# PLOVDIV UNIVERSITY "PAISII HILENDARSKI" FACULTY OF CHEMISTRY DEPARTMENT OF CHEMICAL TECHNOLOGY

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# SYNTHESIS AND INVESTIGATION OF YTTRIUM, LANTHANUM, AND ALUMINUM BORATES DOPED WITH RARE EARTH COMPOUNDS

A dissertation summary for the award of the educational and scientific degree "Doctor"

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The dissertation is written on a total of 181 pages and includes 150 pages of main text. It contains 107 figures, 17 tables, 5 schemes, 5 photographic images, and a list of 273 bibliographic references.

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The public defense of the doctoral dissertation will take place on June 30, 2025, at 2:00 PM in Auditorium I of the Faculty of Chemistry at Paisii Hilendarski University of Plovdiv. All materials related to the dissertation and the defense procedure are available for review at the Central Library of Paisii Hilendarski University of Plovdiv.

#### **I. INTRODUCTION**

In recent decades, there has been a growing interest in rare earth elements and their ions doped into various inorganic matrices due to the unique luminescent properties they exhibit. This research focus is driven by the increasing demand for such materials in high-tech sectors related to energy efficiency–such as light-emitting diodes (LEDs)–as well as in electronics and optics, including sensors and chips for a wide range of devices and machinery, notably in the automotive industry. Additionally, applications extend to medicine, where they are used in novel diagnostic equipment, as well as in the security of identification documents and banknotes, and in many other fields enabling rapid technological advancement.

Among the most widely used luminescent activator ions that emit in the visible spectral range are:  $Eu^{3+}$  (europium),  $Tb^{3+}$  (terbium),  $Ce^{3+}$  (cerium),  $Gd^{3+}$  (gadolinium), and  $Dy^{3+}$  (dysprosium). These ions are employed in a variety of optical applications, including temperature sensors, communication sources, solid-state lasers, and others. Europium (Eu), with atomic number 63, holds a particularly important position among the rare earth elements. In its trivalent oxidation state (+3), it is one of the most extensively used lanthanides. Its compounds exhibit important properties such as high quantum efficiency and chemical stability, making them especially suitable for use in phosphors, catalysts, and optical materials. Considerable attention has been devoted to the luminescence of europium-based compounds due to their potential in the development of novel materials with enhanced efficiency and durability.

The ionic character of the lanthanide–ligand bonding leads to high coordination numbers, which are a result of the shielding of the 4f orbitals and the relatively large ionic radii of the elements. These features determine the structural diversity and the physicochemical properties of compounds containing rare earth ions. In order to improve their functional characteristics, the development of efficient and reproducible synthesis methods is of primary importance. Such methods include the solid-state method, the sol-gel method, and microwaveassisted synthesis–each offering specific advantages depending on the intended application.

The present work focuses on the synthesis and investigation of borates doped and codoped with rare earth elements, with particular emphasis on their luminescence properties. The study involves an analysis of the influence of the synthesis method on the phase composition and microstructure of the obtained materials. The results aim to contribute to the development of a new generation of materials with potential applications in various high-tech fields.

# **II. Aim and Objectives**

The growing interest in novel functional luminescent materials with sensory properties has led to a substantial body of research in the field of solid-state chemistry and the development of efficient synthesis methods. Despite the extensive investigations and the fundamental knowledge accumulated so far, the potential for expanding the application of inorganic borates highlights the need for new scientific advancements aimed at achieving unique material properties in the context of a rapidly evolving technological landscape. The increasing demand for smart, portable, and compact devices in modern technology further emphasizes the need for materials with enhanced functionalities.

In this context, the main aim of the present doctoral dissertation is the synthesis and investigation of borates doped with rare earth compounds in order to obtain materials with luminescent and sensory properties and to evaluate their potential applications. To achieve this aim, the following research objectives were defined:

- 1. To establish a synthesis protocol for powder-form yttrium borates via solid-state and microwave-assisted methods, and to investigate their structural and optical properties with a view toward potential practical applications.
- 2. To study the influence of the synthesis method on the fundamental characteristics of the materials.

- 3. To examine the effect of excess boric acid on the structure and properties of yttrium borates.
- 4. To synthesize lanthanum and aluminum borates doped and co-doped with rare earth elements, to study their crystal structure, and to determine their optical and chemical properties.
- 5. To perform a comparative analysis of the synthesized materials with respect to their luminescent properties.
- 6. To explore the potential of the obtained luminescent samples as smartphone-readable materials.

# III. Results and Discussion

# III.1 Solid-State Synthesis of YBO<sub>3</sub>:Eu

The synthesis and investigation of these materials aim to determine the optimal excess of boric acid required to enhance the fluorescent properties of europium-doped yttrium borates. Due to the limited information available in the scientific literature, a targeted study was carried out to examine the structural changes in these materials as the amount of boric acid in the reaction mixture was gradually increased (Table 1).

Synthesised materials	$Y_2O_3(g)$	H <sub>3</sub> BO <sub>3</sub> (g) (excess, %)	Eu <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (2 mol%) (g)
S10	0,6446	0,3537 (0)	0,1472
S11	0,6446	0,3714 (5)	0,1472
S12	0,6446	0,3890 (10)	0,1472
S13	0,6446	0,4047 (15)	0,1472
S14	0,6446	0,4217 (20)	0,1472
S15	0,6446	0,4387 (25)	0,1472
S16	0,6446	0,4557 (30)	0,1472
S17	0,6446	0,4727 (35)	0,1472
S18	0,6446	0,4897 (40)	0,1472
S19	0,6446	0,5067 (45)	0,1472
S110	0,6446	0,5237 (50)	0,1472
S111	0,6446	0,5407 (55)	0,1472
S112	0.6446	0.5577 (60)	0.1472

Table 1. Composition of YBO3: Eu Materials with Varying Excess of Boric Acid

The materials were synthesized using the solid-state method at a temperature of 900 °C. Boric acid was added in excess, ranging from 5 % to 60 %, and a reference sample, prepared stoichiometrically (without excess acid), was also synthesized. The synthesis was carried out in a MLW LM 212.11 muffle furnace, with a temperature range of 0 - 1200 °C and a heating rate of 22.28 °C/min.

# **III.1.2. X-ray Structural Analysis**

The X-ray diffraction data (Figure 1) indicate that the samples with 5 % to 55 % excess of boric acid exhibit a vaterite-type structure with a hexagonal unit cell and space group P63/m (JCPDF 16-0277). An exception is the stoichiometric sample, whose X-ray data are in good agreement with the structure of yttrium oxide. The most intense peaks in the X-ray diffraction patterns can be described by their 20 positions and corresponding hkl reflections: 20.1508 (002), 27.2483 (100), 29.1052 (101), 34.1245 (102), 40.9610 (004), 48.1569 (110), 49.8952 (104), 52.7078 (112), 60.3361 (202), and 65.0236 (114).



Figure 1. Results of X-ray Structural Analysis of YBO3: Eu Samples

#### **III.1.3.** Fourier Transform Infrared Spectroscopy (FTIR)

The spectra show structural changes with increasing excess of boric acid. From the FTIR spectra of samples S11–S112 (Figure 2 b), overlapping bands are observed with no signals at 1300 cm<sup>-1</sup>, indicating that the YBO<sub>3</sub> phase contains only condensed borate groups in the form of boroxol rings  $[B_3O_9]^{9-}$ .



*Figure 2. a) FTIR Spectra of Yttrium Oxide and Stoichiometric Sample Synthesized via Solid State Method b) FTIR Spectra of Samples S11 – S112* 

The phase transition from the low-temperature (LT) to the high-temperature (HT) phase is associated with the rupture of the boroxol ring and the formation of isolated [BO<sub>3</sub>] and [B–O] groups. The reverse process (HT–LT) leads to the condensation of isolated [BO<sub>3</sub>] groups into [B<sub>3</sub>O<sub>9</sub>]<sup>9-</sup>. Increasing boric acid results in structural densification and the formation of the LT phase with four-coordinate boron. In the stoichiometric sample S10 (Figure 2 a)), bands are observed at 1307 cm<sup>-1</sup> and 1200 cm<sup>-1</sup>, characteristic of isolated [BO<sub>3</sub>]<sup>3-</sup> and BO groups, indicating a high-temperature YBO<sub>3</sub> phase. Additionally, low-frequency peaks at 561 cm<sup>-1</sup> and 464 cm<sup>-1</sup>, associated with yttrium oxide, are present in sample S10 but absent in samples S11–S112.

#### **III.1.4. Raman Analysis**

In order to characterize in detail, the structural variations in the synthesized samples, which cannot be fully established through FTIR, a vibrational Raman spectroscopy analysis was conducted. The vibrational peaks in the range of 250–1150 cm<sup>-1</sup> are associated with different vibrational modes of the [B<sub>3</sub>O<sub>9</sub>]<sup>9-</sup> ring structure in the YBO<sub>3</sub> crystal. The most intense peak at 262 cm<sup>-1</sup> reflects interactions between Y<sup>3+</sup> and oxygen, while the bands at 375 cm<sup>-1</sup> and 414 cm<sup>-1</sup> are characteristic of the cubic structure of Y<sub>2</sub>O<sub>3</sub> and symmetric vibrations of Y<sup>3+</sup>. Vibrations of the tetrahedral [BO<sub>4</sub>]<sup>3-</sup> units show a signal at 513 cm<sup>-1</sup>, and those of trigonal orthoborates appear at 615 cm<sup>-1</sup>. The band at 881 cm<sup>-1</sup> is associated with the asymmetric stretching modes of the boron-oxygen tetrahedra. No spectral activity above 1200 cm<sup>-1</sup> was recorded, indicating the absence of asymmetric stretching of the structural units (Figure 3).



Figure 3. Raman spectra of YBO3: Eu, with identification of peak positions

#### **III.1.5.** Photoluminescent Analysis

The activation of Eu<sup>3+</sup> in yttrium borates has been investigated through excitation using sources in the near ultraviolet region. For the stoichiometric sample S10, excitation at 260 nm leads to the strongest emission peak at ~616 nm, corresponding to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of europium ions (Figure 4 a). When excited at 220 nm, the most intense emission peaks are observed in the infrared region (823 nm and 881 nm). For all samples, the maximum quantum yield was recorded at 220 nm, which corresponds to a higher excitation energy. Spectral analysis shows that as the excitation wavelength increases, the emission bands shift toward longer wavelengths. The most intense emission was recorded at 270 nm (Figure 4 b), in the range of 570–680 nm, with the main peak around 612 nm, characteristic of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition, confirming the efficient energy transfer from Y<sup>3+</sup> to Eu<sup>3+</sup>.

As the excess boric acid content increases, a slight increase in intensity is observed, likely due to the improvement in the crystal structure or optimal conditions for europium activation. This correlation is illustrated in figure 5, where the intensity is plotted on the ordinate and the percentage excess of boric acid on the abscissa.



*Figure 4. a) Fluorescence spectra of sample S10 with maximum emission intensity at 616 nm for different excitation sources. b) Fluorescence spectra of samples S10-S112.* 

From the graph (Figure 5), a maximum is observed at approximately 45 % excess. Beyond this threshold, the intensity remains high but shows a tendency to stabilize or slightly decrease. Based on the obtained data, it was established that the optimal excess of boric acid for the synthesis of samples with maximum luminescence intensity at a wavelength of  $\sim$ 612 nm is 45 %.

### **III.1.6.** Chemical Durability Assessment

The chemical stability of materials plays a crucial role in their application in optoelectronic devices such as lightemitting diodes (LEDs), displays, anticounterfeiting systems, and fluorescent markings. In these applications, the materials are exposed to various environments, including oxidizing agents, moisture, and temperature fluctuations, which can affect their structural and optical properties. For this reason, it is necessary to investigate the stability of materials in different aggressive environments. This study evaluates the chemical stability of YBO3:Eu in three environments with different pH levels - acidic (pH = 1,80),



neutral (pH = 7), and alkaline (pH = 10,85). Two main indicators were used to analyze the results: percentage mass loss (M%) and mass loss rate (V). These indicators were calculated based on the data in Table 2.

Sample	Time, (hours/min)									
YBO3:Eu, SS										
	1/60	2/120	3/180	4/240	24/1440	48/2880	72/4320			
YBO <sub>3</sub> :Eu	0,0653	0,0448	0,0489	0,0408	0,6625	0,6701	0,6778			
$+ H_2O(g)$										
YBO <sub>3</sub> :Eu	0,0432	0,0321	0,0358	0,0312	0,5485	0,5362	0,5683			
+ acid (g)										
YBO <sub>3</sub> :Eu	0,0407	0,032	0,0415	0,0337	0,6598	0,6625	0,5315			
+ basis (g)										

Table 2. Change in sample mass in various environments

The results indicate that during the first 60 minutes, mass loss remains below 1 % for all samples, with the greatest loss observed in the neutral medium. After 1440 minutes (24 hours), the mass loss reaches approximately 2 %, with the sample in the neutral medium exhibiting slightly higher loss compared to those in acidic and alkaline environments. By the end of the study–4320 minutes (72 hours)–the sample in water loses around 6 % of its mass, whereas the losses in alkaline and acidic media are 5.5% and 5%, respectively. This suggests the highest stability in the acidic environment (Figure 6 a).

The rate of mass loss is highest during the first 60 minutes, with the sample in the neutral medium reaching approximately 0.001 g/min, while the rates in acidic and alkaline media are about 0.0007 g/min. After this initial period, the rate decreases and stabilizes after 2880 minutes (48 hours), indicating the formation of a stable surface layer or the depletion of readily soluble components. Toward the end of the study, the mass loss rates in different media converge, suggesting a deceleration of the degradation process (Figure 6 b).

These findings demonstrate that YBO<sub>3</sub>:Eu exhibits high chemical stability, particularly in acidic environments, which is an important consideration for selecting appropriate application conditions in optoelectronic devices.



Figure 6. a) Percentage mass loss of yttrium borate synthesized by SS b) Mass loss rate

#### III.2. Synthesis of YBO<sub>3</sub>:Eu via Microwave-Assisted Method (MWAM)

The synthesis of YBO<sub>3</sub>:Eu samples was carried out using a microwave-assisted decomposition system, aiming to obtain phases with stable structure and maximum luminescence intensity. Sample S20 MW (Table 3) was prepared by mixing stoichiometric amounts of Y<sub>2</sub>O<sub>3</sub> and H<sub>3</sub>BO<sub>3</sub> with 2 mol % Eu<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>x8H<sub>2</sub>O as the doping agent, according to equation (1):

$$Y_2O_3 + 2H_3BO_3 \rightarrow 2YBO_3 + 3H_2O (1)$$

Sample	$Y_2O_3(g)$	H <sub>3</sub> BO <sub>3</sub> (g) (Excess, %)	Eu <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> x8H <sub>2</sub> O (2 mol %) (g)	Dest. H <sub>2</sub> O (ml)
S20 MW	0,6446	0,3537 (0)	0,1472	5
S21 MW	0,6446	0,3714 (5)	0,1472	5
S22 MW	0,6446	0,3890 (10)	0,1472	5
S23 MW	0,6446	0,4047 (15)	0,1472	5
S24 MW	0,6446	0,4217 (20)	0,1472	5
S25 MW	0,6446	0,4387 (25)	0,1472	5
S26 MW	0,6446	0,4557 (30)	0,1472	5
S27 MW	0,6446	0,4727 (35)	0,1472	5
S28 MW	0,6446	0,4897 (40)	0,1472	5
S29 MW	0,6446	0,5067 (45)	0,1472	5
S210 MW	0,6446	0,5237 (50)	0,1472	5
S211 MW	0,6446	0,5407 (55)	0,1472	5
S212 MW	0,6446	0,5577 (60)	0,1472	5

Table 3. Composition of samples synthesized via MWAM with varying excess of H<sub>3</sub>BO<sub>3</sub>

The selected europium content (2 mol %) provides an effective balance between luminescence intensity and the minimization of structural defects. This ensures uniform distribution of the dopant within the host matrix and prevents concentration quenching of luminescence at higher doping levels.

Samples from the S20–S212 MW series were synthesized using the microwave-assisted method, employing the same stoichiometric ratios of precursors as in the solid-state synthesis, with the addition of 5 mL of distilled water. The process was carried out at a temperature of 260 °C, with a ramp time of 15 minutes, a holding time of 10 minutes, and a cooling time of 20 minutes. The microwave system operated at a power of 1500 W. After cooling, the samples were collected in dry form and were ready for subsequent analyses.

# III.2.1. X-ray Structural Analysis

The high intensity of the peaks indicates good crystallinity, achieved through uniform heating and rapid attainment of the target temperature provided by the microwave synthesis (Figure 7).

With increasing excess of boric acid, a rise in peak intensity is observed, indicating structural stabilization. At concentrations above 45–50%, the intensity levels off, suggesting that optimal conditions for crystallization have been reached. These results confirm the effectiveness of microwave synthesis in producing high-quality



synthesis in producing high-quality crystalline structures across a range of boric acid concentrations.

# **III.2.2.** Fourier Transform Infrared (FTIR) Spectroscopy

For the samples synthesized via the microwave-assisted method, the FTIR spectrum of YBO<sub>3</sub>:Eu<sup>3+</sup> exhibits two well-defined groups of doublet peaks (Figure 8). The first group appears

For at 874 cm<sup>-1</sup> and 920 cm<sup>-1</sup>, while the second is observed at 1032 cm<sup>-1</sup> and 1075 cm<sup>-1</sup>, closely resembling the features identified in the samples obtained by solid-state synthesis. The spectrum confirms the presence of  $[B_3O_9]^{9-}$  rings within the



YBO<sub>3</sub> structure. The peaks at 874 and 920 cm<sup>-1</sup> are attributed to the stretching vibrations of boroxol rings, while the peak at 1078 cm<sup>-1</sup> corresponds to the terminal BO stretching vibrations. The vibrations of bridging B–O–B bonds are observed around 710 cm<sup>-1</sup>, and the band at 570 cm<sup>-1</sup> is associated with Y–O stretching in Y<sub>2</sub>O<sub>3</sub>. A broad band at 3217 cm<sup>-1</sup> is related to O–H stretching vibrations of hydroxyl groups.

#### **III.2.3.** Fluorescence Analysis

The fluorescence spectra of the samples synthesized via the microwave-assisted method exhibit intense emission peaks upon excitation with sources at 260 nm and 396 nm, with the latter proving to be more effective. The emission spectra display peaks in the range of 590 nm to 700 nm, corresponding to transitions of europium ions from the excited <sup>5</sup>D<sub>0</sub> state to various <sup>7</sup>F<sub>J</sub> levels.

The identified peaks at 591 nm and 612 nm are assigned to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transitions, which are responsible for orange and red emissions, respectively. The intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition is notably higher under excitation at 396 nm and significantly lower at 260 nm.

The main difference between the samples synthesized via solid-state and microwaveassisted methods lies in the higher fluorescence intensity observed in the MWAM series. This enhancement is likely due to improved crystallinity and more efficient activation of the europium ions (Figure 9 a and 9 b).



*Figure 9.* Fluorescence spectrum of samples excited at a wavelength of 260 nm a) Solid-phase synthesis b) Microwave-assisted method

- ✓ When Eu<sup>3+</sup> ions occupy inversion centers, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transitions are expected to be relatively strong, while the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transitions are relatively weak.
- ✓ The  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, which is of magnetic dipole nature, is largely independent of the host matrix, whereas the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition, which is electric dipole-allowed, is strongly influenced by the local symmetry of the Eu<sup>3+</sup> site.
- ✓ The emission at 696 nm corresponds to the electric dipole transition  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ , which exhibits lower intensity under 260 nm excitation.
- ✓ The main difference between the two series of synthesized samples lies in the emission intensity at 696 nm-samples obtained via the solid-state method show low intensity, while those synthesized by the microwave-assisted method exhibit significantly enhanced luminescence.

The red-to-orange (R/O) emission intensity ratio indicates that, for the samples synthesized via the solid-state route, the R/O ratio increases with increasing boric acid excess, reaching a saturation point at 45 %. For the microwave-assisted samples, the R/O ratio remains stable around 1.75 and increases further under 396 nm excitation. For all samples, fluorescence intensity decreases markedly when the boric acid excess exceeds 60 % (Figure 10 a and 10 b).



*Figure 10.* Comparison between SS and MWAM samples: (a, b) dependences of the R/O ratios on the percentage of excess boric acid for 260 and 396 nm excitations

# **III.2.4.** Chemical Durability Assessment

The microwave-assisted method ensures uniform heating and leads to improved crystallinity compared to the conventional solid-state synthesis, which may contribute to enhanced material stability. The chemical resistance of the samples synthesized via this method was evaluated in three different media: neutral, acidic, and alkaline-buffered. The results show that, at the beginning of the experiment, the mass loss was minimal in all media, with no significant changes observed within the first 240 minutes, indicating high initial chemical stability.

Over the subsequent 24 hours, the mass loss gradually increased, with the greatest loss recorded in the neutral (aqueous) medium (2.26 %), while the acidic and alkaline-buffered environments exhibited comparatively lower increases. After 2880 and 4320 minutes (48 and 72 hours, respectively), the samples demonstrated a more pronounced degradation, with the highest mass loss occurring in water–4.02 % at 2880 minutes and 5.83 % at 4320 minutes. The samples immersed in alkaline-buffered media displayed the highest chemical stability, followed by those in the acidic environment (Figure 11 a).

The rate of mass loss was highest during the initial stages of the experiment but decreased significantly by the 120<sup>th</sup> minute (2 hours) and subsequently stabilized. Samples exposed to the alkaline-buffered environment exhibited a lower initial mass loss rate compared to those in acidic and neutral media. Despite the enhanced fluorescence and improved color purity achieved in the samples synthesized via the microwave-assisted method, their relatively low chemical durability limits their potential applications (Figure 11 b).

Therefore, it is necessary to explore additional strategies aimed at improving color purity. One such approach involves the introduction of a co-dopant with known boosting properties into the host matrix responsible for fluorescence in yttrium borate. Cerium, in the form of various compounds, may serve as a suitable co-dopant for this purpose.



Figure 11. a) Percentage mass loss of yttrium borate synthesized by MWAM b) Mass loss rate

#### III.3. Solid-State Synthesis of YBO3:Eu:Ce

The YBO<sub>3</sub>:Eu:Ce sample series was synthesized via a conventional solid-state reaction under the same conditions as those used for europium-only doped samples. The starting materials included  $Y_2O_3$ ,  $H_3BO_3$ ,  $Eu_2O_3$ , and  $Ce(SO_4)_3x4H_2O$ . The boric acid excess was varied from 5 % to 60 % in 5 % increments, with an undoped reference sample also prepared.

Following thorough homogenization of the raw materials, the mixtures were calcined at 920 °C for 4 hours, followed by slow cooling inside the furnace for 16 hours. The resulting products were white, fine powders. The composition of each sample is presented in Table 4.

Sample	Y <sub>2</sub> O <sub>3</sub>	H <sub>3</sub> BO <sub>3</sub>	Eu <sub>2</sub> O <sub>3</sub>	Ce(SO <sub>4</sub> ) <sub>3</sub> x4H <sub>2</sub> O (1 mol%)
	(g)	(excess, %) (g)	(2 mol %) (g)	(g)
S20	0,6446	0,3537 (0)	0,070704	0,0404
S21	0,6446	0,3714 (5)	0,070704	0,0404
S22	0,6446	0,3890 (10)	0,070704	0,0404
S23	0,6446	0,4047 (15)	0,070704	0,0404
S24	0,6446	0,4217 (20)	0,070704	0,0404
S25	0,6446	0,4387 (25)	0,070704	0,0404
S26	0,6446	0,4557 (30)	0,070704	0,0404
S27	0,6446	0,4727 (35)	0,070704	0,0404
S28	0,6446	0,4897 (40)	0,070704	0,0404
S29	0,6446	0,5067 (45)	0,070704	0,0404
S210	0,6446	0,5237 (50)	0,070704	0,0404
S211	0,6446	0,5407 (55)	0,070704	0,0404
S212	0 6446	0 5577 (60)	0.070704	0.0404

Table 4. Composition of YBO3: Eu: Ce samples with varying excess of boric acid

# **III.3.1. X-ray Diffraction Analysis**

Figure 12 presents the X-ray diffraction (XRD) patterns of the YBO<sub>3</sub>:Eu:Ce samples, compared with reference data from JCPDS cards 01-074-1929 and 00-034-0291. The diffraction peaks match those of the hexagonal YBO<sub>3</sub> phase, with lattice parameters a = 3.778 Å (0.3778 nm) and c = 8.814 Å (0.8814 nm). All observed peaks are indexed to the hexagonal structure with space group P63/mmc.

The most intense diffraction reflections are located within the 20 range of 10° to 35°, and the corresponding crystallographic planes identified include: (002), (100), (101), (102), (004), (110), (104), (112), (200), (202), (006), (106), and (204). The (204) plane, located at 20 =  $36.5257^\circ$ , is confirmed by the reference JCPDS card 00-034-0291.

Above  $2\theta = 35^\circ$ , weaker diffraction peaks are observed, which may be attributed to residual amorphous phases or poorly crystallized domains. The presence of well-defined diffraction peaks indicates a crystalline structure, likely corresponding to various phases of yttrium borate.



Figure 2. XRD analysis of sample YBO3:Eu:Ce

# III.3.2. Fourier-Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of the YBO<sub>3</sub>:Eu:Ce sample series exhibit similarities to those of yttrium borate samples doped solely with europium ions and synthesized via the solid-state method with varying excess of boric acid. The primary differences include the appearance of additional bands corresponding to impurities such as hygroscopically bound water (~3300 cm<sup>-1</sup>) and atmospheric CO<sub>2</sub> (~2300 cm<sup>-1</sup>) (Figure 13).

In the spectral region between 646-712 cm<sup>-1</sup>, peaks associated with



bending vibrations of the bridging B–O–B bonds are observed, which are less pronounced in samples containing only europium. The peaks related to the stretching vibrations of B–O within

 $BO_4$  units (878–920 cm<sup>-1</sup>) display increased amplitude, which may be attributed to the incorporation of cerium ions. The broader absorption bands observed in this sample series suggest a more complex structural environment, influenced by the presence of multiple dopants.

The overlap in structural features between both series of samples indicates good reproducibility of the synthesis procedure and confirms the structural consistency of the doped yttrium borate matrix.

#### **III.3.3.** Photoluminescence Analysis

A comprehensive scan of the emission spectrum in the 220–550 nm range was conducted, identifying effective excitation wavelengths at 245, 320, 395, and 470 nm. Special attention was given to excitation at 395 nm (Figure 14 a), under which characteristic transitions of the europium ions were observed, albeit with lower intensity compared to samples synthesized solely via the solid-state method. A slight shift of the main peaks in the orange and red emission regions (599 and 616 nm) was detected, along with noticeable changes in the peak profiles.

A particularly interesting feature is the difference in the spectral shape of the main emission peaks in the orange (590 nm) and red (620 nm) regions. In the previously synthesized series, the orange emission appeared as a single peak, while the red one was split; in the present series, this pattern is reversed, suggesting a variation in the local environment of the Eu<sup>3+</sup> ions due to cerium co-doping.

To evaluate the excitation efficiency, the fluorescence intensity at  $\lambda = 616$  nm was used as a reference. The highest excitation efficiency was recorded at 250 and 395 nm, with both wavelengths exhibiting nearly equivalent performance. Samples with more than 15 % excess boric acid showed maximum excitation efficiency at 250 nm, followed closely by 395 nm (Figure 15 b). The excitation efficiency does not increase monotonically with increasing boric acid excess; rather, distinct peaks in efficiency were observed at 30 %, 50 %, and 60 % excess. Excitation at 495 nm demonstrated significantly low efficiency, rendering it impractical for application purposes.



*Figure 14. a) Emission spectra at wavelength 395 nm b) Dependence on excitation wavelength at maximum fluorescence intensity at 616 nm* 

After calculating the red-to-orange emission ratio (Table 5), significantly higher values in favor of red emission were observed for the samples co-doped with  $Eu^{3+}$  and  $Ce^{3+}$  ions, compared to those doped solely with europium. This occurs despite the lower overall fluorescence intensity of the co-doped samples. It is possible that  $Ce^{3+}$  ions contribute positively to color enhancement, likely through energy transfer between the two ions ( $Eu^{3+}/Ce^{3+}$ ). When comparing data obtained at similar excitation wavelengths – 395 and 396 nm – for europiumonly doped samples and those co-doped with cerium, an average increase of 96.57 % in the redto-orange ratio was recorded. The average value of this ratio for yttrium borates doped with  $Eu^{3+}$  ions is 1.517, whereas for the co-doped samples ( $Eu^{3+}/Ce^{3+}$ ) it reaches 2.982 at  $\lambda_{exc} = 395$ nm. Literature reports typically show color purity values averaging around 2.

	Wave	length
	245 nm	395 nm
Samples	Ratio	R/O
S20	2,035	3,412
S21	2,184	3,782
S22	1,920	2,994
S23	2,045	2,976
S24	1,752	2,657
S25	1,855	2,856
S26	1,758	2,508
S27	1,834	2,818
S28	1,858	2,767
S29	1,901	3,732
S210	1,816	2,660
S211	1,836	2.817
S212	1,858	2,790

*Table 5* Ratio R/O at  $\lambda_{exc.}$ =245 nm  $\lambda_{exc.}$ =395 nm

#### **III.3.4.** Chemical Durability Assessment

In this study, yttrium borates co-doped with europium ( $Eu^{3+}$ ) and cerium ( $Ce^{3+}$ ) ions were analyzed with regard to their chemical stability in various media and their fluorescent characteristics. The mass loss process was monitored in three different environments: aqueous, acidic, and alkaline-buffered, over a time interval ranging from 60 to 4320 minutes (1 to 72 hours). Based on the data presented in Table 6, the obtained results indicate a significant increase in mass loss with the duration of exposure, with the highest mass loss observed in the alkaline-buffered medium (~5.5 %). The samples exhibit good initial stability; however, over

time, their chemical resistance decreases, with the lowest mass loss recorded in the acidic medium (4 %) (Figure 15 a).

The analysis of the mass loss rate (Figure 15 b) shows the highest values at the initial stage of exposure, particularly in the aqueous medium. Following the initial decrease, the rate of mass loss declines and stabilizes after 1440 minutes (24 hours), with the dissolution dynamics being dependent on the chemical composition of the surrounding medium. The results emphasize the influence of the chemical environment on the dissolution behavior of the borates.

Sample YBO3:Eu <sup>3+</sup> Ce <sup>3+</sup>		Time (hours/min)					
	1/60	2/120	3/180	4/240	24/1440	48/2880	72/4320
SYECe $+$ H <sub>2</sub> O (g)	0,0543	0,0459	0,0444	0,0386	0,6658	0,6641	0,5331
SYECe + acid (g)	0,0409	0,0300	0,0319	0,0284	0,4585	0,4601	0,4770
SYECe + basis (g)	0,0388	0,0324	0,0390	0,0314	0,6145	0,6213	0,6407

Table 6. Change in sample mass in various environments



Figure 15. a) Percentage mass loss of YBO3: Eu: Ce obtained by SS b) Mass loss rate

The fluorescence analysis revealed significant differences in the optical properties of the samples depending on the dopants and the synthesis method. The samples co-doped with europium and cerium ions exhibited enhanced color purity, attributed to energy transfer between the ions. These samples also demonstrated the highest chemical stability in acidic medium, whereas the samples synthesized via the microwave-assisted method showed the lowest stability, followed by yttrium borates doped with europium ions and synthesized by the solid-state (SS) method. These results highlight the complex balance between optical properties and chemical stability, emphasizing the influence of synthesis conditions and dopant selection on the final characteristics of the materials.

# III.4. Solid-State Synthesis of Lanthanum Borates Doped and Co-Doped with Rare Earth Compounds

Lanthanum borates (LaBO<sub>3</sub>:RE = Eu, Tb, Dy, Gd, Ce) were synthesized via a conventional solid-state method. The starting materials used for their preparation were La<sub>2</sub>O<sub>3</sub> and an excess of H<sub>3</sub>BO<sub>3</sub> (45 %), selected according to the optimized synthesis conditions for yttrium borates and based on the stoichiometric formula (2):

 $La_2O_3 + 2H_3BO_3 \rightarrow 2LaBO_3 + 3H_2O$  (2)

The samples in this series were doped and co-doped with rare earth compounds in concentrations ranging from 1 to 3 mol %, as shown in Table 7.

$La_2O_3 + H_3BO_3$	Rare earths compounds (RE)	Doped with (RE), mol %
Al	Eu <sub>2</sub> O <sub>3</sub>	2
A2	$Dy_2O_3$	2
A3	TbF <sub>3</sub>	2
A4	Gd <sub>2</sub> O <sub>3</sub>	2
A5	CeSO <sub>4</sub> x 4 H <sub>2</sub> O	2
A6	$Eu_2O_3 + TbF_3$	2 / 1
A7	Eu <sub>2</sub> O <sub>3</sub> +CeSO <sub>4</sub> x 4 H <sub>2</sub> O	2 / 1
A8	$Eu_2O_3 + Dy_2O_3$	2 / 1
A9	$Eu_2O_3 + Gd_2O_3$	2 / 1
A10	$Eu_2O_3 + Gd_2O_3 + TbF_3$	3 / 2 / 1
A11	$Eu_2O_3 + Dy_2O_3 + TbF_3$	3 / 2 / 1

 

 Table 7. Composition of lanthanum borates doped and co-doped with rare earth compounds, synthesized via the solid-state method (SS)

The synthesis was carried out at a temperature of 1050 °C, maintained for 6 hours, after which the samples were slowly cooled in the furnace over a period of 16 hours to ensure the formation of a homogeneous crystalline structure. The use of a higher temperature compared to the synthesis of yttrium borates (900 °C) is justified by the difference in the ionic radii of lanthanum (1.16 Å) and yttrium (1.02 Å). The larger ionic radius of lanthanum requires a higher temperature to ensure complete reaction and the formation of a stable crystalline structure. At lower synthesis temperatures, a mixture of different lanthanum borate phases is formed.

# III.4.1. X-ray Diffraction (XRD) Analysis

According to the results, the positions of several diffraction peaks are consistent with the standard XRD patterns of LaBO<sub>3</sub> (JCPDS 12-0762). The main diffraction peaks appear at 20.4°, 25.5°, 26.3°, 30.4°, 32.3°, 35.1°, 44.4°, 48.6°, and 51.1°, corresponding to the (001), (111), (120), (200), (210), (002), (122), (231), and (311) planes of LaBO<sub>3</sub>, respectively (Figure 16 a). The bands observed before 20° are attributed to unreacted boric acid. The diffraction peaks are sharp and intense, indicating that the LaBO<sub>3</sub> powder exhibits good crystallinity. The space group is *Pnam* (N 62), and the crystalline phase is orthorhombic of the aragonite type, with lattice parameters a = 0.587 nm, b = 0.825 nm, and c = 0.510 nm. The structure is illustrated in Figure 16 b.



*Figure 16. a)* X-ray diffraction analysis of sample A12 b) Structure of lanthanum borate, (The structure was visualized using software: Crystalmaker 10.6 (CrystalMaker Software Ltd., Oxford, United Kingdom; http://www.crystalmaker.com)

# **III.4.2.** Fourier-Transform Infrared Spectroscopy (FTIR)

The vibrational spectra of the synthesized lanthanum borates doped with rare earth compounds exhibit characteristic vibrational modes of BO<sub>3</sub> and BO<sub>4</sub> structural units. The planar trigonal BO<sub>3</sub> groups are identified by four fundamental vibrational modes: symmetric stretching  $(v_1)$ at approximately 950 cm<sup>-1</sup>, out-ofplane bending (v<sub>2</sub>) at  $\sim$ 740 cm<sup>-1</sup>, asymmetric stretching  $(v_3)$  at  $\sim 1250 \text{ cm}^{-1}$ , and in-plane bending  $(v_4)$  at ~592 cm<sup>-1</sup>. The tetrahedral BO<sub>4</sub> groups are characterized by



symmetric stretching  $(v_1)$  around 1000 cm<sup>-1</sup>, degenerate bending  $(v_2)$  below 950 cm<sup>-1</sup>, triply degenerate stretching  $(v_3)$  near 600 cm<sup>-1</sup>, and bending  $(v_4)$  below 600 cm<sup>-1</sup> (Figure 17).

The analysis indicates that orthoborates with an aragonite-type structure predominantly contain BO<sub>3</sub> groups, whereas those with a vaterite-type structure incorporate BO<sub>4</sub> tetrahedra. For aragonite-type lanthanum borates, the spectral features include absorption bands at 592 and 610 cm<sup>-1</sup> (v<sub>4</sub>) and 707 cm<sup>-1</sup> (v<sub>2</sub>), which are associated with the respective bending vibrations of the [BO<sub>3</sub>]<sup>3-</sup> groups. The symmetric stretching mode (v<sub>1</sub>) at 940 cm<sup>-1</sup> and the most intense peak at 1268 cm<sup>-1</sup>, corresponding to the asymmetric stretching mode (v<sub>3</sub>), confirm the presence of trigonal BO<sub>3</sub> units.

The obtained results contribute to a deeper understanding of the structural characteristics and spectral properties of rare earth-doped lanthanum borates.

#### **III.4.3. Raman Spectral Analysis**

In the present study, the Raman spectra of lanthanum borates synthesized via the solidstate method and doped or codoped with rare earth compounds were analyzed. In the recorded spectrum, the peak at 1375  $cm^{-1}$ is attributed to the asymmetric stretching of B(3)–O bonds, while the bending vibration  $\delta(B-O-H)$  is observed at 1253 cm<sup>-1</sup>. The most intense peak at 943  $cm^{-1}$ corresponds to the symmetric stretching vs(B(3)-O). Metaborate groups, which are characteristic of



ring structures, are identified by the band at  $631 \text{ cm}^{-1}$ , whereas the band at  $605 \text{ cm}^{-1}$  is associated with vibrations of bridging bonds within BO<sub>3</sub> groups.

The stretching of La–O bonds is manifested through low-intensity doublet peaks at 306 and 317 cm<sup>-1</sup>. Additionally, in the region between 113 and 300 cm<sup>-1</sup>, vibrational modes related to La(RE)–O interactions are observed (Figure 18).

#### **III.4.4.** Chemical Durability Assessment

In the present study, the chemical durability of lanthanum borate (LaBO<sub>3</sub>) was evaluated in different media by measuring the percentage of mass loss and the dissolution rate. The investigated samples were immersed in neutral, acidic, and alkaline-buffered solutions, and the mass loss was monitored over a period of up to 4320 minutes (72 hours) (Figure 19 a).

The results indicate that in a neutral medium, the material exhibits the lowest chemical resistance, with a mass loss exceeding 6 % by the end of the experiment and a dissolution rate reaching approximately 0.001 g/min. In acidic conditions, the mass loss is the lowest (below 4 %), and the dissolution rate is around 0.0008 g/min, suggesting weaker interactions with the solution. In the alkaline-buffered medium, both mass loss and dissolution rate ( $\approx 0.0007$  g/min) are intermediate compared to the other environments, indicating moderate stability (Figure 19 b).

The observed decrease in dissolution rate after 240 minutes is associated with the formation of a passivating surface layer, likely composed of poorly soluble borate or hydroxyl complexes. The obtained results confirm that the chemical durability of LaBO<sub>3</sub> is strongly dependent on the surrounding medium, and this information can be utilized to identify its potential applications under specific chemical conditions.



Figure 19. a) Percentage mass loss of lanthanum borate b) Mass loss rate

#### III.5. Solid-State Synthesis of Rare-Earth Doped and Co-Doped Aluminum Borates

The synthesis of aluminum borates (AlBO<sub>3</sub>:RE = Eu, Tb, Dy, Gd, Ce) was carried out via the solid-state method. The starting materials used were Al<sub>2</sub>O<sub>3</sub> and an excess of H<sub>3</sub>BO<sub>3</sub> (45 %), with the reagent ratio adjusted according to the stoichiometric reaction shown in equation (3):

 $Al_2O_3 + 2H_3BO_3 \rightarrow 2AlBO_3 + 3H_2O \qquad (3)$ 

The raw materials were thoroughly homogenized, and the samples were doped and codoped with rare-earth (RE) compounds in concentrations ranging from 1 to 3 mol %, as specified in Table 8.

Table 8.	Composition of	of samples	synthesized	by SS,	aluminum	borates	doped	and	co-d	oped
		ν	vith rare eat	rth con	ipounds					

$Al_2O_3 + H_3BO_3$	Rare earths compounds (RE)	Doped with RE mol %
B1	Eu <sub>2</sub> O <sub>3</sub>	2
B2	Dy <sub>2</sub> O <sub>3</sub>	2
B3	TbF <sub>3</sub>	2
B4	$Gd_2O_3$	2
B5	CeSO <sub>4</sub> x 4 H <sub>2</sub> O	2
B6	$Eu_2O_3 + TbF_3$	2 / 1
B7	$Eu_2O_3$ +CeSO <sub>4</sub> x 4 H <sub>2</sub> O	2 / 1
B8	$Eu_2O_3 + Dy_2O_3$	2 / 1
B9	$Eu_2O_3 + Gd_2O_3$	2 / 1
B10	$Eu_2O_3 + Gd_2O_3 + TbF_3$	3 / 2 / 1
B11	$Eu_2O_3 + Dv_2O_3 + TbF_3$	3/2/1

For the preparation of luminescent materials, the raw materials were heated at 1000 °C for 6 hours, followed by slow cooling inside the furnace over a period of 16 hours. The higher synthesis temperature required for aluminum borates, compared to yttrium borates, is attributed to the structural characteristics of aluminum oxide. The  $Al^{3+}$  ion possesses a small ionic radius (0.53 Å) and high electron density, which stabilizes the bonding within the oxide structure. Consequently, additional energy is required to break the crystalline lattice of  $Al_2O_3$  and facilitate its reaction with boric acid. As a result, a higher temperature is necessary to ensure complete reaction and the formation of a crystalline product.

# **III.5.1. X-ray Diffraction Analysis**

The X-ray diffraction (XRD) results indicate the absence of an amorphous halo, confirming the good crystallinity of the material and the effective incorporation of boron oxide. No diffraction peaks corresponding to residual boric acid (at 14.9° and 28.15°, JCPDS 30-0199) were detected in the diffraction pattern of the aluminum borate, suggesting that the boric acid was fully consumed during synthesis.

The XRD pattern of sample B3 (AlBO<sub>3</sub>:Tb<sup>3+</sup>) exhibits well-defined diffraction peaks in the 2 $\theta$  range of 10° to 50°, with prominent maxima observed at 11.68°, 13.06°, 15.78°, 18.46°, 22.16°, 34.38°, and 41.04°. The crystallographic model reveals that the aluminum borate crystallizes in a rhombohedral structure (space group R-<sub>3C</sub>, No167), characteristic of the calcite-type phase (Figure 20 a).



Figure 20. a) X-ray diffraction analysis of sample B3 b) Structure of AlBO<sub>3</sub> (The structure was visualized using software: Crystalmaker 10.6 (CrystalMaker Software Ltd., Oxford, United Kingdom; http://www.crystalmaker.com)

The structure consists of distorted AlO<sub>6</sub> octahedra connected to BO<sub>3</sub> groups, which are arranged in oppositely oriented layers. The octahedra share vertices with adjacent layers, forming a three-dimensional network. The unit cell parameters (a = 5.334 Å, b = 5.134 Å, c = 6.511 Å,  $\alpha$  = 96.181°,  $\beta$  = 90.541°,  $\gamma$  = 106.101°) confirm a slightly distorted triclinic structure (Figure 20b). The intense diffraction peak at 13.06° indicates a high degree of crystallinity, while the observed peak shifts suggest an influence of the rare-earth dopants on the structure. Similar peak shifts were observed in the XRD patterns of lanthanum borates, indicating analogous structural effects.

# **III.5.2.** Fourier-Transform Infrared Spectroscopy

The Fourier-transform infrared (FTIR) spectra of rare-earth-doped aluminum borates reveal characteristic bands in the mid-infrared region, associated with the vibrational modes of boron–oxygen (BO) groups. In the 1400–1100 cm<sup>-1</sup> range, bands are observed that correspond to the asymmetric stretching vibrations (v<sub>3</sub>) of triangular BO<sub>3</sub> groups, occupying two distinct structural positions. Weak bands in the 1060–800 cm<sup>-1</sup> region are attributed to symmetric

stretching vibrations ( $v_1$ ), while those between 820–450 cm<sup>-1</sup> are associated with bending modes ( $v_2$ and  $v_4$ ) (Figure 21).

In the case of aluminum borates doped and co-doped with rare-earth ions, additional peaks were identified, corresponding to both BO<sub>3</sub> and BO<sub>4</sub> units. A band in the range 448–505 cm<sup>-1</sup> is assigned to bending vibrations of BO<sub>4</sub> groups, while the band at 547 cm<sup>-1</sup> is associated with the formation of borate linkages. Peaks at 648 cm<sup>-1</sup> and 717 cm<sup>-1</sup> are characteristic of



europium ions

B–O–B bending modes in the BO<sub>3</sub> network and in amorphous B<sub>2</sub>O<sub>3</sub>. The stretching vibrations of Al–O bonds in AlO<sub>4</sub> units appear near 780 cm<sup>-1</sup>, while peaks in the 884–1200 cm<sup>-1</sup> region are related to the stretching vibrations of B–O bonds in BO<sub>4</sub> groups. The high-frequency band at 1437 cm<sup>-1</sup> corresponds to the asymmetric stretching vibrations of B–O bonds in BO<sub>3</sub> units.

# **III.5.3. Raman Spectral Analysis**

The Raman analysis of the synthesized aluminum borates reveals characteristic peaks associated with both dialuminum trioxide and boric acid. The spectral data can be divided into three main frequency regions:

- ✓ Boson region (20–200 cm<sup>-1</sup>): A peak at 120 cm<sup>-1</sup> is observed in this region, attributed to the excess vibrational density of states at low frequencies, known as the boson peak. This feature is associated with the rotational motion of tetrahedral units.
- ✓ Region 200-800 cm<sup>-1</sup>: This range is dominated by vibrational modes related to dialuminum trioxide. The peak at 500 cm<sup>-1</sup> corresponds to symmetric motion around the bridging oxygen atoms in Al–O–Al linkages, while the low-intensity band at 340 cm<sup>-1</sup> is assigned to O–Al–O bending modes.
- ✓ Region 800–1700 cm<sup>-1</sup>: This region contains vibrational modes of boron-containing groups. The most intense peak at 881 cm<sup>-1</sup> is related to the substitution between Al and B atoms and is characteristic of

orthoborate triangular BO<sub>3</sub> units. A less intense peak at  $807 \text{ cm}^{-1}$  indicates the formation of boroxol rings. The presence of Al<sub>2</sub>O<sub>3</sub> as [AlO<sub>4</sub>]<sup>5-</sup> units requires charge compensation by RE<sup>3+</sup> cations, which affects the abundance of BO<sub>4</sub> groups.

All synthesized samples exhibit boroxol ring features at 807 cm<sup>-1</sup>, confirming the specific structural characteristics of the aluminum borates (Figure 22).



#### **III.5.4.** Determination of Chemical Durability

The chemical durability of aluminum borate (AlBO<sub>3</sub>), doped and co-doped with rareearth compounds, was investigated in three different environments – alkaline-buffered, neutral, and acidic. Based on the data presented in Table 9, the percentage weight loss and dissolution rate were calculated.

As shown in Figure 23 a, during the initial 240 minutes (4 hours), the weight loss remained below 1%, with the highest value recorded in the neutral environment. After 1440 minutes (24 hours), samples immersed in water showed a weight loss exceeding 2 %. By 4320 minutes (72 hours), the highest loss (close to 8 %) was observed in the acidic medium, indicating substantial dissolution of the borate components.

The alkaline-buffered medium exhibited an intermediate effect, with weight loss exceeding 7 % by the end of the experiment. In all media, the dissolution rate decreased over time, which corresponds to a kinetically controlled process, likely limited by the availability of reactive material or the formation of a protective surface layer.

Analysis of the dissolution rate (Figure 23 b) showed that during the initial 120 minutes (2 hours), the rate was highest in the neutral aqueous medium ( $\approx 0.0012$  g/min), likely due to the dissolution of the surface layer and the presence of easily soluble phases. After 120 minutes, the rate significantly decreased and remained stable, suggesting the formation of a protective layer composed of insoluble oxides or borate complexes.

Sample AlBO <sub>3</sub> :Eu <sup>3+</sup>	Time (hours/min)							
	1/60	2/120	3/180	4/240	24/1440	48/2880	72/4320	
SAlBO <sub>3</sub> + $H_2O(g)$	0,0673	0,0474	0,0539	0,0436	0,7409	0,8133	0,6382	
$SAlBO_3 + acid (g)$	0,0561	0,0403	0,0376	0,0350	0,6215	0,5986	0,7222	
SAlBO <sub>3</sub> + basis (g)	0,0396	0,0360	0,0371	0,0313	0,6689	0,6121	0,7704	

Table 9. Change in sample mass in various environments

In the acidic medium, the initial dissolution rate is slightly lower ( $\approx 0.001$  g/min), which may be attributed to the relative stability of aluminum oxides and borates at low pH. In the alkaline-buffered environment, the initial rate is approximately 0.0008 g/min, likely due to the stability of borate phases and the formation of sparingly soluble alkaline borate compounds. In all media, a peak in the dissolution rate is observed at 1440 minutes (24 hours), after which the values decrease and stabilize.



Figure 23. a) Percentage mass loss of aluminum borate; b) Mass loss rate

#### **III.6. Fluorescence Analysis of Lanthanum and Aluminum Borates**

LaBO<sub>3</sub>:Eu<sup>3+</sup> & AlBO<sub>3</sub>:Eu<sup>3+</sup>

This study focuses on the spectral characteristics of lanthanum and aluminum borates doped with europium ions ( $Eu^{3+}$ ), aiming to elucidate the relationship between crystal structure and luminescent properties of these materials. Excitation–emission spectral measurements reveal the characteristic f–f transitions of  $Eu^{3+}$ , with the most intense emission peaks observed at 592 nm (orange region) and 615 nm (red region) upon excitation at 284 and 395 nm.

In LaBO<sub>3</sub>:Eu<sup>3+</sup> (Figure 24 a), the emission peak at 615 nm corresponds to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition, which is highly sensitive to the symmetry of the local coordination environment around the Eu<sup>3+</sup> ions. An energy transfer process is observed under excitation around 290 nm, involving interactions between the 2p orbitals of O<sup>2-</sup> and the 4f orbitals of Eu<sup>3+</sup>. The efficiency of this transfer is influenced by the local electrostatic stability of Eu<sup>3+</sup> within the crystal lattice.

In AlBO<sub>3</sub>:Eu<sup>3+</sup> (Figure 24 b), a strong red emission is observed, with the most intense peak at 612 nm also assigned to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition. This suggests that Eu<sup>3+</sup> ions in AlBO<sub>3</sub> occupy non-centrosymmetric sites, as further supported by the broadening of the emission bands. The broadening is attributed to the presence of different microenvironments around Eu<sup>3+</sup> within the crystal structure, leading to inhomogeneous energy level distributions.

Of particular interest is the transition from the excited  ${}^{5}\text{H}_{3}$  state of Eu<sup>3+</sup> at 319 nm observed in AlBO<sub>3</sub>:Eu<sup>3+</sup>. This transition is typically associated with fluoride-based matrices or systems exhibiting high-energy charge-transfer bands. Its presence in aluminum borate indicates that the octahedral coordination of Eu<sup>3+</sup> in this matrix provides a local environment similar to that in fluoride hosts, effectively suppressing non-radiative relaxation processes.



*Figure 24. Graphical representation of the emission intensity versus the excitation wavelength for a)* LaBO<sub>3</sub>:*Eu*<sup>3+</sup> *and b)* AlBO<sub>3</sub>:*Eu*<sup>3+</sup>

# LaBO3:Dy<sup>3+</sup> & AlBO3:Dy<sup>3+</sup>

The emission-excitation spectrum of LaBO<sub>3</sub> doped with  $Dy^{3+}$  ions is presented in Figure 25 a. The spectral measurements reveal characteristic excitation and emission peaks associated with the intraconfigurational f–f transitions of  $Dy^{3+}$  ions. The dominant emission peaks observed at 477 nm and 569 nm correspond to magnetic dipole and electric dipole transitions, respectively.

The intensities of these transitions provide insight into the symmetry of the local environment surrounding the  $Dy^{3+}$  ions in the synthesized samples. Spectral analysis indicates that the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$  transition, observed at 477 nm, is more prominent in highly symmetric environments, whereas the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  transition at 569 nm becomes more intense in environments with lower symmetry. In the synthesized LaBO<sub>3</sub>-based material, the enhanced

intensity of the 569 nm transition suggests a locally distorted, lower-symmetry coordination around  $Dy^{3+}$ .

Additionally, in the spectra of AlBO<sub>3</sub> doped with  $Dy^{3+}$  ions (Figure 25 b), emission peaks at 591 nm and 612 nm are observed. Although these wavelengths are typically associated with  $Eu^{3+}$  transitions, in this context they can be attributed to distinct electronic transitions of  $Dy^{3+}$  ions. The differences in spectral features between the lanthanum and aluminum borates are primarily attributed to variations in the crystal structure and the specific site occupancy of  $Dy^{3+}$  ions within the respective host lattices.



*Figure 25.* Graphical representation of the emission intensity versus the excitation wavelength for a) LaBO<sub>3</sub>:Dy<sup>3+</sup> and b) AlBO<sub>3</sub>:Dy<sup>3+</sup>

# LaBO<sub>3</sub>:Tb<sup>3+</sup> & AlBO<sub>3</sub>:Tb<sup>3+</sup>

The luminescence spectra of aluminum and lanthanum borate hosts doped with terbium ions  $(Tb^{3+})$  are shown in Figure 26 a and 26 b. The emission spectra of  $Tb^{3+}$  ions arise from intraconfigurational 4f transitions, whose intensity and position are strongly influenced by the crystal field environment of the host material.

The peak observed at 270 nm is attributed to the spin-allowed  $4f^8 \rightarrow 4f^75d$  transition of Tb<sup>3+</sup>. Additional excitation bands in the range of 270–380 nm correspond to transitions from the ground state <sup>7</sup>F<sub>6</sub> to higher excited levels such as <sup>5</sup>H<sub>7</sub> (320 nm), <sup>5</sup>L<sub>9</sub> (350/357 nm), and <sup>5</sup>G<sub>6</sub> (380/377 nm).

The emission spectrum of  $Tb^{3+}$  in the lanthanum borate matrix includes four main transitions:  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$  (491 nm),  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  (545 nm),  ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$  (589 nm), and  ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$  (621 nm), with the 545 nm transition dominating the emission, indicating green luminescence under excitation at 380 nm. In the aluminum borate matrix, three emission transitions have been identified:  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  (543 nm),  ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$  (587 nm), and  ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$  (613 nm), the latter being slightly blue-shifted compared to its counterpart in LaBO<sub>3</sub>.

The luminescence intensity is significantly higher in LaBO<sub>3</sub>:Tb<sup>3+</sup> (approximately 20,000 a.u.) compared to AlBO<sub>3</sub>:Tb<sup>3+</sup> (about 9,000 a.u.). These results suggest that the lanthanum borate matrix provides a more favorable crystal environment for efficient emission, minimizing energy losses and enhancing the quantum yield of luminescence relative to the aluminum borate counterpart.



*Figure 26. Graphical representation of the emission intensity versus the excitation* wavelength for a) LaBO<sub>3</sub>:*Tb*<sup>3+</sup> and b) AlBO<sub>3</sub>:*Tb*<sup>3+</sup>

LaBO<sub>3</sub>:Eu<sup>3+</sup>:Tb<sup>3+</sup> & AlBO<sub>3</sub>:Eu<sup>3+</sup>:Tb<sup>3+</sup>

The spectra of lanthanum and aluminum borates co-doped with europium ( $Eu^{3+}$ ) and terbium ( $Tb^{3+}$ ) ions display the characteristic spectral features of both dopants, as shown in Figure 27 a and 27 b. Spectral analysis reveals that the co-doped samples exhibit distinctive luminescent bands and interactions between the two types of ions, which significantly influence the optical properties of the materials.



**Figure 27.** Graphical representation of the emission intensity versus the excitation wavelength for a)  $LaBO_3:Eu^{3+}:Tb^{3+}$  and b)  $AlBO_3:Eu^{3+}:Tb^{3+}$ 

At a Eu<sup>3+</sup>:Tb<sup>3+</sup> molar ratio of 1:2, transitions corresponding to  ${}^{5}D_{0} \rightarrow {}^{7}F_{j}$  (J = 1 to 4) of Eu<sup>3+</sup> and the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition of Tb<sup>3+</sup> are observed. The luminescent bands in the 587–673 nm range confirm the occurrence of an energy transfer process from Tb<sup>3+</sup> to Eu<sup>3+</sup>, while no evidence of the reverse transfer (Eu<sup>3+</sup> $\rightarrow$  Tb<sup>3+</sup>) is detected. This results in a dominant red emission at 613 nm under excitation at 395 nm.

The spectral profiles indicate that  $Tb^{3+}$  ions enhance the red emission of  $Eu^{3+}$  ions through an efficient energy transfer mechanism. This leads to an increase in red luminescence intensity (613 nm) at the expense of green emission, making these materials particularly suitable for applications that require precise tuning of the emitted color.

LaBO<sub>3</sub>:Eu<sup>3+</sup>:Dy<sup>3+</sup> & AlBO<sub>3</sub>:Eu<sup>3+</sup>:Dy<sup>3+</sup>

The luminescence spectra of samples co-doped with  $Eu^{3+}/Dy^{3+}$  in a molar ratio of 2:1 exhibit four emission bands at 591, 615, 683, and 701 nm for the lanthanum borate matrix (Figure 28 a), and three bands at 586, 612, and 698 nm for the aluminum borate matrix (Figure 28 b).



**Figure 28.** Emission intensity as a function of excitation wavelength for a)  $LaBO_3:Eu^{3+}:Dy^{3+}$ and b)  $AlBO_3:Eu^{3+}:Dy^{3+}$ 

The most intense luminescent peak in the lanthanum borate sample is observed upon excitation at 290 nm. Samples doped with  $Dy^{3+}$  alone show insufficient emission intensity in the red region of the spectrum. Therefore,  $Eu^{3+}$  ions, known for their strong red emission, were introduced alongside  $Dy^{3+}$  to enhance luminescent efficiency.

In the visible spectral range,  $Dy^{3+}$  ions produce blue and yellow emissions corresponding to the  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ ,  ${}^{6}H_{13/2}$ , and  ${}^{6}H_{11/2}$  transitions. Yellow emission is typically observed when  $Dy^{3+}$  ions occupy non-centrosymmetric lattice sites. For  $Eu^{3+}$  ions, red emission arising from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition is attributed to an electric dipole mechanism, and it becomes most intense when  $Eu^{3+}$  ions also reside in non-centrosymmetric environments.

# LaBO<sub>3</sub>:Eu<sup>3+</sup>:Gd<sup>3+</sup> & AlBO<sub>3</sub>:Eu<sup>3+</sup>:Gd<sup>3+</sup>

Upon direct excitation of  $Eu^{3+}$  ions at 396 nm, non-radiative relaxation leads to population of the <sup>5</sup>D<sub>0</sub> emitting level. Spectral analysis reveals efficient energy transfer from Gd<sup>3+</sup> to Eu<sup>3+</sup>, significantly enhancing luminescence intensity.

Under 396 nm excitation,  $Eu^{3+}$  ions are directly excited and relax to the <sup>5</sup>D<sub>0</sub> state, from which characteristic emission occurs (Figure 29 a). Excitation of Gd<sup>3+</sup> at 290 nm induces the  ${}^{8}S_{7/2} \rightarrow {}^{6}I_{7/2}$  transition, followed by either photon emission or energy transfer to  $Eu^{3+}$ . Additionally, excitation at 270 nm activates both  $Eu^{3+}$  and Gd<sup>3+</sup> ions, further intensifying the emission through a combined charge and energy transfer mechanism.



**Figure 29.** Emission intensity as a function of excitation wavelength for a)  $LaBO_3:Eu^{3+}:Gd^{3+}$ and b)  $AlBO_3:Eu^{3+}:Gd^{3+}$ 

The most intense emission peak, observed at 613 nm, corresponds to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of Eu<sup>3+</sup>. Comparison of emission intensities shows that the Gd<sup>3+/</sup>Eu<sup>3+</sup> combination

results in stronger luminescence in the AlBO<sub>3</sub> matrix than in LaBO<sub>3</sub> (Figure 29 b). This suggests that AlBO<sub>3</sub> provides a more favorable environment for efficient energy transfer and enhanced emission intensity, making it advantageous for applications requiring bright red luminescence.

# LaBO<sub>3</sub>:Eu<sup>3+</sup>:Gd<sup>3+</sup>:Tb<sup>3+</sup> & AlBO<sub>3</sub>:Eu<sup>3+</sup>:Gd<sup>3+</sup>:Tb<sup>3+</sup>

Figures 30 a and 30 b present excitation-emission plots for samples co-doped with  $Eu^{3+}$ ,  $Gd^{3+}$ , and  $Tb^{3+}$  ions in a molar ratio of 3:2:1, embedded in LaBO<sub>3</sub> and AlBO<sub>3</sub> matrices. The samples were excited using a source with wavelengths ranging from 200 to 600 nm, and the dependence of the emission peak intensities on the excitation wavelength was examined. Fluorescence analysis reveals that, for both samples, the most intense emission peak appears at 612 nm (red region), attributed to the characteristic electronic transitions of  $Eu^{3+}$  ions. Emissions observed at 589 nm for LaBO<sub>3</sub> and 592 nm for AlBO<sub>3</sub> are associated with transitions of  $Tb^{3+}$  ions, but their intensity is notably low.



*Figure 30.* Emission intensity as a function of excitation wavelength for a)LaBO<sub>3</sub>:Eu<sup>3+</sup>:Gd<sup>3+</sup>:Tb<sup>3+</sup> and b) AlBO<sub>3</sub>:Eu<sup>3+</sup>:Gd<sup>3+</sup>:Tb<sup>3+</sup>

The typical emission peaks of  $Gd^{3+}$ , located around 303 nm, 321 nm, and 398 nm– corresponding to the  ${}^{6}P_{7/2} \rightarrow {}^{8}S_{7/2}$ ,  ${}^{6}P_{5/2} \rightarrow {}^{8}S_{7/2}$ , and  ${}^{6}P_{3/2} \rightarrow {}^{8}S_{7/2}$  transitions–are not detected in the synthesized samples due to the high energy gap. In this case,  $Gd^{3+}$  ions act as sensitizers, enhancing the luminescence of Eu<sup>3+</sup> ions. Additional peaks are identified at 290/270 nm, 320 nm, 365/360 nm, 386/380 nm, 420 nm, 466 nm, and 535/540 nm, although their intensities are significantly lower compared to the main peak at 612 nm.

It is also observed that the excitation peak intensity at 395/400 nm is substantially higher than that at 290/270 nm for both samples, indicating a more efficient energy transfer when excited at longer wavelengths. Eu<sup>3+</sup> ions appear to be better incorporated into the crystal lattice of AlBO<sub>3</sub> compared to LaBO<sub>3</sub>, which may explain the differences in the observed luminescent properties.

# LaBO<sub>3</sub>:Eu<sup>3+</sup>:Dy<sup>3+</sup>:Tb<sup>3+</sup> & AlBO<sub>3</sub>:Eu<sup>3+</sup>:Dy<sup>3+</sup>:Tb<sup>3+</sup>

The maximum emission intensity of LaBO<sub>3</sub> co-doped with  $Eu^{3+}$ ,  $Dy^{3+}$ , and  $Tb^{3+}$  ions is significantly higher (~25,000 a.u.) compared to AlBO<sub>3</sub> (~18,000 a.u.), suggesting that the LaBO<sub>3</sub> matrix is more effective in enhancing luminescence signals (Figures 31 a and 31 b). The emission spectra show prominent peaks in the red region (616/611 nm), with LaBO<sub>3</sub> exhibiting a gradual decrease in intensity with increasing excitation wavelength, whereas AlBO<sub>3</sub> displays the opposite trend–an increase in intensity at longer wavelengths. Additional emission bands detected at 591, 684, and 696/701 nm are attributed to transitions of  $Eu^{3+}$ ,  $Dy^{3+}$ , and  $Tb^{3+}$  ions. Their contributions help to broaden the spectral coverage of the materials.



*Figure 31.* Emission intensity as a function of excitation wavelength for a) LaBO<sub>3</sub>:Eu<sup>3+</sup>:Dy<sup>3+</sup>:Tb<sup>3+</sup> and b) AlBO<sub>3</sub>:Eu<sup>3+</sup>:Dy<sup>3+</sup>:Tb<sup>3+</sup>

The larger ionic cavities in LaBO<sub>3</sub> allow for easier incorporation and more favorable positioning of rare-earth ions, which enhances emission efficiency. In contrast, the tighter coordination spaces in AlBO<sub>3</sub> generate strong local electrostatic fields, reflected in a blue-shift of the main emission peak. Co-doping with  $Dy^{3+}$  and  $Tb^{3+}$  further contributes to specific emission features. In LaBO<sub>3</sub>,  $Tb^{3+}$ -related transitions show higher intensity compared to those in AlBO<sub>3</sub>, suggesting more efficient integration of  $Tb^{3+}$  into the LaBO<sub>3</sub> structure and more effective energy transfer to Eu<sup>3+</sup>.

#### **III.7.** Luminescence Measurements Using a Smartphone

#### Spectral Characteristics of the Smartphone

The present study investigates the spectral response characteristics of a smartphone (Samsung A51) in comparison to a conventional spectrometer (Ocean Optics), focusing on the accuracy and linearity of the acquired data. The smartphone's spectral sensitivity is determined by the transmission spectra of the color filter array (RGB) corresponding to red, green, and blue pixels. This inherent filter design leads to characteristic distortions in the recorded spectra.

An experimental setup involving a diffraction grating (1000 lines/mm) and broadband white light emitted through a monochromator was used to determine the spectral ratio  $r(\lambda)$ , defined as the ratio between the signal recorded by the smartphone and that of the spectrometer.

The results reveal a non-uniform distribution of  $r(\lambda)$ , with pronounced minima at spectral regions corresponding to the crossover points of the RGB transmission curves. The linearity of the smartphone's response was further assessed by replacing a fixed-intensity laser source with a white LED of variable optical power. It was observed that the intensity measured by the smartphone tends to saturate with increasing optical power, an effect most prominent in the blue spectral region and least pronounced in the red.

A comparison of spectra recorded by the two devices confirms that distortions in smartphone-based measurements are primarily due to the spectral efficiency of the RGB filters. This highlights the need for appropriate calibration procedures. The results underscore the limitations of smartphones as spectral sensors, while also pointing to the potential for improvement through algorithmic correction techniques.

Figure 32 presents the topographic emission spectra of a)  $LaBO_3:Eu^{3+}:Tb^{3+}$ ; b) AlBO<sub>3</sub>:Eu<sup>3+</sup>:Tb<sup>3+</sup>; c) LaBO<sub>3</sub>:Eu<sup>3+</sup>:Dy<sup>3+</sup>; and d) LaBO<sub>3</sub>:Eu<sup>3+</sup>:Dy<sup>3+</sup>:Tb<sup>3+</sup>, as measured by the Ocean Optics spectrometer (OO) and the smartphone (MT). The comparison between these spectra allows for the following observations:



**Figure 32.** Topographic spectra of a) LaBO3:Eu<sup>3+</sup>:Tb<sup>3+</sup>, b) AlBO3:Eu<sup>3+</sup>:Tb<sup>3+</sup>, c) LaBO3:Eu<sup>3+</sup>:Dy<sup>3+</sup>, d) LaBO3:Eu<sup>3+</sup>:Dy<sup>3+</sup>:Tb<sup>3+</sup>, recorded by the Ocean Optics (OO) spectrometer and by a mobile phone (MT)

Based on the comparison between the two detection methods, the following observations can be made:

- ✓ The mobile phone camera accurately reproduces the narrow excitation-emission peaks within the range of 400–700 nm, enabling reliable identification of the main fluorescent transitions.
- ✓ Intensities above 700 nm are not detected by the mobile phone, and signals above 650 nm are weakly detectable. This limits the analysis in the infrared region of the spectrum. However, the phone effectively suppresses excitation light signals at wavelengths ≤ 395 nm, which is a significant advantage for fluorescence measurements.
- ✓ There are changes in the ratio of adjacent emission peaks, which requires prior knowledge of the spectrum measured by a standard spectrometer, especially when using relative intensity for sample identification.
- ✓ A smartphone, when equipped with a low-cost diffraction grating, can be used for both contact and non-contact detection of fluorescent materials.
- ✓ The mobile phone allows three-dimensional visualization of the excitation-emission spectra, with individual peaks of the samples being accurately identifiable. However, it should be noted that the relative intensities may differ from those measured by a standard spectrometer due to the spectral transmission properties of the phone's RGB filters.
- ✓ The smartphone enables simultaneous detection of spectra from arrays of fluorescent markers, with their spatial distribution appearing differently depending on the excitation wavelength.
- ✓ In the case of phosphorescent materials, the smartphone shows between 7 and 15 times faster response compared to a standard spectrometer, making it suitable for dynamic measurements.

# **IV. CONCLUSION**

- 1. The yttrium borates (YBO<sub>3</sub>) were synthesized via two methods solid-state synthesis and microwave-assisted process with control over key synthesis parameters (temperature, time, and boric acid excess).
- 2. The optimal synthesis conditions were found to be 45 % boric acid excess, a synthesis temperature of 900 °C, a holding time of 4 hours, and a cooling rate of 0.9375 °C/min.
- 3. All the obtained materials were in a white, powdery form, which is advantageous for practical applications.
- 4. The red-orange emission ratio was improved by co-doping the yttrium borates with europium and cerium ions (Eu<sub>2</sub>O<sub>3</sub>, Ce(SO<sub>4</sub>)<sub>2</sub>x4H<sub>2</sub>O), achieving a maximum red emission purity with an average value of 2.98. This minimized the unwanted orange emission.
- 5. X-ray structural analysis showed that YBO<sub>3</sub> forms a vaterite-type crystal structure, with polymorphic transformation observed depending on the boric acid content.
- 6. A comparative study of the fluorescence spectra of yttrium borates doped with europium ions, synthesized via both methods, revealed that those obtained via microwave-assisted synthesis exhibited stronger fluorescence and a higher red-to-orange (R/O) ratio. The enhanced red emission is attributed to better structural substitution of europium ions into the yttrium host lattice.
- 7. Chemical stability studies revealed differences between the two synthesis methods. Although microwave-assisted synthesis showed stability, the samples obtained through this method demonstrated lower chemical resistance. This emphasizes the advantages of solid-state synthesis, which was selected for the synthesis of lanthanum and aluminum borates doped and co-doped with rare earth elements to ensure better operational properties.
- 8. X-ray analysis was performed to study the crystal structure of lanthanum borates doped and co-doped with rare earth ions. The main crystal phase identified was orthorhombic, of the aragonite type. A correlation was found between the structural features of the materials and their luminescent properties.

- 9. Lanthanum borate (LaBO<sub>3</sub>), doped and co-doped with rare earth ions, demonstrated stability and effective charge transfer, leading to higher light intensity compared to other synthesized materials. This makes it one of the most promising materials for various practical applications.
- 10. Aluminum borate (AlBO<sub>3</sub>), co-doped with europium and gadolinium, showed the highest luminescence intensity and demonstrated significant potential for applications in optoelectronic technologies due to its stability and effective charge transfer.
- 11. The crystal structure of aluminum borates was determined to be rhombohedral, of the calcite-type.
- 12. Chemical stability results showed that the most stable in aqueous environment was the yttrium borate co-doped with europium and cerium ions, while the aluminum borate dissolved to a large extent. This trend was also observed in acidic media. In alkaline-buffered solution, the most stable borate was the yttrium one doped with europium ions, synthesized by the microwave-assisted method, while the aluminum borate exhibited the lowest stability.
- 13. Fluorescence spectra of the synthesized materials measured with the smartphone camera demonstrated the potential of using affordable and compact devices for rapid and convenient fluorescence analysis, expanding the possibilities for quick spectroscopic characterization of materials.
- 14. A comparative evaluation of the synthesized materials in terms of their luminescent properties revealed significant differences based on the synthesis method and the doped elements, highlighting the importance of optimizing the synthesis conditions.

This research demonstrates that doped borate materials synthesized under controlled conditions offer significant potential for applications in optoelectronics, photonics, and sensor technologies. The obtained results contribute to both the fundamental understanding of the structure-property relationships in borate materials and the development of functional materials for practical use.

# V. CONTRIBUTIONS

# **Scientific Contributions**

- 1. At the first time, a detailed study was conducted on the effect of boric acid in high excess (from 5 % to 60 %) on the structural and optical properties of europium-doped yttrium borate. The dependencies were established, the structure was identified, and the main composition-property functions for the studied materials were derived; the optimal boric acid excess for achieving maximum fluorescent efficiency was determined.
- 2. At the first time, a microwave-assisted method for synthesizing europium-doped yttrium borates was implemented, with increasing boric acid excess (from 5 % to 60 %). A detailed comparative analysis was performed between yttrium borates synthesized by solid-state and microwave-assisted methods, from which fundamental conclusions were drawn regarding changes in optical and chemical properties.
- 3. The general patterns of luminescence of the doping components in the three types of matrices were established, along with the synergistic effect of co-doping multiple components in a single matrix.

# **Scientific and Practical Contributions**

- 1. The chemical stability of yttrium, aluminum, and lanthanum borates was evaluated, providing valuable information for their respective practical applications.
- 2. At the first time, fluorescence measurements of materials were conducted using a smartphone camera. The potential for non-contact, rapid, and reliable measurement of luminescent materials was assessed.

This dissertation is part of a research project funded by contracts with international companies. Some of the newly synthesized luminescent materials have been used to develop specialized compositions and devices, which are confidential due to patent considerations. *Guidelines for Continuing the Current Work:* 

- 1. Doping of the synthesized matrices with other rare-earth compounds.
- 2. Synthesis of yttrium borates doped and co-doped with other rare-earth compounds.
- 3. Synthesis of analogous borate materials with nanoscale dimensions, which would contribute to a deeper understanding of the influence of size effects on their luminescent, structural, and chemical properties, as well as expand their potential applications in the fields of nanotechnology and functional materials.
- 4. Expanding the research on the integration of the obtained materials into composite systems and their application in sensors, lasers, and displays.

# VI. PUBLICATIONS RELATED TO THE DISSERTATION:

- 1. K. Hristova, S. Nachkova, A. Peltekov, Zh. Simeonova, I. P. Kostova, Synthesis of inorganic luminescent materials applicable for valuable documents protection, *Technics*. *Technologies*. *Education*. *Safety*. 2021. VOL. 2, 128-130.
- T.A. Eftimov, I. P. Kostova, A. Peltekov, K. Hristova, D. Brabant, S. Fouzar, K. Nikolov, A study of strontium aluminates for all optical contactless sensing applications using smartphone interrogation, *Optics & Laser Technology, Volume* 176, *2024*, 110965, ISSN 0030-3992, https://doi.org/10.1016/j.optlastec.2024.110965. Impact Factor: 4.6, Quartile: Q1
- **3.** K. Hristova, I. P. Kostova, T.A. Eftimov, D. Brabant, S. Fouzar. Rare-Earth-Ion (RE<sup>3+</sup>)-Doped Aluminum and Lanthanum Borates for Mobile-Phone-Interrogated Luminescent Markers. *Photonics 2024, 11, 434*. https://doi.org/10.3390/photonics11050434 Impact Factor: 2.1, Quartile: Q2
- 4. I.P. Kostova, T. A. Eftimov, **K. Hristova**, S. Nachkova, S. Tsoneva, and A. Peltekov. "An Effect of Boric Acid on the Structure and Luminescence of Yttrium Orthoborates Doped with Europium Synthesized by Two Different Routines" *Crystals 14, no. 6: 575, 2024*, https://doi.org/10.3390/cryst14060575 Impact Factor: 2.4, Quartile: Q2
- K. Hristova, I. Kostova, T. Eftimov, D. Tonchev, Synthesis and luminescence characteristics of yttrium, aluminum and lanthanum borates doped with europium ions (Eu<sup>3+</sup>), *Bulgarian Chemical Communications, Volume 56, Special Issue D (pp. 121-127) 2024* https://doi.org/10.34049/bcc.56.D.S1P44, SJR 2023 – 0.15 Quartile: Q4

# Noted citations:

Publication 4 is cited in:

- Wibawa, T., Diharjo, K., Ariawan, D., Raharjo, W.W., Wibowo, C.H., Saputro, F.N., Rakhman, A., Muharam, A., Kaleg, S., Hapid, A. and Zulkefly, M. "Enhancing the Mechanical and Fire-Resistant Properties of GFRP Composite using Boric Acid and Sodium Silicate Fillers" *Engineering, Technology & Applied Science Research.* 14, 6, 18911–18922, 2024. doi.org/10.48084/etasr.9271.
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- Alena Aslandukova\*, Andrey Aslandukov, Yuqing Yin, Maxim Bykov, Valerio Cerantola, Anna Pakhomova, Natalia Dubrovinskaia, Leonid Dubrovinsky, "High-Pressure Yttrium Borate *oC*20-YBO<sub>3</sub> and Yttrium Orthocarbonate *hR*39-Y<sub>3</sub>(CO<sub>4</sub>)<sub>2</sub> Synthesized at Megabar Pressures", *Inorganic Chemistry*, **2025**, doi: 10.1021/acs.inorgchem.4c05308.

Publication 3 is cited in:

• Xiaoqing Du, Hong Chen, Xiaohua Lei, Yu Xiong and Xiaoyang Liu, "Enhanced EQE of rare earth-doped fluorescent glass by micro-patterning light incident and emission interface for highly efficient white LEDs", *Applied Physics Express*, **2025**, doi: 10.35848/1882-0786/adc8f8

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# **VII. PARTICIPATIONS IN CONFERENCES**

- 9<sup>th</sup> International Scientific Conference "Technology. Technologies. Education. Security," Borovets Resort, June 7, 2021 – June 10, 2021. K. Hristova, S. Nachkova, A. Peltekov, Zh. Simeonova, I. P. Kostova, "Synthesis of inorganic luminescent materials applicable for valuable documents protection" (oral presentation).
- 3<sup>rd</sup> National Scientific Conference on Chemical and Pharmaceutical Sciences, Sofia University "St. Kliment Ohridski", Sofia, October 5, 2022 – October 6, 2022. K. Hristova, I. P. Kostova, D. Tonchev, "Innovative method for protecting the authenticity of pharmaceutical products using photoluminescent encoding" (poster presentation).
- 12<sup>th</sup> Scientific Conference on Chemistry with International Participation, Plovdiv, October 13, 2023 – October 14, 2023. K. Hristova, I. P. Kostova, T. A. Eftimov, D. Tonchev, "Luminescent analysis of yttrium, aluminium, and lanthanum borates doped with europium ions (Eu3+)" (poster presentation).
- 2024 International Workshop on Optoelectronic Perception (IWOP 2024), September 18<sup>th</sup>-22<sup>nd</sup>, 2024, Xi'an Yohol Hotel (西安悦豪酒店), Xi'an, China. T. A. Eftimov, I. P. Kostova, K. Hristova, G. Dyankov, K. Nikolov, P. Kolev, "Use of smartphones as affordable sensor interrogation instruments for measurements in the spectral and in the time domain" (oral presentation).
- 7<sup>th</sup> Scientific Conference for Students, PhD Students, and Young Researchers "Challenges in Chemistry," Plovdiv, October 18, 2024 – October 19, 2024. K. Hristova, I. P. Kostova, T. A. Eftimov, D. Tonchev, "Effect of boric acid on the structure and luminescence of europium-doped yttrium orthoborates" (oral presentation).
- National Scientific Conference on Physics, Engineering, and Technology with International Participation, organized by the Physics and Technology Faculty of Plovdiv University "Paisii Hilendarski", in collaboration with the "Eureka" Foundation, Plovdiv, November 27, 2024 – November 28, 2024. K. Hristova, K. Nikolov, I. P. Kostova, T. Eftimov, D. Tonchev, "Synthesis of lanthanum and aluminum borates for smartphone-readable fluorescent sensors" (poster presentation).

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