

Effect of temperature on luminescence properties of Eu^{2+} -doped calcium chloroborate

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Calcium chloroborate $\text{Ca}_2\text{BO}_3\text{Cl}$ doped with Eu^{2+} ions is known as the promising phosphor for white LEDs. Recently, this material has attracted additional attention due to its very long persistent luminescence. In the present work, the luminescence properties of Eu^{2+} ions in $\text{Ca}_2\text{BO}_3\text{Cl}$ were studied for the first time at cryogenic temperatures. It is shown that with increasing temperature from 80 K (10 K) to 293 K, the maximum of the $\text{Eu}^{2+} 4f^65d \rightarrow 4f^7$ emission is shifted to shorter wavelengths from ~ 590 nm to 576 nm and the full width at half maximum of the emission band increases from 2185 to 2980 cm^{-1} . The blue shift of the Eu^{2+} emission maximum is ascribed to temperature induced population of higher energy $\text{Eu}^{2+} 4f^65d$ states. At 80 K, the decay time of the Eu^{2+} emission in $\text{Ca}_2\text{BO}_3\text{Cl}$ was found to be somewhat smaller than that recorded at 293 K (1.05 μs vs. 1.14 μs). Possible explanations for this unusual observation are also discussed.

Keywords: calcium chloroborate, europium, luminescence, defects.

Вплив температури на люмінесцентні властивості хлорборату кальцію, легованого Eu^{2+} .
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Хлороборат кальцію $\text{Ca}_2\text{BO}_3\text{Cl}$, легований іонами Eu^{2+} , відомий як перспективний люмінофор для білих світлодіодів. Останнім часом цей матеріал привертає до себе додаткову увагу через його дуже тривале післясвічення після припинення збудження. У цій роботі вперше досліджено люмінесцентні властивості іонів Eu^{2+} у $\text{Ca}_2\text{BO}_3\text{Cl}$ при низьких температурах. Показано, що з підвищенням температури від 80 К (10 К) до 293 К максимум випромінювання, яке обумовлено переходами $4f^65d \rightarrow 4f^7$ іонів Eu^{2+} , зміщується в короткохвильову область від ~ 590 нм до 576 нм, а півширина смуги випромінювання збільшується з 2185 до 2980 см^{-1} . Зсув максимуму випромінювання Eu^{2+} приписується температурному заселенню високоенергетичних станів $4f^65d$ -конфігурації Eu^{2+} . При 80 К час загасання випромінювання Eu^{2+} в $\text{Ca}_2\text{BO}_3\text{Cl}$, виявився трохи меншим, ніж при 293 К (1,05 мкс проти 1,14 мкс). Можливі пояснення цього незвичайного спостереження також обговорюються.

1. Introduction

In last decades, a number of Eu^{2+} doped alkaline-earth borates were presented as promising phosphors for white light emitting diodes (LEDs) and specific applications in medicine, particularly for phototherapy and bio-imaging [1, 2]. Some of these materials, e.g., $\text{Sr}_5(\text{BO}_3)_3\text{Cl}:\text{Eu}^{2+}$ [3] and $\text{Ca}_2\text{BO}_3\text{Cl}:\text{Eu}^{2+}$ [4], were also shown to exhibit persistent luminescence (PersL), i.e. long-time afterglow after ceasing excita-

tion. This type of luminescent materials has been the subject of increasing interest during the recent years due to numerous applications, such as luminous paints for road markers, safety signs and luminescent markers for bio-imaging [5, 6].

Among phosphors of borate family, calcium chloroborate $\text{Ca}_2\text{BO}_3\text{Cl}$ doped with Eu^{2+} ions is still one of the most attractive for researchers due to its favorable luminescent properties, and a possibility to improve

the luminescent characteristics by co-doping with other lanthanides [7, 8] or by modification of the anion sublattice [9]. According to Zak and Hanic [10], $\text{Ca}_2\text{BO}_3\text{Cl}$ crystallizes in a monoclinic structure with the $\text{P}2_1/c$ space group. The crystal structure of this compound can be described as a three-dimensional framework built up of calcium polyhedra. There are two types of calcium polyhedra, $\text{Ca(I)}\text{O}_4\text{Cl}_3$ and $\text{Ca(II)}\text{O}_5\text{Cl}_2$, with sevenfold coordination of the calcium atoms. The mean Ca–O bond length for the Ca(I) and Ca(II) polyhedra are 2.35 and 2.38 Å, respectively [10]. The boron atoms form isolated BO_3^{3-} groups.

The luminescent properties of Eu^{2+} ions in $\text{Ca}_2\text{BO}_3\text{Cl}$ were studied upon excitation in the range from vacuum ultraviolet (VUV) to visible region of the spectrum [11–14]. Eu^{2+} -doped $\text{Ca}_2\text{BO}_3\text{Cl}$ was found to show a broadband emission with a maximum at about 576 nm, which is due to the $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} ions. Since this emission is efficiently excited by photons in the 360–400 nm region, quite efficient white LEDs were fabricated by using a combination of (In,Ga)N chips emitting around 395 nm and $\text{Ca}_2\text{BO}_3\text{Cl}:\text{Eu}^{2+}$ as a yellow phosphor [13, 14]. Taking into account that the centroid shift and the crystal-field splitting of the $5d$ configuration of Eu^{2+} and Ce^{3+} ions in a compound are linearly related to one another [15], the luminescent characteristics of Ce^{3+} ions in $\text{Ca}_2\text{BO}_3\text{Cl}$ were used to interpret those of Eu^{2+} [16]. It was shown that the long-wavelength position of the Eu^{2+} emission in $\text{Ca}_2\text{BO}_3\text{Cl}$ ($\lambda_{\text{max}} = 576$ nm) is caused by two factors: the large crystal-field splitting of the Eu^{2+} $4f^65d$ configuration and the effect of covalence [16].

In 2013, the yellow PersL of Eu^{2+} -doped $\text{Ca}_2\text{BO}_3\text{Cl}$ after exposure to 254 nm light was reported [4]. It was also shown that co-doping with Dy^{3+} ions leads to an essential increase of the PersL duration. These authors proposed the conventional electron trapping-detrapping model as a possible mechanism of the PersL in this phosphor [4, 8]. Later, the vacuum referred binding energy (VRBE) diagram of $\text{Ca}_2\text{BO}_3\text{Cl}$ with location of Eu^{2+} and Ce^{3+} levels was constructed based on the combined theoretical and experimental results [16]. In particular, the VRBE diagram supported the involvement of the conduction band in the charging process, and a key role of electron traps in the appearance of the PersL. Very recently, the influence of substitution of Ca^{2+} with Sr^{2+} on the PersL

of Eu^{2+} -doped $\text{Ca}_2\text{BO}_3\text{Cl}$ has been studied [17]. The $\text{Sr}^{2+} \rightarrow \text{Ca}^{2+}$ substitution has been shown to result in an essential improvement of the PersL performance of the $\text{Ca}_2\text{BO}_3\text{Cl}:\text{Eu}^{2+}$, Dy^{3+} phosphor. In particular, the afterglow duration, defined as the time when the luminance decreases to a benchmark level of 0.32 mcd/m², was found to increase from 12 to 46 h. The distinct positive effect of the substitution was attributed to an increase in the concentration of the oxygen vacancies (i.e. electron traps) in the samples studied.

Despite the practical importance of $\text{Ca}_2\text{BO}_3\text{Cl}:\text{Eu}^{2+}$ phosphor, no research on the luminescence properties of Eu^{2+} ions in this compound has been done at cryogenic temperatures. In this paper, the results of the luminescence study of Eu^{2+} -doped $\text{Ca}_2\text{BO}_3\text{Cl}$ at 80 K are reported and discussed. They are anticipated to be useful for predicting and interpretation of the influence of different substitutional ions and anionic groups (Sr^{2+} , F^- , PO_4^{3-} etc.) on the luminescence properties of Eu^{2+} -doped $\text{Ca}_2\text{BO}_3\text{Cl}$.

2. Experimental

Two samples of the general formula $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{BO}_3\text{Cl}$ ($x = 0.001, 0.01$) were prepared by the solid state reaction method and used for luminescent measurements. The choice of Eu nominal concentrations was dictated also by the fact that optimal concentrations of Eu^{2+} in LED phosphors are typically larger than the ones in PersL materials. Indeed, the authors of [4, 8, 17] reported the longest afterglow in $(\text{Ca,Sr})_2\text{BO}_3\text{Cl}:\text{Eu}^{2+}$, Dy^{3+} upon doping with 0.1 at.% ($x = 0.001$) of Eu^{2+} , whereas the optimal concentration of Eu^{2+} in $\text{Ca}_2\text{BO}_3\text{Cl}:\text{Eu}^{2+}$ phosphors for LEDs was found to be 1–2 at.% [11, 13].

The synthesis procedure was as follows: starting mixtures of CaCO_3 , $\text{CaCl}_2 \cdot n\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and H_3BO_3 were fired at a temperature of about 400°C for 1 h and then at 850°C for 3 h in a nitrogen stream. The specimens were cooled, mortared to insure homogeneity and fired again at 850°C for 3 h in a reducing atmosphere of CO. Boric acid was used in excess (5 %) of the stoichiometric amount to compensate for B_2O_3 losses due to its high volatility at temperatures above 700°C .

The samples were characterized by X-ray diffraction (XRD) using Cu $\text{K}\alpha$ radiation (Rigaku Ultima IV). The results indicate

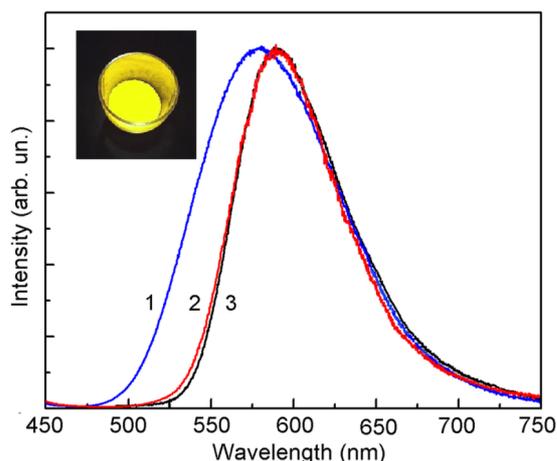


Fig. 1. Normalized emission spectra of $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{B}_2\text{O}_7\text{Cl}$ ($x = 0.001$) upon excitation with $\lambda_{exc} = 330$ nm at: (1) — 293 K; (2) — 80 K; (3) — 10 K. The image of the sample under excitation with a UV LED ($\lambda_{max} = 330$ nm) is presented as the insert.

that the final products were formed in a homogenous form and their XRD patterns were well matched with JCPDS File No. 70-0181 for $\text{Ca}_2\text{B}_2\text{O}_7\text{Cl}$. No impurity phases were detected in the XRD patterns. The emission and excitation spectra in UV-visible region were obtained at 80 and 293 K using a Fluorolog FL-3-22 (Horiba Jobin Yvon) spectrofluorometer equipped with a xenon lamp. The decay curves of the Eu^{2+} emission were recorded using the time correlated single photon counting method upon excitation with nanosecond LEDs with λ_{max} at 330 and 450 nm.

3. Results and discussion

At room temperature, both the samples exhibited an intense yellow luminescence, especially upon excitation in the 290–410 nm range, and the recorded emission spectra were found to be practically independent on the Eu^{2+} concentration and the excitation wavelength. Since the luminescence properties of the $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{B}_2\text{O}_7\text{Cl}$ ($x = 0.001, 0.01$) samples appeared very similar (but not identical), we will discuss mainly those of the sample with $x = 0.001$.

Fig. 1 shows the emission spectra of $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{B}_2\text{O}_7\text{Cl}$ ($x = 0.001$) recorded upon excitation with $\lambda_{exc} = 330$ nm at three different temperatures. At 293 K the emission band extends from 480 to 750 nm and has a maximum at about 576 nm (17361 cm^{-1}). It is known that this emission is due to the $4f^65d \rightarrow 4f^7$ transitions of Eu^{2+} ions occupying the two nonequivalent Ca(I,II) sites [11–13].

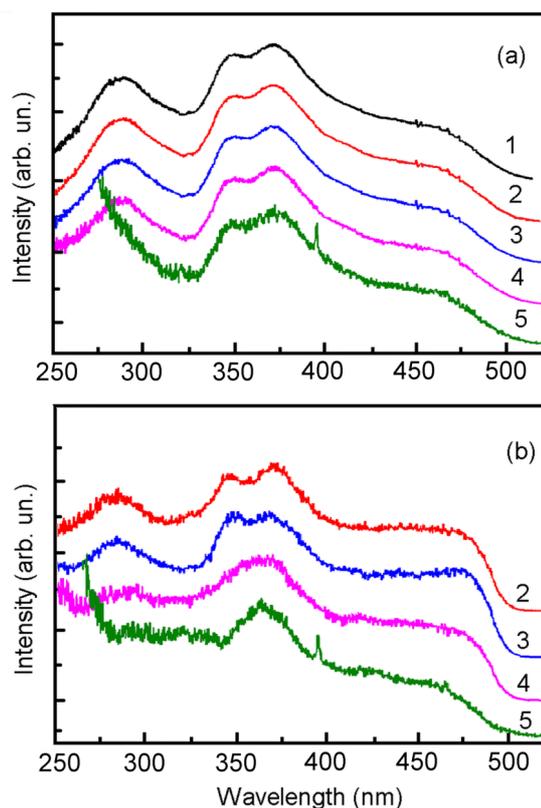


Fig. 2. Excitation spectra of $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{B}_2\text{O}_7\text{Cl}$ ($x=0.001$) recorded at (a) 293 K and (b) 80 K for the emission at (1) — 520 nm, (2) — 540 nm, (3) — 600 nm, (4) — 650 nm, (5) — 700 nm.

The full width at half maximum (FWHM) of this band amounts to 2980 cm^{-1} , which is comparable with the typical bandwidths ($800\text{--}3200 \text{ cm}^{-1}$) for Eu^{2+} -doped compounds [18]. At 80 K, the sample exhibits a red-shifted luminescence with a maximum at ~ 590 nm (16949 cm^{-1}). Besides, the emission band of the Eu^{2+} -doped $\text{Ca}_2\text{B}_2\text{O}_7\text{Cl}$ is strongly narrowed and its FWHM is only 2185 cm^{-1} . From Fig. 1 one can also see that further decrease in temperature to 10 K does not produce any appreciable changes in the position of the emission maximum and the FWHM value. We also note that the emission spectrum at 10 K was obtained earlier by some of us [12] upon excitation with synchrotron radiation ($\lambda_{exc} = 330$ nm), but has not been published. Thus, with increasing temperature from 10 to 293 K, the Eu^{2+} emission maximum is shifted towards shorter wavelengths by 412 cm^{-1} and the FWHM value of the emission band increases from 2185 to 2980 cm^{-1} .

The luminescence excitation spectra of the $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{B}_2\text{O}_7\text{Cl}$ ($x = 0.001$) sample at

80 and 293 K are compared in Fig. 2. The spectra recorded at 293 K consist of strongly overlapping bands at 288, 346, 370, ~ 390 nm and a shoulder at about 470 nm. These bands are evidently due to direct excitation of the Eu^{2+} ions via transitions from the $^8S_{7/2}$ ground state ($4f^7$ configuration) to the components of the Eu^{2+} $4f^65d$ configuration [11, 12]. It is worth noting that the optical absorption edge of $\text{Ca}_2\text{BO}_3\text{Cl}$ is known to locate at ~ 185 nm (6.70 eV) [12, 16], which is close to typical values for alkaline-earth borates [19]. From Fig. 2 one can see that the spectra are practically independent on the emission wavelength, although the spectrum for the emission at 700 nm contains also a narrow line at 395 nm. Besides, in contrast to other spectra in the 250–290 nm range, the emission intensity increases steadily with decreasing excitation wavelength. These features are due to the presence of some amount of Eu^{3+} ions. In the case of Eu^{2+} -doped materials, the coexistence of Eu^{2+} and Eu^{3+} is an almost inevitable situation, even if they were synthesized under strong reducing conditions [2, 20]. The emission and excitation spectra of Eu^{3+} in the $\text{Ca}_2\text{BO}_3\text{Cl}$ samples appeared very similar to those reported in detail previously [12]. Upon excitation in the 240–280 nm range, in addition to the intense and broad $4f^65d \rightarrow 4f^7$ emission band of Eu^{2+} ions, the emission spectra contain several groups of relatively narrow bands in the region of 580–710 nm. There is no doubt that these features are due to the $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) transitions of Eu^{3+} ions at the Ca sites. The corresponding excitation spectra are strongly dominated by a broad band extending from 220 nm to 290 nm with a maximum at about 242 nm, which was attributed to the $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ charge transfer (CT) transition [12]. Since the Eu^{3+} emission manifests in the obtained spectra only upon excitation into this Eu^{3+} CT band, it can be assumed that in the samples under study only a small fraction of the europium ions was stabilized in the +3 oxidation state. Nevertheless, the presence of even small amounts of Eu^{3+} is expected to influence the native point-defect concentrations in $\text{Ca}_2\text{BO}_3\text{Cl}$ [8, 16] and to contribute to inhomogeneous broadening of the Eu^{2+} emission band. Indeed, the presence of Eu^{3+} at the Ca^{2+} sites requires a charge compensation, which can be provided by an oxygen ion on a chlorine site ($\text{O}_{\text{Cl}'}$),

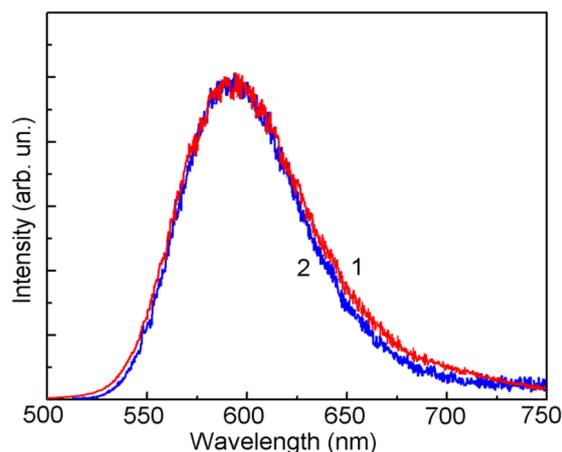


Fig. 3. Normalized emission spectra of $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{BO}_3\text{Cl}$ ($x = 0.001$) upon excitation with $\lambda_{exc} = 370$ nm (1) and 500 nm (2) at 80 K.

and thereby should promote the formation of $\text{O}_{\text{Cl}'}$ at a relatively high concentration.

It should be noted that since the $4f^7 \rightarrow 4f^65d$ excitation bands strongly overlap with each other and merge into one broad continuum, accurate determination of the position of the lowest energy $4f^65d$ state and Stokes shift for the Eu^{2+} emission in $\text{Ca}_2\text{BO}_3\text{Cl}$ is very difficult. The excitation spectra recorded at 80 K for the emissions at 540, 600 and 650 nm (Fig. 2, curves 2–4) have the same structure as those at 293 K. However, the superposition character of the excitation bands becomes more obvious, and the relative intensity of the band at ~ 470 nm increases compared to that at 293 K. Meanwhile, the emission spectra at 80 K remain practically unchanged upon varying the excitation wavelength. As an example, the emission spectra of $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{BO}_3\text{Cl}$ ($x = 0.001$) upon excitation into the most intense band at 370 nm and near the long-wavelength edge of the excitation spectra ($\lambda_{exc} = 500$ nm) are compared in Fig. 3. One can see that these spectra are similar to that recorded under 330 nm excitation (see Fig. 1, curve 2), but in the case of $\lambda_{exc} = 500$ nm, the FWHM of the emission band was estimated at ~ 2015 cm^{-1} , which is close, but somewhat smaller than those of the bands in the spectra recorded at $\lambda_{exc} = 330$ or 370 nm (~ 2185 cm^{-1}). This observation can be interpreted as a consequence of inhomogeneous broadening caused by the presence of point defects. The most probable candidates are chlorine and oxygen vacancies ($\text{V}_{\text{Cl}'}$, $\text{V}_{\text{O}^{\cdot\cdot}}$) and, as mentioned

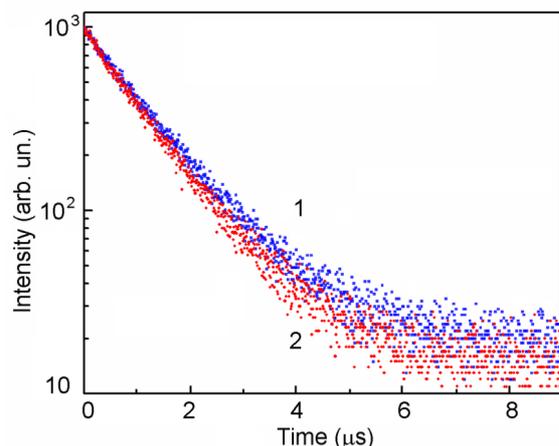


Fig. 4. Decay curves of the Eu^{2+} emission ($\lambda_{em} = 570$ nm) in $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{BO}_3\text{Cl}$ ($x = 0.001$) at (1) — 293 K and (2) — 80 K. The curves were obtained upon excitation at 450 nm.

above, oxygen ions on chlorine sites (O_{Cl}). These defects are expected to induce local crystal-field fluctuations leading to inhomogeneous broadening of the Eu^{2+} emission band.

The decay curves of the Eu^{2+} emission in $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{BO}_3\text{Cl}$ ($x = 0.001$) at 293 and 80 K are presented in Fig. 4. At 293 K, the decay curve deviates from a single exponential function, suggesting the multicenter nature of the emission band. The various fitting procedures resulted in slightly different parameters, but in an one-exponential approximation, the main stage of decay can be generally described by a time constant (τ) of 1.14 ± 0.02 μs . This decay time value agrees well with those reported previously for the Eu^{2+} emission in $\text{Ca}_2\text{BO}_3\text{Cl}$ at room temperature [12, 21] and is quite typical for $\text{Eu}^{2+} 5d \rightarrow 4f$ transitions in inorganic compounds [22]. The decay curves of the emissions in the 540–650 nm range appeared to be analogous to that obtained for $\lambda_{em} = 570$ nm.

At 80 K, the decay is also not strictly one-exponential, but, in a first approximation, it can be characterized by a decay time of $\tau = 1.05 \pm 0.02$ μs , which is somewhat smaller than that recorded at 293 K. In this context, it is worth noting that usually the decay time of $\text{Eu}^{2+} 5d \rightarrow 4f$ emission decreases with increasing temperature, due to an increase in the efficiency of nonradiative relaxation processes with temperature.

In the $\text{Ca}_{2(1-x)}\text{Eu}_{2x}\text{BO}_3\text{Cl}$ ($x = 0.001, 0.01$) samples, Eu^{2+} occupy two nonequivalent Ca(I,II) sites [11–14]. As mentioned in Introduction, the crystal structure of

$\text{Ca}_2\text{BO}_3\text{Cl}$ contains two types of Ca polyhedra: Ca(I) is surrounded by four oxygen ions and three chlorine ions, whereas Ca(II) is surrounded by five oxygen ions and two chlorine ions. Since the average Ca–O and Ca–Cl distances for the Ca(II) site (2.38 and 2.98 Å, respectively) are somewhat larger than those for the Ca(I) site (2.35 and 2.94 Å) [9, 10], and the optical electronegativity of the borate anions is higher than that of Cl^- , the weaker crystal-field splitting and smaller centroid shift of the $4f^6 5d$ configuration are expected for Eu^{2+} ions at the Ca(II) site as compared to the Ca(I) site. This should be accompanied by the blue shift of the lowest energy $4f^7 \rightarrow 4f^6 5d$ excitation band. But the spectral differences between the Eu^{2+} centers turned out to be too small to be detected in our experiments. In other words, the strong overlapping of the emission and excitation bands prevented selective excitation and detection of individual Eu^{2+} -related centers in the $\text{Ca}_2\text{BO}_3\text{Cl}$.

In a recent review paper [23], the temperature dependent luminescent properties of different Eu^{2+} -doped phosphors were analyzed. It has been concluded that some popular explanations for the blue shift of the Eu^{2+} emission maxima with increasing temperature are highly questionable. Among the most probable explanations, the following should be mentioned [23]:

1. A lower quenching temperature of the longer wavelength (low-energy) emission compared to its shorter wavelength counterpart.
2. An electron tunneling from the low-energy site to the high-energy site.
3. A decrease in crystal-field splitting and an increase in energy of $\text{Eu}^{2+} 4f^6 5d$ emitting state with increasing temperature as a result of thermal expansion of the crystal lattice.
4. A temperature induced population of higher energy $4f^6 5d$ states.

The first explanation generally assumes that only one of the two Eu^{2+} centers can participate in the luminescence process of Eu^{2+} -doped $\text{Ca}_2\text{BO}_3\text{Cl}$ at elevated temperatures. It is evident that this contradicts the experimental observations, since no temperature quenching process was observed in the 80–293 K range, and the $\text{Eu}^{2+} 4f^6 5d \rightarrow 4f^7$ luminescence in $\text{Ca}_2\text{BO}_3\text{Cl}$ is still quite efficient even at high temperatures up to 500 K [9, 13]. The second explanation suggests a sufficient wave-function overlapping for electron initial and final

states. It seems unlikely that this condition can be realized at such low concentrations of Eu^{2+} ions as in the samples under study. As mentioned above, the emission and excitation spectra of the samples with $x = 0.001$ and 0.01 appeared very similar, suggesting that the increased Eu^{2+} concentration does not influence significantly on the distribution of Eu^{2+} ions between the Ca(I) and Ca(II) sites, nor does it lead to the formation of Eu^{2+} - Eu^{2+} pairs. It should be also noted that this explanation (in our opinion, without proper justification) was used to interpret the blue shift of the emission maximum of Eu^{2+} -doped $\text{Ca}_2\text{BO}_3\text{Cl}$ by 12 nm with increasing temperature from 293 to 500 K [13]. On the contrary, we suggest that this shift may be associated with the combined effect of thermal quenching of the Eu^{2+} luminescence in $\text{Ca}_2\text{BO}_3\text{Cl}$, which, as reported, begins at ~ 350 K [9, 13], and thermal expansion of the crystal lattice. Undoubtedly, an increase in the unit cell size and distances between Eu^{2+} and ligand with increasing temperature can generally result in a blue shift of the Eu^{2+} emission band in $\text{Ca}_2\text{BO}_3\text{Cl}$, due to a decrease in both the crystal-field splitting of the $\text{Eu}^{2+} 4f^65d$ configuration and the nephelauxetic effect. The crystal-field splitting for Ce^{3+} is typically larger (by a factor of 1.30) than that for Eu^{2+} in the same compound [15], and no blue shift of the emission band was observed in Ce^{3+} -doped $\text{Ca}_2\text{BO}_3\text{Cl}$ in the 20–293 K range [16, 24]. Therefore, one can conclude that at least in this temperature region, thermal expansion of the crystal lattice does not influence significantly on the position of the Eu^{2+} emission maximum in $\text{Ca}_2\text{BO}_3\text{Cl}$.

At this stage of the study of Eu^{2+} -doped $\text{Ca}_2\text{BO}_3\text{Cl}$, the most plausible explanation for the blue shift of the Eu^{2+} emission maximum with increasing temperature from 80 to 293 K is the temperature induced population of higher energy $4f^6(^7F_J)5d$ states. Indeed, the thermal excitation from the lowest 7F_0 level into the energetically closely lying 7F_J levels ($J = 1, 2$) of the excited $4f^6(^7F_J)5d$ ($J = 0-6$) configuration can be responsible for the blue shift by ~ 400 cm^{-1} . Note, that this model was used earlier to interpret blue shifts of the Eu^{2+} emission maximum in some Eu^{2+} -doped ternary bromides [25] and alkaline earth siliconitrides [23]. In the 80–293 K range, the FWHM value of the Eu^{2+} emission band in $\text{Ca}_2\text{BO}_3\text{Cl}$ increases by 800 cm^{-1} ; furthermore, the position of its long-wavelength

edge (~ 750 nm) remains unchanged (see Fig. 1). This increase in the FWHM can be explained by a combined effect of enhancement of the electron-phonon coupling with temperature and the thermal population of the higher 7F_1 level within the excited $4f^6(^7F_J)5d$ configuration.

More difficult to interpret is the fact that at 80 K the decay time of the Eu^{2+} emission turned out to be somewhat shorter than at 293 K (1.05 μs vs 1.14 μs). In general, an increase in τ with temperature can be due to the so-called self-absorption effect [26], i.e. the luminescence reabsorption. Since the spectral overlap between the excitation and emission bands of Eu^{2+} ions in $\text{Ca}_2\text{BO}_3\text{Cl}$ increases with temperature (see Figs. 1 and 2), the reabsorption will also increase, which in principle can lead to a slight change in the measured decay time. However, taking into account the low concentration of Eu^{2+} in the samples under study, this effect is expected to be negligible. In accordance with the theoretical model [27], this unusual behavior can also be due to the thermal population of states for which the transition probability to the $\text{Eu}^{2+} ^8S_{7/2}$ ground state is lower than for the lowest energy $4f^65d$ state. By the way, this idea was firstly proposed by Meijerink and Blasse [28] to interpret an increase in the decay time of the Eu^{2+} emission with temperature in barium halosilicates $\text{Ba}_5\text{SiO}_4\text{X}_6$ ($\text{X} = \text{Cl}, \text{Br}$).

It is known that in some compounds, the high energy $^6P_{7/2}$ state of the $\text{Eu}^{2+} 4f^7$ configuration turns out to be involved in luminescence processes [18, 26, 28], and its thermal population at elevated temperatures can result in an increase in the decay time of Eu^{2+} emission with temperature. However, it is obviously not the case of $\text{Ca}_2\text{BO}_3\text{Cl}$. Indeed, regardless of the chemical composition of the compound, the $^6P_{7/2}$ state of Eu^{2+} is located at ~ 27600 cm^{-1} (362 nm). On the other hand, the position of the lowest energy $4f^6(^7F_0)5d$ state in $\text{Ca}_2\text{BO}_3\text{Cl}$ can be roughly estimated from the beginning of the long-wavelength edge of the excitation spectra as ~ 20000 cm^{-1} (500 nm). Therefore, in $\text{Ca}_2\text{BO}_3\text{Cl}$, the energy gap between the $^6P_{7/2}$ state and the lowest energy state of the $4f^65d$ configuration is 7600 cm^{-1} , which excludes the possibility of thermal population of $^6P_{7/2}$ state even at 500 K.

4. Conclusions

Calcium chloroborate $\text{Ca}_2\text{BO}_3\text{Cl}$ doped with Eu^{2+} ions is still the promising phosphor for white LEDs. Recently, this material has attracted additional attention because of its very long afterglow after ceasing the excitation and a possibility to improve the PersL characteristics by modification of the cation sublattice or by codoping with other lanthanides. In the present work, the luminescence properties of Eu^{2+} ions in $\text{Ca}_2\text{BO}_3\text{Cl}$ were studied for the first time at cryogenic temperatures. It is shown that with increasing temperature from 80 K (10 K) to 293 K, the maximum of the $\text{Eu}^{2+} 4f^65d \rightarrow 4f^7$ emission is shifted to shorter wavelengths from ~ 590 nm to 576 nm, and the full width at half maximum of the emission band increases from 2185 to 2980 cm^{-1} . The distinct shift of the Eu^{2+} emission maximum is ascribed to the temperature induced population of higher energy $\text{Eu}^{2+} 4f^65d$ states. At 80 K, the decay time of the Eu^{2+} emission was found to be somewhat smaller than at 293 K (1.05 μs vs. 1.14 μs). This observation may be caused by the thermal population of states for which the transition probability to the $\text{Eu}^{2+} {}^8S_{7/2}$ ground state is lower than for the lowest energy $4f^65d$ state, but its reliable interpretation requires additional studies. The results obtained are anticipated to be useful for predicting and interpretation of the influence of different substitutional ions and anionic groups on the luminescence properties of Eu^{2+} -doped $\text{Ca}_2\text{BO}_3\text{Cl}$.

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