminescence maximum (Fig. 4). The decay curve had a pure exponential character up to 2 orders of magnitude with a decay time of 140 μ s.

The most chemically stable valence of bismuth is 3+, and it corresponds to an electronic configuration that consists only of complete electronic shells. We believe that the most intense absorption band centered at 360 nm is due to the $^1S_0 \rightarrow ^3P_1$ intraconfiguration transition from the 6s shell to the 7p shell, because the band centered at the same wavelength is attributed to this transition in Bi^{3+} ion doped to the RbCl crystal [8]. So as this band absolutely dominated in the absorption spectrum of the RPC:Bi crystal and the ionic radius of the Bi^{3+} ion is close to an Pb^{2+} ionic radius (131 and 143 pm, correspondingly [9]), we consider that bismuth ions in the RPC crystal have predominantly a 3+ valence state and replace Pb^{2+} ions in the crystal lattice. It is unlikely that Bi^{3+} ions replace Rb^+ ions, as the ionic radius of Rb^+ is rather large (175 pm [9]).

The NIR luminescence might be attributed to a transition in an incomplete electronic shell, because it corresponds to relatively low energies of excitation and luminescence photons. Electronic radii of Bi^{2+}

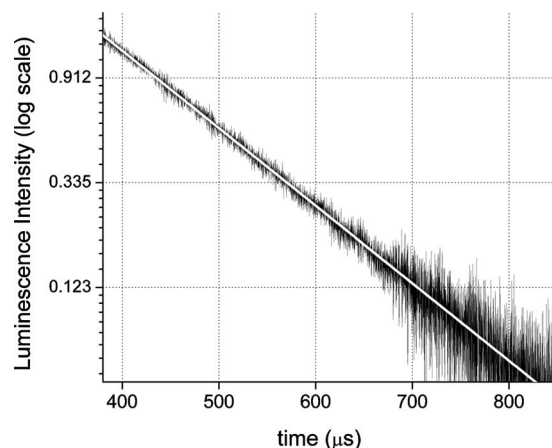


Fig. 4. Kinetics of RPC:Bi luminescence measured under 808 nm excitation, and the exponential approximation.

Table 1. Energies of Multiplets for Free Bi⁺ and Pb⁺ Ions Having the Same Normal Configuration as the Bi²⁺ Ion^a

Bi ⁺			Pb ⁺		
Configuration	Multiplet	Energy (cm ⁻¹)	Configuration	Multiplet	Energy (cm ⁻¹)
6s ² 6p ²	³ P ₀	0	6s ² 6p	² P ⁰ _{1/2}	0
	³ P ₁	13325.401		² P ⁰ _{3/2}	14081.074
	³ P ₂	17031.698	6s6p ²	⁴ P _{1/2}	57910.48
	¹ D ₂	33938.718		⁴ P _{3/2}	66124.53
	¹ S ₀	44173.768		⁴ P _{5/2}	73905.708
6s ² 6p7s	³ P ⁰ ₀	69133.891			
	³ P ⁰ ₁	69598.475			

^aNormal configuration is 6s²6p¹.

and Bi⁺ ions should be higher than a radius of Bi³⁺, and so as the Bi³⁺ radius is less than the Pb²⁺ radius, the Bi⁺ and Bi²⁺ ions probably conform well to the Pb²⁺ site in the crystal lattice. Bi²⁺ is favorable because it has the same valence as Pb²⁺ has, and no charge compensation is required in this case. On the other hand, the +1 state is a likely state, because the Bi⁺ ion is a relatively negatively charged crystal lattice and compensates positively charged Bi³⁺ ions. Thus we should narrow our choice of the valence state of bismuth ions responsible for the luminescence within +2 and +1. Spin-orbital interaction gives the main contribution to the energy-level splitting of unfilled electronic shells of the heavy ions, and the crystal field gives minor contribution. Thus at the first approach we could compare measured spectra with the energy structure of the free ions. In Table 1 electronic energies of multiplets of free Bi⁺ ions and free Pb⁺ ions are presented [10]. The last has the same electronic configuration as Bi²⁺ ions.

No analogous NIR luminescence was observed in RPC crystals doped with Dy³⁺, Pr³⁺, or Er³⁺. Thus the nature of the luminescence centers should be connected with electronic transition in bismuth ions and not with structural defects of an RPC crystal lattice, which can be induced by IR-inactive Bi³⁺ ions.

As many as eight transitions in NIR and the visible are allowed by spin-selection rules for a Bi⁺ ion that is from the ground ³P₀ state to the three-fold degenerated ³P₁ and to the five-fold degenerated ³P₂ state. The crystal field might further split multiplets, and the number of bands in the visible and NIR for RPC:Bi⁺ can be as high as eight. Only two bands in NIR and the visible could be observed for the Bi²⁺ ion, because the ground state ²P⁰_{1/2} cannot be split by the crystal field (according Kramers's theorem), and the ²P⁰_{3/2} excited state can be split to two Stark's sub-levels only. As mentioned above, the five bands relevant to the excitation of the NIR luminescence were identified (415, 630, 715, 767, and 915 nm). All five bands should belong to one luminescence center, because the emission spectrum has a perfect Gaussian shape, and the kinetics of the luminescence is single exponential. Energy transfer to the emitted center from other hypothetical centers absorbed in the visible and NIR should be excluded from consideration,

because concentration of all these centers cannot be enough for effective energy transfer. Thus such a large amount of observed bands is inconsistent with Bi²⁺ ions, and only the Bi⁺ ion could correspond to the observed structure in the absorption and excitation spectra. Our assumption is supported by the spectroscopy investigation of M²⁺BPO₅:Bi²⁺ crystals (M²⁺=Ba²⁺, Sr²⁺, and Ca²⁺) [11]. Contrary to the RPC:Bi crystal, the emission spectrum of M²⁺BPO₅:Bi²⁺ crystals lay in the red region, and there were only two absorption bands in NIR and the visible, as it should be for Bi²⁺ ions. Additional fine structures of RPC:Bi absorption and excitation bands could be due to the electron–vibration interaction.

In conclusion, we have found a wideband NIR luminescence centered at 1080 nm that is associated with bismuth-doped RbPb₂Cl₅ crystals. We tend to assign this luminescence to the ³P₁→³P₀ transition in the 6p electronic shell of a Bi⁺ ion, and absorption in the range 10000–25000 cm⁻¹ to transitions from the ground ³P₀ state to other high-spin states of the 6p shell of a Bi⁺ ion, which are ³P₁ and ³P₂.

References

1. Y. Fujimoto and M. Nakatsuka, Jpn. J. Appl. Phys. **40**, L279 (2001).
2. V. V. Dvoyrin, V. M. Mashinsky, L. I. Bulatov, I. A. Bufetov, A. V. Shubin, M. A. Melkumov, E. F. Kustov, E. M. Dianov, A. A. Umnikov, V. F. Khopin, M. V. Yashkov, and A. N. Guryanov, Opt. Lett. **31**, 2966 (2006).
3. M. Peng, D. Chen, J. Qiu, X. Jiang, and C. Zhu, Opt. Mater. **29**, 556 (2007).
4. X. Meng, J. Qiu, M. Peng, D. Chen, Q. Zhao, X. Jiang, and C. Zhu, Opt. Express **13**, 1635 (2005).
5. V. G. Truong, L. Bigot, A. Lerouge, M. Douay, and I. Razdobrevev, Appl. Phys. Lett. **92**, 041908 (2008).
6. T. Ohkura, Y. Fujimoto, M. Nakatsuka, and S. Y. Seok, J. Am. Ceram. Soc. **90**, 3596 (2007).
7. N. V. Lichkova, V. N. Zagorodnev, L. N. Butvina, A. G. Okhrimchuk, and A. V. Shestakov, Inorg. Mater. **42**, 81 (2006).
8. S. Radhakrishna and R. S. S. Setty, Phys. Rev. B **14**, 969 (1976).
9. <http://www.webelements.com>.
10. J. E. Sansonetti and W. C. Martin, J. Phys. Chem. Ref. Data **34**, 1559 (2005).
11. A. M. Srivastava, J. Lumin. **78**, 239 (1998).