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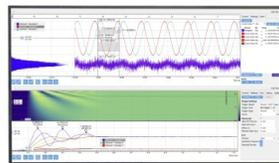
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Luminescent Properties of BaBrI:Sm²⁺ Scintillation Crystals

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Abstract. The optical spectra of BaBrI crystals activated by divalent samarium were studied. The samples exhibit bright luminescence in the red region of spectra due to 4f⁶–4f⁶ and 4f⁵5d¹–4f⁶ transitions of Sm²⁺ ions. Luminescence exhibits strong temperature dependence in the range 7–300 K. At low temperatures, luminescence associated with parity-forbidden 4f⁶–4f⁶ transitions from ⁵D₀ and ⁵D₁ states is observed. Coloring of the crystals after irradiation by ultraviolet light and long afterglow luminescence of BaBrI:Sm²⁺ were detected.

INTRODUCTION

Fast scintillator crystals with high light output in the red region of the spectrum are especially in demand in the production of gamma and x-ray detection devices based on scintillator and photodiode assemblies. Recent studies show [1–3], that BaBrI crystals doped with Eu²⁺ ions are promising scintillators with 4f⁶5d¹–4f⁷ luminescence in the blue region of the spectrum. Now there is a need of scintillators emitting in the red region of spectra [4] for scintillation detectors based on modern avalanche photodiodes and silicon photomultipliers (Si-PM) with a large sensor area and high quantum efficiency. According to the Dorenbos model [5] constructed for BaBrI in [1], Sm²⁺ should be the red light emitting activator for BaBrI. According to the model, 5d level of Sm²⁺ should have approximately the same energy relative to the bottom of the conduction band as Eu²⁺ and the fast 4f⁵5d¹–4f⁶ luminescence of Sm²⁺ ions should be observed at room temperature.

METHODOLOGY

Crystal Growth

The crystals were grown by the vertical Bridgman method in sealed quartz ampoules in vacuum. The temperature gradient was about 10–15°C/cm, and the growth rate was 1 mm/hour. The reagents used for the growth were BaBr₂ and BaI₂ (purity 99.9%, Lanhit, LTD). Utilized stoichiometric mixture of BaBr₂ + BaI₂ was doped with SmBr₃. Because the material is hygroscopic, the batch was thoroughly dried prior to sealing the ampoule of diameter 10–30 mm. The melting points, the level of hydration and the possible dehydration temperatures of the materials were determined by thermogravimetric and differential scanning calorimetry methods prior to the crystal growth. The melting point for BaBrI is about 783°C. The concentration of Sm²⁺ ions in the sample was determined by inductively coupled plasma mass spectrometry (ICP-MS) and amounted to 3·10⁻³ mol. %. The plates about 1–2 mm

of thickness and 5 mm in diameter were cut and polished in glovebox for optical absorption and luminescence spectra studies. In between experiments, the crystals were stored in an ampoule filled with liquid paraffin, in order to exclude the effect of natural humidity.

Optical Measurements

The photoluminescence and excitation spectra were recorded by double monochromator SDL-1 (LOMO) with 600 lines/mm grating and photosensor module Hamamatsu H10720-01. Luminescence was excited by emission of high pressure 150 W xenon arc lamp DKSH-150 passed through MDR-2 monochromator with a diffraction grating of 1200 lines/mm. The photoluminescence excitation (PLE) spectra were reduced for comparison due to varying intensity of exciting light. Photoluminescence decay curves were registered by an oscilloscope Rigol 1202 under pulse nitrogen laser excitation (337 nm) with pulse duration about 10 ns. Measurements were carried out at temperatures 7, 77 and 298 K using vacuum cold-finger cryostat. The optical absorption spectra were obtained by Perkin-Elmer Lambda 950 UV/VIS/NIR spectrophotometer.

RESULTS AND DISCUSSION

Luminescence of Sm^{2+}

The BaBrI excitation spectrum (Fig. 1) was observed at a temperature of 77 K at a recording wavenumber of 14640 cm^{-1} (683 nm), the absorption spectrum was recorded at 298 K. In the region of $16000\text{--}35000 \text{ cm}^{-1}$ we observed absorption bands related to transitions from ground state $4f^6$ to $4f^55d^1$ states of the Sm^{2+} ion, which are split by the influence of the crystal field and spin-orbit interaction [6,7].

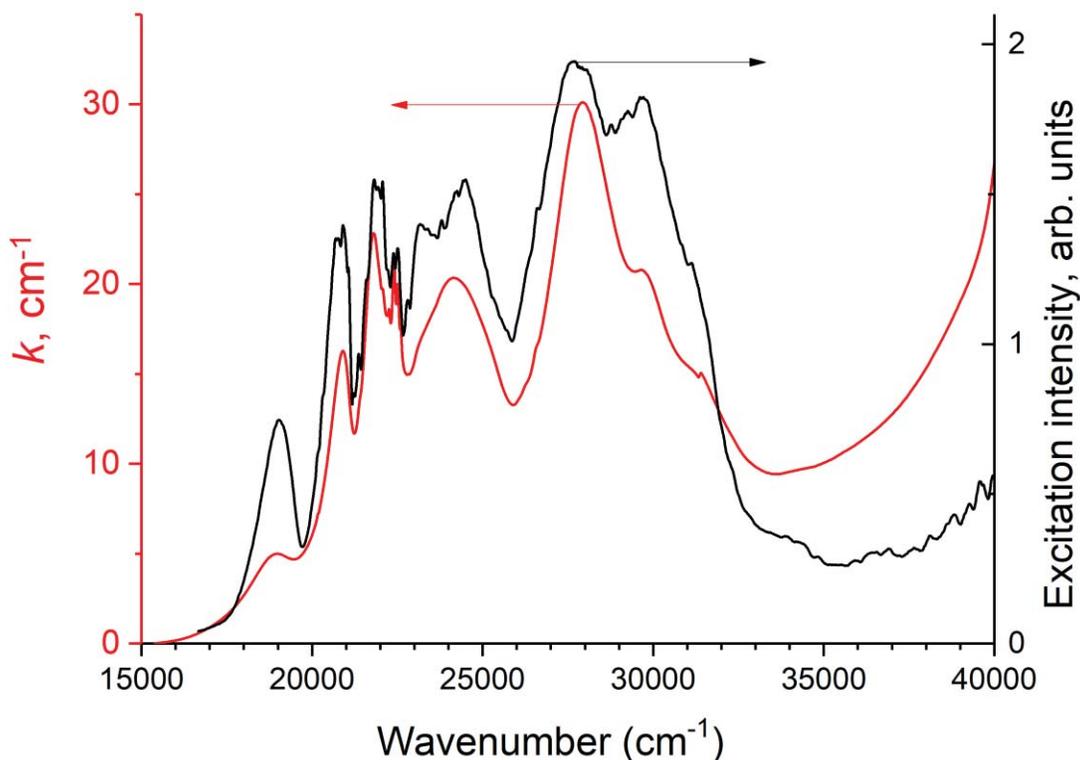


FIGURE 1. Absorption and excitation spectra of BaBrI:Sm²⁺ at 298 K and 77 K respectively

BaBrI:Sm²⁺ crystals show bright red luminescence under the excitation of ultraviolet radiation (Fig. 2). The luminescence spectra were recorded with excitation by light with wavelength of 365 nm (27397 cm^{-1}), which

corresponds to the maximum in the excitation spectrum. Measurements were carried out at temperatures 7, 77 and 298 K. The emission spectrum at room temperature (Fig. 2 (a)) consists of a multiplicity of lines corresponding to intraconfigurational $4f^6-4f^6$ transitions of Sm^{2+} ions.

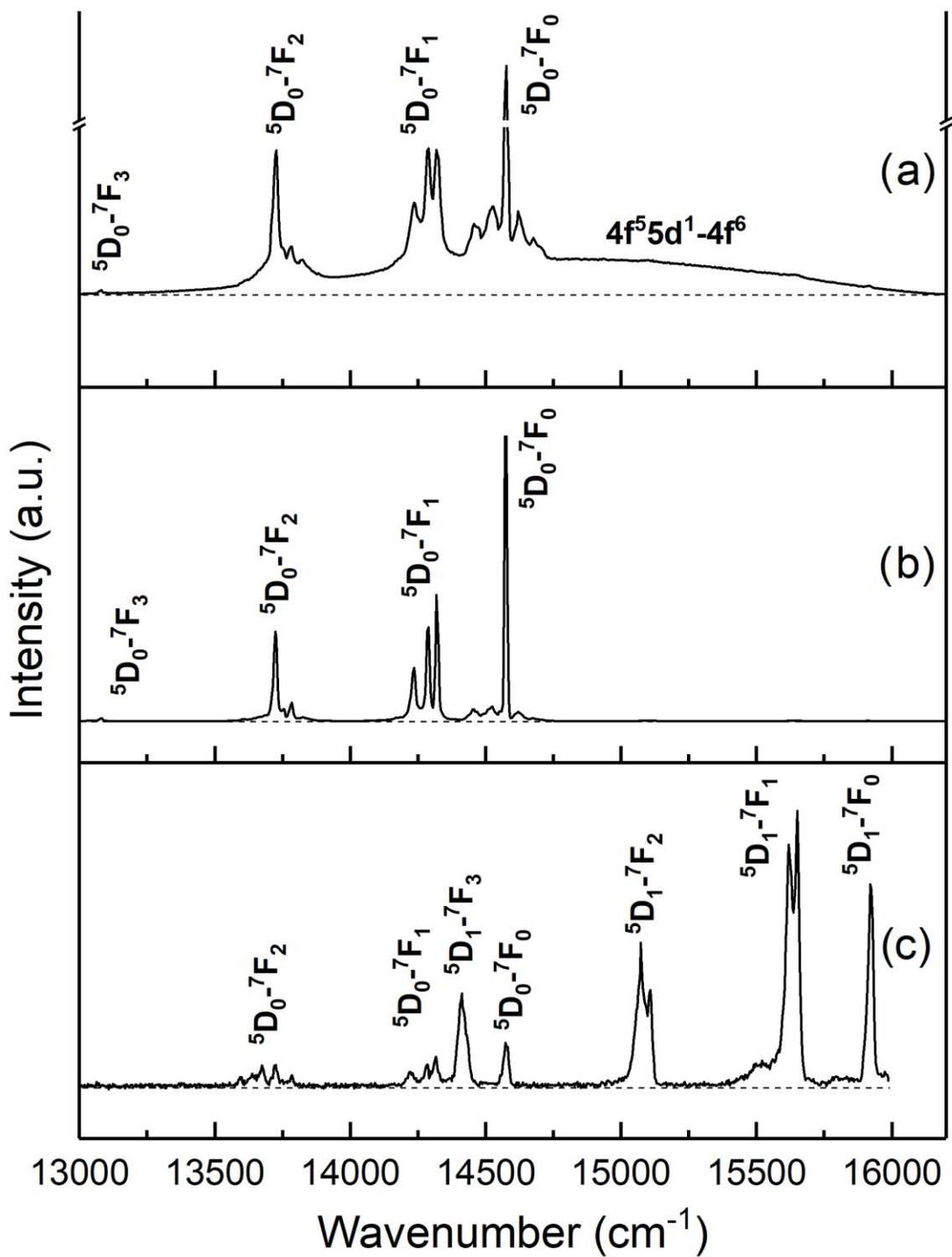


FIGURE 2. Luminescence spectra of BaBrI:Sm²⁺ at 298 K (a), 77 K (b) and 7 K (c), excited at 27397 cm⁻¹ (365 nm)

At room temperature $4f^6-4f^6$ transitions from the lower excited level 5D_0 to the group of levels of the ground state 7F_J occur. The $^5D_0-^7F_0$ transition appears in the emission spectrum as a line at 14641 cm^{-1} and has the highest intensity among the other lines. Typical full width at half maximum (FWHM) of this line is 10 cm^{-1} . This zero-phonon line is accompanied by multiple vibronic lines located on either side of the band. We note that $^5D_0-^7F_0$ transition for cubic sites with center of symmetry is further forbidden by symmetry selection rules [8]. This reveals that in BaBrI the Sm^{2+} ions occupied only one site without central symmetry. Also, we observed the bands related to transitions from the 5D_0 level to excited levels of the ground state: 7F_1 , 7F_2 , 7F_3 , in the range $14340-14210$, $13850-13560$ and $13100-13050\text{ cm}^{-1}$. The transitions $^5D_0-^7F_1$ and $^5D_0-^7F_2$ are split into three and five components, respectively. Such line splitting may correspond to the monoclinic syngony of the crystalline environment of the samarium ion [9].

Also, a wide band in the region of $13000-17000\text{ cm}^{-1}$ is visible in the spectrum. When the temperature descends below 200 K , this band disappears completely. As shown in [7], the wide band can relate to $4f^55d^1-4f^6$ transitions of Sm^{2+} ions. The FWHM of this band is 1700 cm^{-1} , which is in good agreement with the data from [10]. Only bands associated with $4f^6-4f^6$ transitions from the lower 5D_0 excited state of the Sm^{2+} ion are observed in the luminescence spectra at liquid nitrogen temperature (Fig. 2 (b)). The luminescence spectrum recorded at 7 K shows new narrow luminescence bands, shifted to the short-wavelength region relative to the $^5D_0-^7F_J$ transitions (Fig. 2 (c)). They correspond to transitions from the 5D_1 state of Sm^{2+} to the ground state: 7F_0 (15900 cm^{-1}), 7F_1 (15650 cm^{-1}), 7F_2 (15100 cm^{-1}), 7F_3 (14400 cm^{-1}), 7F_4 (13650 cm^{-1}). The spectrum shows that the number of stark components of each band is determined by splitting of the sublevels of the ground state and does not depend on which level of the excited state the radiative transition occurs [11].

The decay time of the wide luminescence band, recorded at 15000 cm^{-1} , consists of two components, fast – 18 ns and slow – 2.15 ms . The slow and fast decay curves of this band are shown in Fig. 3. Sm^{2+} ions in some matrices have a complex interaction between $5d$ and $4f$ shells [10]. In the case of BaBrI: Sm^{2+} , luminescence of parity-allowed $4f^55d^1-4f^6$ transitions is observed at room temperature together with bands of parity-forbidden $4f^6-4f^6$ transitions from the lower excited state 5D_0 . At the same time, the $5d$ level can be thermally populated from the 5D_0 state, this is the reason the short and long components in decay are observed.

The decay curves of luminescence excited by laser radiation and recorded at 14600 cm^{-1} ($^5D_0-^7F_0$) and 15900 cm^{-1} ($^5D_1-^7F_0$) are presented in Fig. 4. All of the collected decay curves are reduced for comparison. The decay time of the $^5D_0-^7F_0$ band (14600 cm^{-1}) is 1.9 ms at temperature of 285 K and decay is exponential. When the sample is cooled, an increase in the decay time of luminescence is observed, with maximum of 4.8 ms at temperature of 25 K . Also, an increase in the luminescence rise time in the range of $35-55\text{ K}$ is observed. For the $^5D_1-^7F_0$ band (15900 cm^{-1}) the shape of the decay curve has a slight deviation from the exponential at low temperatures; the decay time was 3.1 ms at 7 K . At temperature of 195 K , the decay time of the $^5D_1-^7F_0$ transition was 0.55 ms . With decreasing temperature, the degree of thermal population of the $5d$ level decreases, and luminescence of $4f^6-4f^6$ transitions begins to prevail. At temperature of 7 K transitions from the upper excited 5D_1 level predominate in the luminescence spectrum because the probability of nonradiative relaxation $^5D_1-^5D_0$ decreases and the $^5D_1-^7F_J$ luminescent transitions are more probable relaxation path.

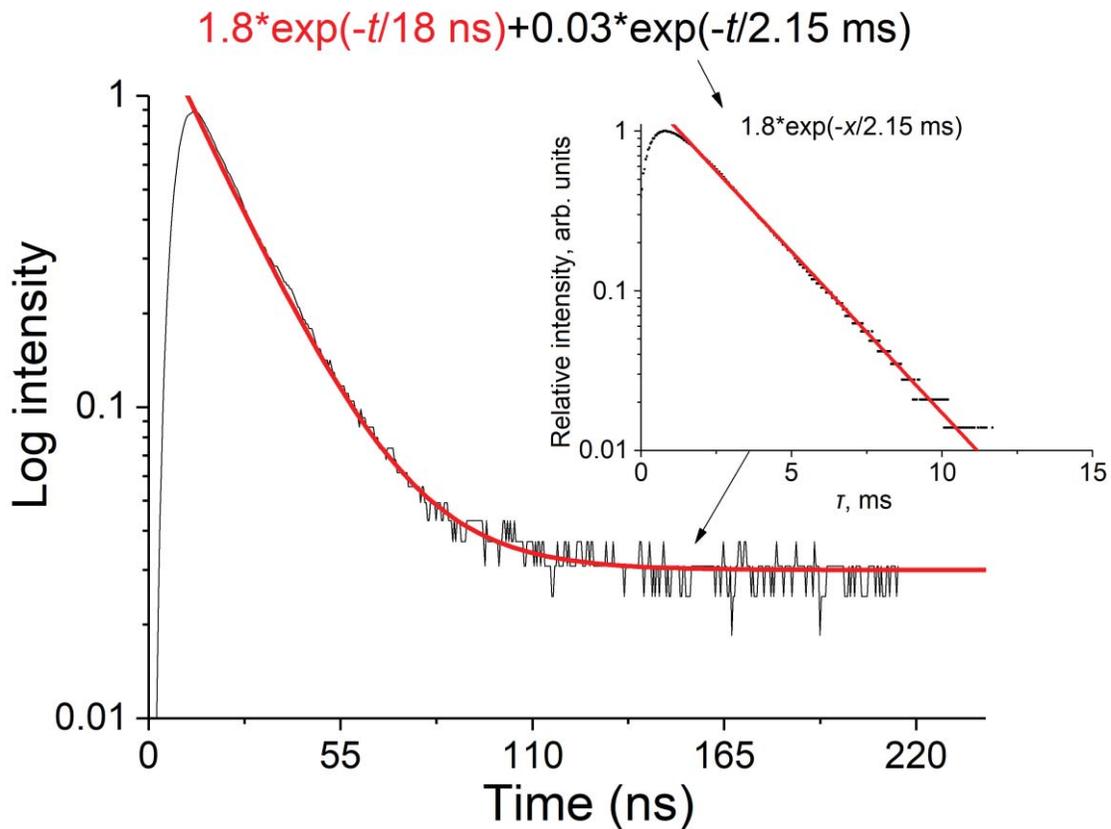


FIGURE 3. $4f^5 5d^1 - 4f^6$ luminescence decay curves of BaBrI: Sm^{2+} excited by nitrogen laser (337 nm) and recorded at 15000 cm^{-1}

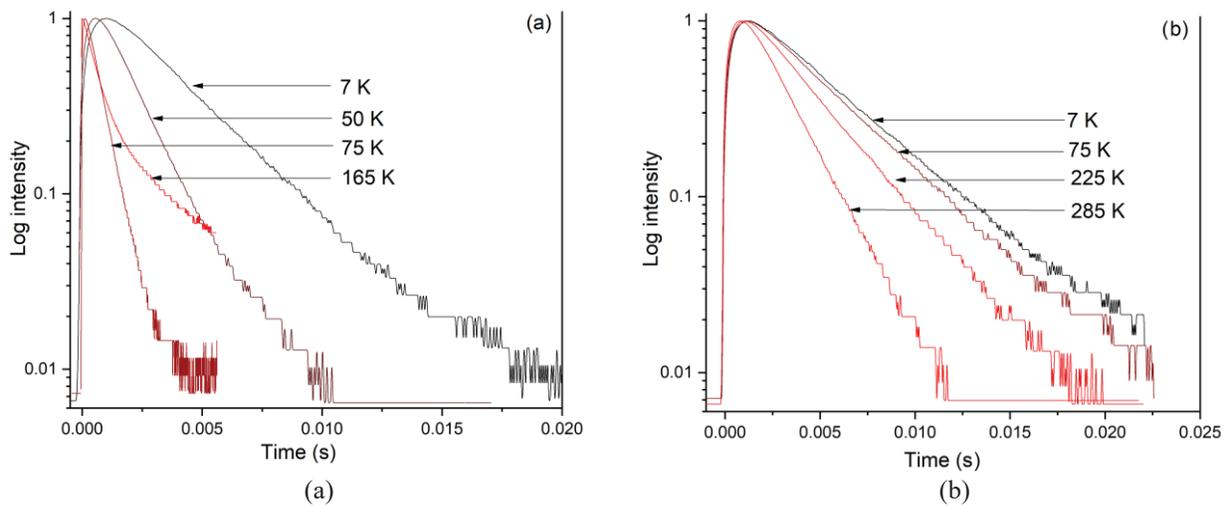


FIGURE 4. $^5\text{D}_0 - ^7\text{F}_0$ (a) and $^5\text{D}_1 - ^7\text{F}_0$ (b) luminescence decay curves of BaBrI: Sm^{2+} excited by nitrogen laser. Arrows indicate sample temperature

Afterglow Luminescence of BaBrI:Sm²⁺

BaBrI: Sm²⁺ crystals are colored by exposition to ultraviolet radiation at room temperature acquiring greenish color. Within an hour, the crystal returns its original color, while afterglow is observed in the region of 13000–17000 cm⁻¹. The afterglow spectrum is shown in Fig. 5. This afterglow is associated with 4f⁵5d¹–4f⁶ and 4f⁶–4f⁶ transitions of Sm²⁺.

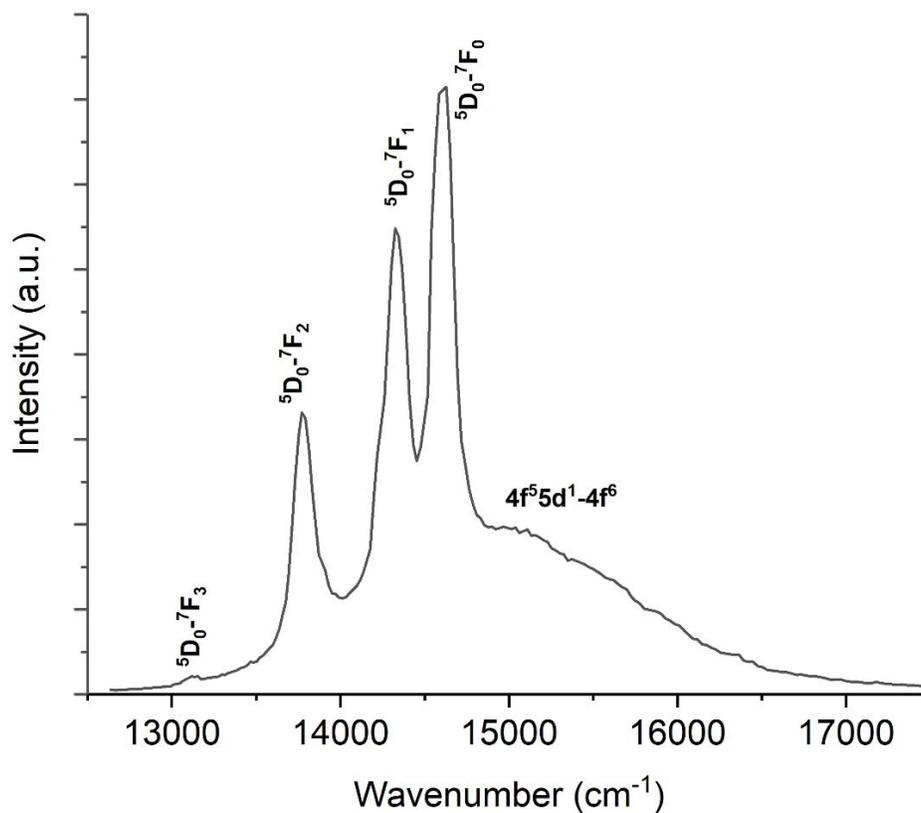


FIGURE 5. Afterglow luminescence spectra of BaBrI: Sm²⁺, irradiated at 34000 cm⁻¹ for 10 minutes

Figure 6 shows the results of measurements of the integrated intensity of the afterglow, which varies with the wavelength of light used to irradiate the crystal. The afterglow of Sm²⁺ ions is most efficiently excited in the region of 28000–43000 cm⁻¹, and has a peak in the region of 38400 cm⁻¹ close to the fundamental absorption edge, and also a peak at 32000 cm⁻¹ located near the edge of the short-wavelength absorption of Sm²⁺ ions.

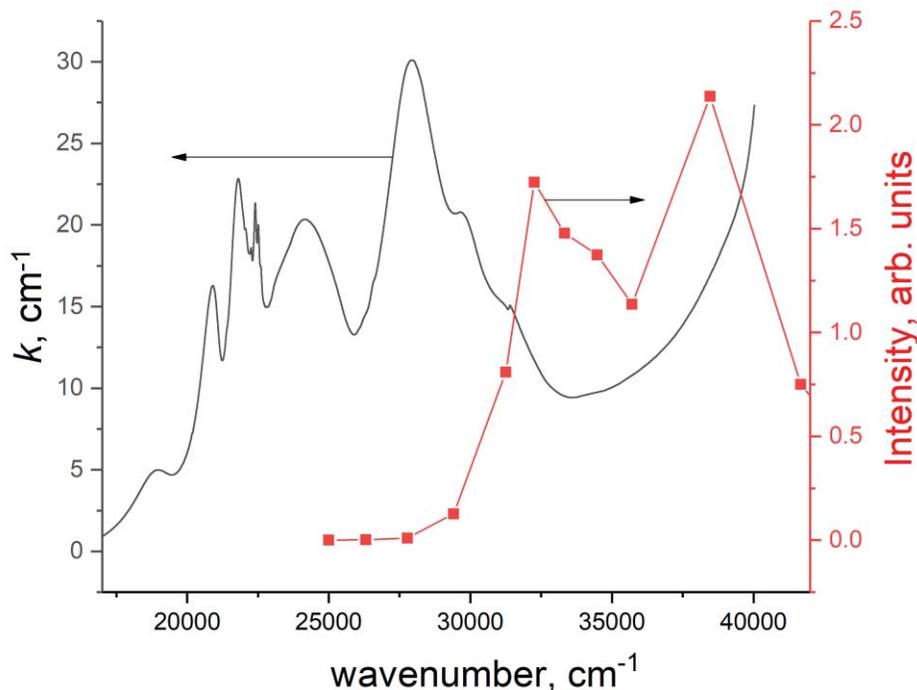


FIGURE 6. Integral intensity of the afterglow luminescence at 14600 cm^{-1} as a function of the wavelength of light used to irradiate the sample (red curve). Absorption spectra of BaBrI: Sm^{2+} at room temperature (black curve)

CONCLUSIONS

Studies of the luminescent properties of BaBrI: Sm^{2+} crystals showed that the luminescence spectrum contains bands of $4f^6-4f^6$ and $4f^55d^1-4f^6$ transitions of divalent samarium ions. Luminescence have a strong temperature dependence due to small energy gaps between the levels of the excited states of the 4f shell and the lower level 5d of the Sm^{2+} ions. A long afterglow was detected in crystals irradiated by ultraviolet. The photon energy threshold necessary for afterglow excitation was determined, which amounted to 28000 cm^{-1} . In this paper the scintillation properties of BaBrI: Sm^{2+} have not been studied, however, its use as a room temperature scintillator seems doubtful due to the presence of intense afterglow.

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REFERENCES

1. R. Shendrik, A. A. Shalaev, A. S. Myasnikova, A. Bogdanov, E. Kaneva, A. Rusakov, A. Vasilkovskiy, *J. Lumin.* **192**, 653–660 (2017).
2. A. A. Shalaev, A. I. Rusakov, R. Yu. Shendrik, A. K. Subanakov, Yu. V. Sokol’nikova, A. S. Myasnikova, *Fiz. Tv. Tela* **61**, 892–897 (2019) [*Phys. Solid State* **61**, 789–794 (2019)].
3. A. I. Rusakov, A. A. Shalaev, R. Yu. Shendrik, A. S. Myasnikova, A. K. Subanakov, *AIP Conference Proceedings* **2069**, 020002 (2019).

4. D. R. Schaart, H. T. van Dam, S. Seifert, R. Vinke, P. Dendooven, H. Löhner, F. J. Beekman, [Phys. Med. Biol.](#) **54**, 3501–3512 (2009).
5. P. Dorenbos, [Phys. Rev. B](#) **85**, 165107 (2012).
6. P. Pal, H. Hagemann, H. Bill, J. Zhang, [J. Lumin.](#) **161**, 323–329 (2015).
7. C. Wickleder, [J. Lumin.](#) **94-95**, 127–132 (2001).
8. Q. Zeng, N. Kilah, M. Riley, H. Riesen, [J. Lumin.](#) **104**, 65–76 (2003).
9. Z. Qinghua, P. Zhiwu, W. Shubing, S. Qiang, L. Shaozhe, [J. Phys. Chem. Solids](#) **60**, 515–520 (1999).
10. L. C. Dixie, A. Edgar, M. F. Reid, [J. Lumin.](#) **132**, 2775–2782 (2012).
11. H. V. Lauer Jr., F. K. Fong, [J. Chem. Phys.](#) **65**, 3108–3117 (1976).