ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (Ph.D.) on the educational program 8D07104 - Chemical technology of inorganic substances

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on the topic: "Synthesis of luminescent materials in the $R_2O_3 – MeO – M_2O – B_2O_3$ system (R = Sc, Y, Ce, Eu, Tb, Yb; Me = Sr, Ba; M = Na, K)"

General overview of the work. The dissertation is devoted to the development of new luminescent compounds based on rare-earth borates. Various approaches to the synthesis of compounds in the $R_2O_3 – MeO – M_2O – B_2O_3$ system were investigated, producing both fine-crystalline powders and bulk crystals. Optimal conditions for synthesis and doping were determined, as well as the influence of the crystal structure features of $KSrY(BO_3)_2$ and $NaBaSc(BO_3)_2$ on their luminescent properties.

Relevance of the research topic. The current generation of LED lamps follows the principle of gas-discharge devices, in which ultraviolet (UV) radiation is first generated, then used to excite the phosphor, followed by re-emission in the visible light range. The advantages of LED lighting lie in its higher energy efficiency and environmental friendliness. Further optimization of LED performance involves the search for more efficient phosphors capable of generating visible light with minimal losses. In the $R_2O_3 – MeO – M_2O – B_2O_3$ system, a family of complex borates with the general formula $MMeR(BO_3)_2$ has been identified. These compounds exhibit luminescent properties and have attracted attention as host matrices for the development of new luminescent materials. The crystal structure of these borates provides optimal distances between luminescent centers, which, in turn, leads to a high luminescence yield. In addition, their relatively low synthesis temperature and excellent mechanical and chemical stability make them promising candidates for use as host matrices in the production of LED and PDP devices.

Degree of Development of the Topic. The aim of this dissertation is to obtain new phosphors based on borate matrices $NaBaSc(BO_3)_2$ and $KSrY(BO_3)_2$ and to study the relationship between their crystal structure and luminescent properties.

Research objectives:

1. Solid-state and flux synthesis of compounds based on alkali and rare-earth borates.
2. Determination of the phase composition and structural characteristics of the synthesized compounds depending on the cationic composition and type/concentration of the dopant impurity.
3. Investigation of the luminescent and colorimetric properties of the obtained compounds.
4. Determination of the synthesis procedure and optimal phosphor composition for creating a prototype LED matrix.

Subject of the study: Solid-state and flux synthesis of borates containing alkali, alkaline-earth, and rare-earth ions, as well as the investigation of their morphology, phase composition, and luminescent properties.

Methods of investigation: Solid-state and flux synthesis, X-ray structural and phase analyses, scanning electron microscopy with energy-dispersive spectroscopy, thermal analysis, photoluminescence measurements.

Scientific novelty:

- Doped borate compounds were synthesized using solid-state and flux methods. The conditions (temperature and time regimes) under which the solid-state reactions provide the maximum yield of the target product were determined.
- The CIE chromaticity diagram for $KSrY_{0.1}Tb_{0.9}(BO_3)_2$ and $KSrY_{0.9}Tb_{0.1}(BO_3)_2$ samples synthesized by methods I, II, and III and excited at 375 nm showed that samples obtained by methods I and II emit in the green range, while method III shifts the emission toward the blue range. By changing the synthesis method, the emission color can be controlled, covering the spectrum from green to blue.
- A prototype LED based on the phosphor $KSrY(BO_3)_2:0.2Eu^{3+}$ was developed and combined with a UV LED lamp. At a current of 421 mA and a voltage of 3.86 V, the LED emits bright red light with the following characteristics: (x = 0.2570, y = 0.1691, color rendering index Ra = 52.9, purity = 49.6%).

Theoretical significance lies in establishing the crystal-chemical features of the formation of new borate compounds containing cations of valences I, II, and III, as well as revealing the influence of synthesis conditions on the structural and luminescent properties of the obtained compounds. These results expand fundamental understanding of phase formation mechanisms and luminescence in borate matrices.

The practical significance of the study is that the established synthesis conditions allow obtaining materials with predetermined spectral characteristics, phase purity, and controllable structural parameters. This ensures their potential use as components in luminescent optical systems, photonic devices, and other applied technologies.

Scientific novelty of the study:

- A series of new families of borate compounds containing cations of valences I, II, and III has been investigated.
- Crystal-chemical principles for forming stable structures involving alkali, alkaline-earth, and rare-earth elements have been established, enabling targeted design of matrices with specified compositions and concentrations of luminescent centers.

Main provisions submitted for defense:

- Among the synthesis methods used, a monotonic change of the unit cell parameter (β-angle) in the solid solutions $KSr(Y,Tb)(BO_3)_2$ depending on the sample composition is ensured only by annealing in a hydrogen atmosphere followed by slow cooling at a rate of 5°C/hour.

- In the studied borates $KSr(Y,Tb)(BO_3)_2$, the maximum terbium luminescence intensity at the wavelength of 552 nm is observed for the sample with composition $KSrY_{0.9}Tb_{0.1}(BO_3)_2$, obtained by solid-state synthesis followed by annealing in a hydrogen atmosphere and slow cooling at 5°C/hour.
- Changing the cooling rate after annealing in the hydrogen atmosphere for samples $KSrY_{0.1}Tb_{0.9}(BO_3)_2$ and $KSrY_{0.9}Tb_{0.1}(BO_3)_2$ leads to a shift in the luminescence color under UV excitation (λ_ex = 375 nm) from the green to the blue spectral region.

The main results of the dissertation research were published in 9 scientific papers, including:

- One article published in a peer-reviewed scientific journal indexed in the first quartile (Q1) of the Web of Science database. The doctoral candidate's contribution involved conducting experimental work on the synthesis of $KSrY(BO_3)_2$: Tb^{3+}, Tb^{4+} crystals using solid-phase and solution-melt synthesis methods with KF solvent, as well as participating in sample characterization and data interpretation.
- One article published in a peer-reviewed scientific journal indexed in the first quartile (Q1) of the Web of Science database. The doctoral candidate's contribution involved conducting experimental work on the synthesis of $K_7MIn_{2-x}Yb_x(B_5O_{10})_3$ (M = Ca, Sr, Ba; x = 0…2) crystals.
- Two articles published in a journal recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan. The doctoral candidate's contribution included conducting experimental work on the synthesis of $KSrY(BO_3)_2$: Ce^{3+} crystals and compounds formed in the $YbBO_3$-$GaBO_3$ system, participating in physicochemical studies, and interpreting the obtained results.
- One patent issued by the National Institute of Intellectual Property of the Republic of Kazakhstan for a utility model, related to the development of a synthesis method for luminescent materials based on a complex borate doped with terbium and europium ions. The doctoral candidate's contribution involved conducting the experimental part of the research.
- Four abstracts presented at international conferences and symposia. The doctoral candidate's role in preparing publications included conducting experimental research on the synthesis of crystals and participating in physicochemical analysis.

The following conclusions were made based on the results of the dissertation research:

1. The results of X-ray phase analysis (XPA) and crystal structure refinement showed that $NaBaSc(BO_3)_2$ and its doped compounds ($NaBaSc_{1-a-b}(BO_3)_2$: aTb^{3+}, bEu^{3+}) are isostructural to $KBaY(BO_3)_2$, isotypic with the mineral bütschliite $K_2Ca(CO_3)_2$, and crystallize in the trigonal system with the space group R3¯\bar{3}3¯m; $KSrY(BO_3)_2$ and its mono- and co-doped compounds ($KSrY_{1-a-b}(BO_3)_2$: aTb^{3+}, bYb^{3+} (a = 0.05; b = 0.02, 0.05, 0.07) and $KSrY_{1-x}(BO_3)_2$: xCe^{3+} (x = 0.03, 0.05, 0.07)) crystallize in the monoclinic space group $P2_1/m$.

2. The synthesis of solid solutions $KSrY_{1-x}Tb_x(BO_3)_2$ was carried out using two different methods: solid-state synthesis and flux growth with KF as the solvent. The obtained samples contain Tb ions in both Tb^{3+} and Tb^{4+} oxidation states.

3. It was established that among the applied synthesis conditions, only annealing in a hydrogen atmosphere followed by slow cooling at a rate of 5 °C/h provides a monotonic change of the β angle in the structure of $KSr(Y,Tb)(BO_3)_2$ solid solutions depending on the terbium concentration.

4. It was shown that the highest intensity of green terbium luminescence (λ = 552 nm) is observed for the sample with composition $KSrY_{0.9}Tb_{0.1}(BO_3)_2$ obtained by solid-state synthesis followed by annealing in a reducing atmosphere and controlled cooling.

5. Rapid cooling of $KSrY_{1-x}Tb_x(BO_3)_2$ samples leads to an incomplete phase transition to the low-temperature modification. Slowly cooled samples undergo only the low-temperature modification with space group $P2_1/m$.

6. The CIE chromaticity diagram for $KSrY_{0.1}Tb_{0.9}(BO_3)_2$ and $KSrY_{0.9}Tb_{0.1}(BO_3)_2$ synthesized by methods I, II, and III and excited at 375 nm showed that samples obtained by methods I and II emit in the green region, while method III shifts the emission toward the blue region. By changing the synthesis method, it is possible to control the emission color covering the spectrum from green to blue.

Assessment of the completeness of the tasks performed.

All tasks formulated to achieve the objectives of this dissertation were successfully completed. Doped borate compounds were synthesized both in powder and crystalline forms using solid-state and flux methods. The optimal synthesis temperature and time parameters were determined: for $NaBaSc(BO_3)_2$, the samples were annealed at 700°C, and for $KSrY(BO_3)_2$ at 650°C, followed by calcination at 850°C and 900°C, respectively, ensuring the maximum yield of the target product.

CIE chromaticity diagrams for the samples $KSrY_{0.1}Tb_{0.9}(BO_3)_2$ and $KSrY_{0.9}Tb_{0.1}(BO_3)_2$ demonstrated the possibility of controlling the emission color, covering the spectrum from green to blue depending on the synthesis method.

Thus, the goals of the dissertation research were achieved, as evidenced by the development of effective synthetic methods and the study of the optical properties of various doped borates.

Assessment of the technical and economic efficiency of the solutions proposed in the dissertation work. The solutions outlined in this dissertation have high potential for application in the industry for the production of fluorescent materials. The developed methods for the synthesis of doped borates contribute to the optimization of crystal production processes, which, in turn, reduces the cost of components and energy resources.

Compliance with scientific development directions or state programs. The dissertation work was carried out within the framework of the grant funding projects of the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan: “Crystal-chemical design of new phosphors based on

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