

Luminescent properties and stability of Eu^{2+} ions in SrBPO_5 and $\text{SrAl}_2\text{B}_2\text{O}_7$

P.V.Pir, V.P.Dotsenko, N.P.Efryushina, Z.D.Klimenko

O.Bogatsky Physico-Chemical Institute,
National Academy of Sciences of Ukraine,
Lustdorfskaya Road 86, 65080 Odesa, Ukraine

Received July 31, 2006

Using the luminescence spectroscopy, the stability of Eu^{2+} ions in SrBPO_5 has been shown to exceed significantly that in $\text{SrAl}_2\text{B}_2\text{O}_7$. The luminescence spectrum of Eu^{2+} in SrBPO_5 and $\text{SrAl}_2\text{B}_2\text{O}_7$ consists of a broad band with a maximum at 390 and 490 nm, respectively. In contrast to SrBPO_5 , the stabilization of Eu^{2+} ions in $\text{SrAl}_2\text{B}_2\text{O}_7$ requires an annealing in reducing medium. It is supposed that this is caused by the difference in the effectiveness of the excess charge compensating processes for Eu^{3+} which can be quantified by the formal volume per oxygen atom (V_O) in the compound structure.

Методами люминесцентной спектроскопии показано, что устойчивость ионов Eu^{2+} в SrBPO_5 существенно выше, чем в $\text{SrAl}_2\text{B}_2\text{O}_7$. Спектр люминесценции Eu^{2+} в SrBPO_5 и $\text{SrAl}_2\text{B}_2\text{O}_7$ представляет собой широкую полосу с максимумом при 390 и 490 нм, соответственно. В отличие от SrBPO_5 для стабилизации ионов Eu^{2+} в $\text{SrAl}_2\text{B}_2\text{O}_7$ требуется отжиг в восстановительной среде. Предполагается, что это обусловлено различием в эффективности процессов компенсации избыточного заряда Eu^{3+} , критерием которой может служить величина формального объёма (V_O), приходящегося на один атом кислорода в структуре соединения.

The effect of crystal structure on stabilization of elements in a particular electronic configuration (oxidation state) is among the most important issues in the physical chemistry of imperfect crystals. It is supposed [1–3] that it is just the element coordination polyhedron nature that plays a key role defining the stability of its oxidation state, i.e. the stability of an oxidation state depends primarily on the inherent features of metal-ligand bonds. A review of chemical and physical experimental techniques used to determine the oxidation state of transition metals has been given in [4]. In the case of lanthanide compounds, the most informative method is luminescence spectroscopy, since the appropriate calculation approaches and analysis procedures are well developed. One drawback to luminescence spectroscopy is that, in contrast to chemical methods, it allows only qualitative evalu-

ation of the concentration ratio of lanthanides being in different oxidation states, for example, $\text{Ln}^{2+}/\text{Ln}^{3+}$.

Recently, some of us have found that the stability of Ln^{2+} ions ($\text{Ln} = \text{Eu}, \text{Yb}$) increases significantly in the sequence $\text{Sr}_3(\text{BO}_3)_2$, $\text{Sr}_2\text{B}_2\text{O}_5 < \text{SrB}_2\text{O}_4$, $\text{SrB}_6\text{O}_{10}$, $\text{Sr}_2\text{B}_5\text{O}_9\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) $< \text{SrB}_4\text{O}_7$ [5]. It was shown that the stability of Ln^{2+} in strontium borates depends on the borate anions surrounding it and on the effectiveness of the Ln^{3+} excess charge compensation, which can be quantified by the formal volume per oxygen atom (V_O), in the borate structure. V_O can be determined as

$$V_O = V/Zn, \quad (1)$$

where V is the unit cell volume of the compound; Z , the number of formula units per unit cell; and n , the number of oxygen

atoms per formula unit of the compound. If the structural data are unknown, the values of V_O can be determined from the densities of compounds or solid solutions.

Within the strontium borate family, the value of V_O increases from 14.33 Å³ for SrB₄O₇ to ~25 Å³ for Sr₂B₂O₅, Sr₃(BO₃)₂ [5]. It is supposed that the relatively large V_O value for Sr₂B₂O₅, Sr₃(BO₃)₂ promotes the formation and diffusion of the interstitial oxygen atoms and therefore reduces the stability of Ln²⁺ ions in these compounds. The purpose of this work was to study the possibility to use V_O to predict the stability of Ln²⁺ ions in more complex strontium compounds.

Strontium borophosphate SrBPO₅ ($V_O = 17.92$ Å³) and a cubic modification (c) of strontium aluminoborate SrAl₂B₂O₇ ($V_O = 25.87$ Å³) were used as the investigation objects. Since V_O for SrAl₂B₂O₇ is close to those for Sr₂B₂O₅ and Sr₃(BO₃)₂, the stability of Ln²⁺ ions in SrAl₂B₂O₇ (c) is expected to be low. The smaller value of V_O for SrBPO₅ evidences a higher atomic packing density in this compound. It allows one to expect that the Ln²⁺ stability in SrBPO₅ is relatively high.

It is widely accepted that the crystal structure of MBPO₅ is similar to that of mineral stillwellite CeBO(SiO₄) described in detail in [6]. In the crystal structure of CeBO(SiO₄), each BO₄ group is connected with two SiO₄ groups and has two common edges with a cerium polyhedron. The Ce³⁺ ions are surrounded by nine oxygen ions which belong to the borosilicate radical. It is important to note that in the stillwellite structure, the anions of different nature (SiO₄ and BO₄) are connected with each other by oxygen bridges. This is a most prominent structural feature of stillwellite (and SrBPO₅, too), because in compounds with mixed oxide anions the anion groups of various nature are usually isolated. It is also known that the luminescence spectrum of Eu²⁺ ions in SrBPO₅ consists of a relatively broad band with a maximum at $\lambda_{max} = 390$ nm, which is due to the $4f^65d \rightarrow 4f^7$ transition [7, 8].

It is known that strontium aluminoborate SrAl₂B₂O₇ crystallizes in two modifications, namely, a hexagonal (h) phase and a cubic (c) one [9,10]. The structure of hexagonal modification consists of [Al₂O(BO₃)₂]²⁻ layers made up of corner-sharing Al₂O₇ and BO₃ groups. The Sr atoms, located between these layers, are

surrounded by six oxygen atoms at a distance of 2.547 Å and six ones at a distance of 3.292 Å [10]. The emission spectrum of Eu²⁺ ions in SrAl₂B₂O₇ (h) solid solutions prepared in a H₂ flow consists of a broad band with a maximum at $\lambda_{max} = 415$ nm, which is due to the $4f^65d \rightarrow 4f^7$ transition [10]. To our knowledge, the data on the crystal structure and luminescent properties of SrAl₂B₂O₇ (c) are absent in literature.

Eu-doped SrBPO₅ has been prepared by solid-state reaction. The starting materials were special purity grade H₃BO₃, SrCO₃, Eu(NO₃)₃·mH₂O and (NH₄)₂HPO₄ (chemical purity grade). The blended reactants were heated at 400°C for 1 h and then at 900°C for 9 h in air. To prepare SrAl₂B₂O₇ (c) activated with Eu, stoichiometric amounts of special purity grade Sr(NO₃)₂, H₃BO₃, Al(NO₃)₃·9H₂O and Eu₂O₃ were dissolved in HNO₃ (chemical purity grade) followed by evaporation to dryness. After thorough grinding and homogenization, the mixture was heat-treated at 650°C for 40 min. After cooling to room temperature and homogenization, the mixture was fired again at 900–920°C for 10 h. In both cases, the amount of Eu-containing reagent in the starting mixture corresponded to a 0.01 mole fraction of Eu in the final product.

The synthesized samples were checked by X-ray diffraction (XRD) using a DRON-0.5 diffractometer operated with Ni-filtered Cu K_α radiation. The XRD patterns of the samples agreed with JCPDS data: No.18-1270 (SrBPO₅), No.47-0182 (SrAl₂B₂O₇ (c)). No impurity phases were detected within the present experimental sensitivity. The luminescence emission and excitation spectra were recorded for $\lambda > 240$ nm using a SDL-1 spectrometer equipped with a DKSSh 150 xenon arc lamp. The diffuse reflectance spectra were recorded using a Perkin-Elmer LAMBDA 9 spectrometer. All the measurements were carried out at room temperature. The luminescence spectrum of the Sr_{1-x}Eu_xBPO₅ ($x = 0.01$) solid solution upon excitation at $\lambda_{exc} = 272$ nm is presented in Fig. 1. The choice of λ_{exc} is caused by the fact that both Eu²⁺ and Eu³⁺ ions show an efficient luminescence upon excitation in this region. It is seen that in the spectrum, a relatively broad band with a maximum at $\lambda_{max} = 390$ nm predominates, which is due to the Eu²⁺ $4f^65d \rightarrow 4f^7$ transition [8]. Besides, there is a group of bands in the 580–700 nm range. It is evident that these fea-

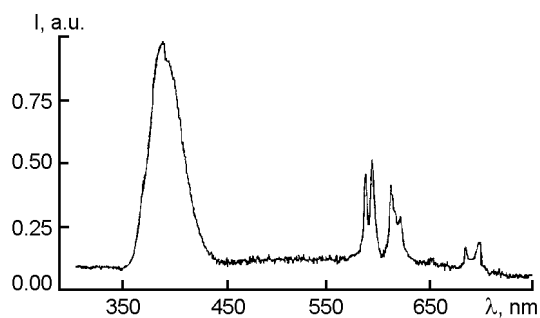


Fig. 1. Luminescence spectrum of $\text{Sr}_{1-x}\text{Eu}_x\text{BPO}_5$ ($x = 0.01$) solid solution upon excitation at $\lambda_{exc} = 272$ nm.

tures are due to the $4f \rightarrow 4f$ transitions of Eu^{3+} ions. The most intense bands at 588 and 594 nm correspond to the ${}^5D_0 \rightarrow {}^7F_1$ transition. The excitation spectrum of this luminescence consists of a broad band at 200–290 nm, which is caused by a charge transfer transition from oxygen $2p$ orbitals to $4f^6$ orbitals of Eu^{3+} ions. The Eu^{2+} luminescence ($\lambda_{max} = 390$ nm) excitation spectrum consists of a broad band extending from 240 nm to 370 nm. Its maximum is at $\lambda_{max} = 305$ nm. This spectrum corresponds to that reported in [8]. Thus, as can be seen from Fig. 1, the $\text{Sr}_{1-x}\text{Eu}_x\text{BPO}_5$ ($x = 0.01$) solid solution prepared in air contains both Eu^{2+} and Eu^{3+} ions.

Fig. 2 illustrates the effect of additional annealing in a reducing atmosphere (CO) at 900°C for 3 h on the luminescence spectrum of $\text{Sr}_{1-x}\text{Eu}_x\text{Al}_2\text{B}_2\text{O}_7$ ($x = 0.01$) solid solution. The luminescence spectrum of the as prepared sample (curve 1) contains several groups of bands in the 580–700 nm range, corresponding to the ${}^5D_0 \rightarrow {}^7F_j$ transitions of Eu^{3+} . The excitation spectrum of this luminescence (see Fig. 3, curve 1) consists of a broad, intense band with a maximum at $\lambda_{max} \approx 248$ nm and a number of lower intensity bands at 363, 382, 394, 414, and 465 nm. It is obvious that the dominating band is due to a charge transfer transition from oxygen $2p$ orbitals to $4f^6$ orbitals of Eu^{3+} ions, whereas the bands in the 360–470 nm region are caused by the ${}^7F_0 \rightarrow {}^5D_4$, ${}^5G_{2,6}$, 5L_6 , 5D_3 , 5D_2 transitions. Note that no change of the spectrum is observed when varying λ_{exc} . In other words, no evidence of Eu^{2+} luminescence in the as-prepared sample is found.

As is seen from Fig. 2, additional annealing in a reducing atmosphere results in a relatively broad band in the range 450–560 nm with a maximum at $\lambda_{max} \approx 490$ nm

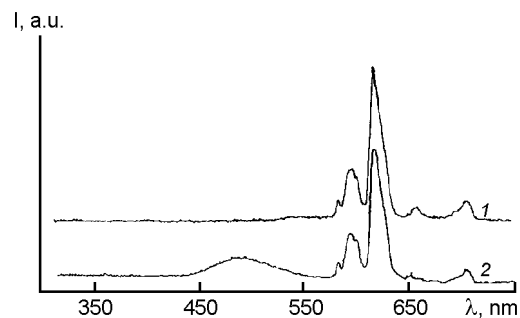


Fig. 2. Effect of additional annealing in a reducing atmosphere of CO at 900°C for 3 h on the luminescence spectrum of $\text{Sr}_{1-x}\text{Eu}_x\text{Al}_2\text{B}_2\text{O}_7$ ($x = 0.01$) solid solution at $\lambda_{exc} = 272$ nm. (1), as-prepared sample; (2), "reduced" sample.

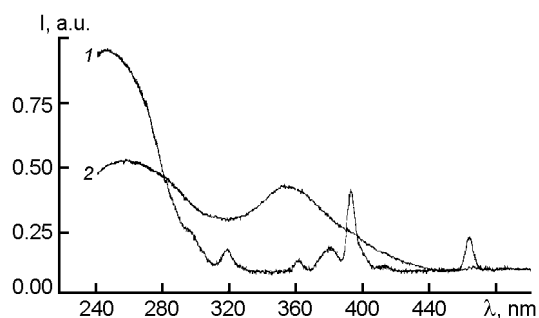


Fig. 3. Excitation spectra of $\text{Sr}_{1-x}\text{Eu}_x\text{Al}_2\text{B}_2\text{O}_7$ ($x = 0.01$) for the luminescence at $\lambda_{em} = 614$ nm (1) and 482 nm (2).

in the luminescence spectrum, while the relative intensity of the bands at 580–700 nm reduces. The excitation spectrum for the $\lambda_{max} = 490$ nm luminescence (see Fig. 3, curve 2) consists of two broad bands with maxima at 260 and 355 nm. Since undoped $\text{SrAl}_2\text{B}_2\text{O}_7$ (c) has no absorption bands in this region, the bands at 260 and 355 nm should be attributed to the $4f^7 \rightarrow 4f^65d$ transitions of Eu^{2+} ions. Such a spectrum is typical for Eu^{2+} ions in many crystals and glasses and it can be considered as a result of transitions from the $4f^7({}^8S_{7/2})$ ground state to the e_g and t_{2g} crystal field components of the $4f^65d$ configuration of Eu^{2+} ions. Thus, it follows from Fig. 2 that additional annealing of the as-prepared $\text{Sr}_{1-x}\text{Eu}_x\text{Al}_2\text{B}_2\text{O}_7$ ($x = 0.01$) in a reducing atmosphere results in the reduction of some amount of Eu^{3+} .

It is to note also that the maximum of the $\text{Eu}^{2+} 4f^65d \rightarrow 4f^7$ luminescence (λ_{max}) in $\text{SrAl}_2\text{B}_2\text{O}_7$ (c) is shifted towards longer wavelengths as compared to that of hexagonal $\text{SrAl}_2\text{B}_2\text{O}_7$ modification (for which $\lambda_{max} =$

415 nm [10]) and lies between the λ_{max} values for SrB_4O_7 (367 nm), $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ (420 nm) and $\text{Sr}_3(\text{BO}_3)_2$ (580 nm), $\text{Sr}_2\text{Mg}(\text{BO}_3)_2$ (590 nm) [11]. It is known that the spectral position of λ_{max} depends mainly on the ionicity of the metal-ligand bond and splitting of the $\text{Eu}^{2+} 4f^6 5d$ -configuration due to crystal field [11]. In view of lack of the detailed structural data for $\text{SrAl}_2\text{B}_2\text{O}_7$ (c) it is impossible to determine now the factors causing the λ_{max} shift to longer wavelengths when passing from hexagonal modification of $\text{SrAl}_2\text{B}_2\text{O}_7$ to cubic one.

From the results presented, one can conclude that, in contrast to SrBPO_5 , the stabilization of Eu^{2+} ions in $\text{SrAl}_2\text{B}_2\text{O}_7$ (c) requires a reducing atmosphere, i.e. the stability of Eu^{2+} ions in $\text{SrAl}_2\text{B}_2\text{O}_7$ (c) is lower than in SrBPO_5 . This can be explained by the difference in the effectiveness of the charge compensating mechanism for Eu^{3+} , which can be quantified by the formal volume per oxygen atom (V_O) in the compound

structure. The luminescence spectrum of Eu^{2+} ions in $\text{SrAl}_2\text{B}_2\text{O}_7$ (c) consists of a broad band with a maximum at 490 nm, which is due to the $4f^6 5d \rightarrow 4f^7$ transition.

References

1. Yu.M.Kiselev, *Zh. Neorg. Khim.*, **43**, 759 (1998).
2. Yu.M.Kiselev, Yu.D.Tretyakov, *Usp. Khim.*, **68**, 401 (1999).
3. Yu.M.Kiselev, *Zh. Neorg. Khim.*, **47**, 540 (2002).
4. Yu.M.Kiselev, *Zh. Neorg. Khim.*, **43**, 2010 (1998).
5. P.V.Pir, V.P.Dotsenko, N.P.Efryushina et al., *Inorg. Mater.*, **42**, 901 (2006).
6. A.A.Voronkov, Yu.A.Pyatenko, *Kristallografiya*, **12**, 258 (1967).
7. Q.Su, H.Liang, T.Hu et al., *J. Alloys. Comp.*, **344**, 132 (2002).
8. A.Karthikeyani, R.Jagannathan, *J. Luminescence*, **86**, 79 (2000).
9. J.F.MacDowell, *J. Am. Ceram. Soc.*, **73**, 2287 (1990).
10. F.Lucas, S.Jaulmes, M.Quarton et al., *J. Phys. Chem. Solids*, **150**, 404 (2000).
- 11 P.Dorendos, *J. Luminescence*, **104**, 239 (2003).

Люмінесцентні властивості та стійкість іонів Eu^{2+} у SrBPO_5 і $\text{SrAl}_2\text{B}_2\text{O}_7$

П.В.Пір, В.П.Доценко, Н.П.Єфрюшина, З.Д.Кліменко

Методами люмінесцентної спектроскопії показано, що стійкість іонів Eu^{2+} у SrBPO_5 істотно вища, ніж у $\text{SrAl}_2\text{B}_2\text{O}_7$. Спектр люмінесценції іонів Eu^{2+} у SrBPO_5 і $\text{SrAl}_2\text{B}_2\text{O}_7$ являє собою широку смугу з максимумом відповідно при 390 і 490 нм. На відміну від SrBPO_5 , для стабілізації іонів Eu^{2+} у $\text{SrAl}_2\text{B}_2\text{O}_7$ потрібен відпал у відновлюючому середовищі. Припускається, що це обумовлено відмінностями у ефективності процесів компенсації надлишкового заряду Eu^{3+} , критерієм якої може служити величина формального об'єму (V_O), на один атом кисню у структурі сполуки.