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Sol-Gel Synthesis of Fluorescent Materials Based on Barium Aluminate

Liliya Selyunina^{a)}, Liudmila Mishenina^{b)}, Ekaterina Kuznetsova^{c)} and Tat'yana Belyaninova^{d)}

Tomsk State University, 36 Lenina Avenue, Tomsk 634050 Russian Federation

^{a)}corresponding author: SelyuninaLA@mail.ru

^{b)}lnm@xf.tsu.ru

^{c)}katerina94_nsk@mail.ru

^{d)}belyaninova_tv@mail.ru

Abstract. Barium aluminate was obtained by sol-gel method. We used a heat treatment in an oven at 130°C, and microwave radiation for drying the gel. To obtain a crystalline product all samples were calcined in the muffle furnace at the temperatures up to 1100°C. Complex studies were used to identify the dynamics of phase and structural transformations in the synthesis of barium aluminate. The main stages of formation BaAl₂O₄ were determined by thermal analysis; evolution of phase composition and crystal structure were studied using X-ray diffraction and IR-spectroscopy. The morphology of surface of the barium aluminate was investigated by scanning electron microscope. In the work fluorescent material with composition Ba_{1-x}Eu_xAl₂O₄ was obtained. The maximum of luminescent intensity is achieved with content of Eu³⁺ equal 0.75 mol in the case of processing of gel by microwaves. The phosphor obtained by heat treatment in an oven gel has a composition Ba_{0.9}Eu_{0.1}Al₂O₄.

INTRODUCTION

Currently, much importance is given to alkaline earth metal aluminates, which are the basis of luminescent materials. Prominent among this class of compounds take barium aluminate doped with rare earth elements. Of great interest to the luminescent materials based on barium aluminate is associated with their thermal stability, environmental safety, radiation intensity and long afterglow time [1, 2].

The chemical industry is often used solid-phase method to obtain luminescent materials based on alkaline earth metal aluminates [3,4]. Its main disadvantage is the high temperature of synthesis. It leads to high energy costs and makes necessary to use special high-temperature furnaces. Also, due to the fact that mixing is in the solid phase, it is difficult to achieve uniform distribution of the activator in the phosphor matrix. In order to eliminate the disadvantages of this method scientists use other methods. The method of co-precipitation eliminates the problem of heterogeneity [5]. In this method, all reactants are used in liquid state and then they are precipitated by common reagent. But the synthesis temperature remains high. To reduce the temperature the scientists use the method of self-propagating high temperature synthesis (SHS) [6]. In this method, a substance with high combustion heat is introduced into reaction mixture. But this method does not lead to uniform distribution of the rare earth ion. Thus, for the best results, we need a method in which the reactants must be in the liquid phase and in the synthesis must be an additional source of energy. The sol-gel synthesis satisfies these conditions. The energy source is a polymeric complex which is destroyed with heat. Also, sol-gel synthesis allows to control the properties of the final product by varying the process parameters such as the composition and ratio of the starting reactants, conditions gel processing, synthesis temperature and time of heat treatment, etc.

The aim of this work was to develop a method of preparing a hexagonal barium monoaluminate and luminescent materials based on it. Also the aim was to investigate the effect of microwave irradiation and thermal processing on

the process of phase formation of the desired product and to determine the optimal conditions for the providing the single-phase product.

EXPERIMENTAL PART

Barium carbonate (chemically pure, Russian grade), aluminum nitrate nonahydrate (analytical reagent grade, Russian grade) and citric acid (chemically pure, Russian grade) were used for the synthesis of barium aluminate. Barium carbonate, aluminum nitrate nonahydrate were used as metal sources. Citric acid was used as a chelating agent and polymerizing agent. The choice of the molar ratio of the starting reagents $\text{Me}^{2+} : \text{Al}^{3+} : \text{H}_4\text{Cit}$ we made on the basis of the phase diagram [7]. There are three chemical compounds on the phase diagram: $\text{BaAl}_{11}\text{O}_{19}$, BaAl_2O_4 , $\text{Ba}_3\text{Al}_2\text{O}_6$, melting congruently at 2188, 2088 and 1893°C respectively and there are four eutectic points at 2148, 1893, 1753, 1698°C. Barium monoaluminate is formed at the molar ratio of $\text{BaO} : \text{Al}_2\text{O}_3$ equal of 1 : 1. Thus, the starting components containing cations barium and aluminum were taken in stoichiometric ratio, the molar ratio $\text{H}_4\text{Cit} : \text{total number of cations } (\text{Ba}^{2+} + \text{Al}^{3+})$ was 2 : 1 [8]. The luminescent material based on barium aluminate was obtained by introducing an ion of europium in an amount from 0.01 mol to 0.1 mol. A certain amount of Eu_2O_3 was dissolved in the nitric acid. Citric acid was dissolved in distilled water. The $\text{Al}(\text{OH})_3$ obtained from aluminum nitrate and calcium carbonate was separately dissolved in a solution of citric acid. The resulting clear solutions were mixed together and stirred for 1.5 hours using a magnetic stirrer. Heat treatment at 130°C in the oven and microwave radiation with a frequency 2450 ± 49 MHz were used for drying the gel. The sample volume was 10 ml. Exposure time per sample was 15 minutes. Synthesis scheme is shown in Figure 1.

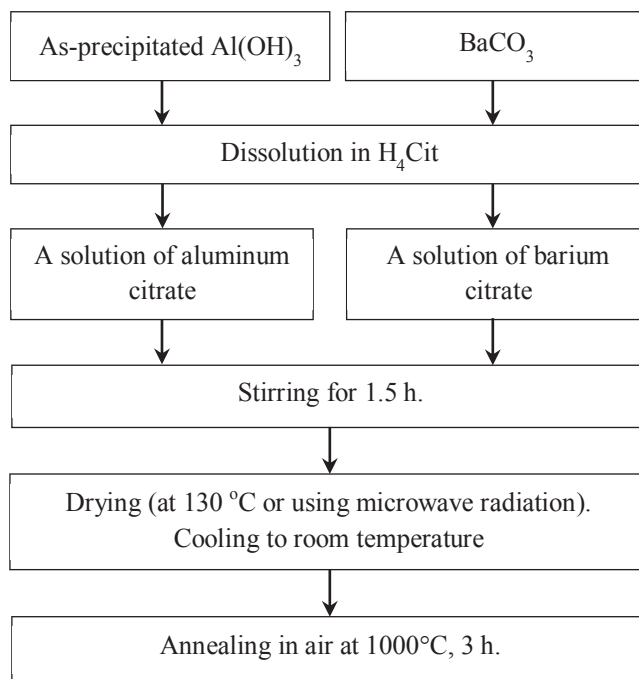


FIGURE 1. Synthesis scheme of barium aluminate

Thermal analysis of untreated xerogels was done using a NETZSCH STA 449C thermoanalyser (“NETZSCH “ Germany) at a rate of 5 °/min in air, the temperature range was from 25 to 1000 °C to define the main stages of the synthesis process. The structure of prepared powders was determined by X-ray analysis (XRD) using Rigaku MiniFlex 600 (Japan) ($\text{Cu K}\alpha$ radiation $\lambda = 1.5406\text{\AA}$) at room temperature with the range of angles 2θ from 3 to 80°) at the scanning speed of 2 °/min. The phase identification was carried out using the literature [9–11] and PDF-2 database. Infrared (IR) spectroscopy was done by IR spectrometer Agilent Technologies Cary 600 Series FTIR Spectrometer (made in USA) on the heat-treated samples at different temperatures to identify the nature of the bonding. The surface morphology of the final compounds was studied by scanning electron microscopy (SEM) on a Hitachi TM 3000 (Japan) equipment at accelerating voltage of 15 kV while removing the charge from the sample

(electron gun $5 \cdot 10^{-2}$ Pa, specimen chamber: 30–50 Pa). The ratio of the elements and the evenness of their distribution on the surface of the sample was determined by X-ray microanalysis using Quantax 70 (Japan) instrument. In order to form the crystalline aluminate precursor were annealed in a muffle furnace at the temperatures up to 1200 °C. The luminescent properties were investigated using a spectrofluorometer Solar CM 2203 (Belarus).

RESULTS AND DISCUSSION

The peculiarity of microwave radiation is a good penetration and interaction of radiation with molecules and ions throughout the volume of the irradiated object. This leads to the formation of uniform particle size of the final products. The best results we achieved when using the microwave exposure capacity of 360 watts. Scanning electron microscopy data indicate the formation of a well-formed round granules with the size from 350 to 550 nm. Therefore, further studies of phase formation we performed using this power.

Analysis of DSC and TG curves and the results of infrared spectroscopic analysis (Fig. 2) showed that the formation of barium aluminate proceeds in several steps separated from each other. Microwaves stabilize the complex at temperatures up to 200°C and prevent oxidation of the organic component. Therefore, an exothermic peak on the DTG curve is absent. The width of the exothermic peak in the temperature range from 350 to 500°C increases. This peak indicates the destruction of the polymer backbone with a simultaneous oxidation of organic substances. In the IR spectra the intensity of the absorption bands, which correspond to the groups $-\text{COO}-$ at 1578 cm^{-1} increase. The released carbon dioxide forms carbonate ions with water vapor, whose presence is associated with oscillations at a frequency 1100 and 1500 cm^{-1} . Formation of barium aluminate begins above 800°C. Fluctuations of tetrahedra $[\text{AlO}_4]$ appear, intensity and resolution of the absorption bands which characteristic of communication $\text{Al}-\text{O}-\text{Al}$ in barium aluminate increase. Due to the fact that the release of energy occurs in a narrow range, the temperature of the synthesis is reduced. This is evidenced by an endothermic peak which appears at 800°C. Precursor obtained by drying in the oven begins to oxidize to 200°C. In both cases above 200°C the band intensity at 3600–3100 and 1360 cm^{-1} belonging to adsorbed water and crystal water is reduced. In the process of drying the gel under the influence of microwave radiation, the nitrate decomposition accompanied by the release of large quantities of brown gas. Therefore fluctuations $\text{C}-\text{NO}_2$ bond in the IR spectra at 1350, 1550, 900 cm^{-1} were less intense for the sample and disappear above 250°C. In the sample obtained by thermal treatment of the gel at 130°C these bands are more intense and remain to 350°C. Assignment of IR spectra bands barium aluminate and synthetic intermediates are shown in Table 1.

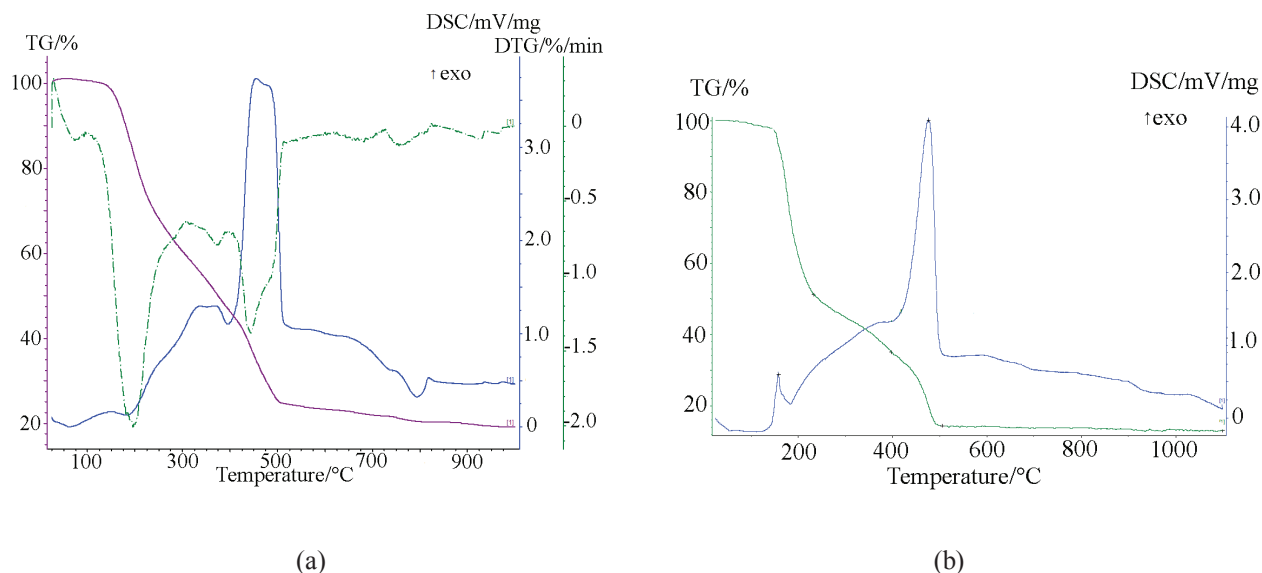


FIGURE 2. DSC and TG curves of samples, obtained: (a) – using heat treatment at 130°C in the oven, (b) - using microwave radiation

TABLE 1. Assignment of IR spectra bands barium aluminate and synthetic intermediates

Temperature, °C						Type fluctuations
250	350	650	700	900	1000	
The oscillation frequency, cm ⁻¹						
3600–3100	3600–3100	3600–3100	3600–3100	3600–3100	3600–3100	crystal water
1640–1615	1640–1615	1640–1615	1640–1615	1640–1615	1640–1615	
3444	3450	3450	3450	3450	3450	–OH
1550,1350, 900	1550,1350, 900	-	-	-	-	C–NO ₂ ⁻
1605	1578	1578	-	-	-	COO ⁻
1500, 1100	1500, 1100	1500, 1100	-	-	-	CO ₃ ²⁻
1419.5	1419.5	1413.2		-		C=C
1074	1074	1074.4, 1023.7		-		O–C–O
906.6, 874.9	906.6, 874.9	897.1	868.6	872	897.1	Al–O–Al
814.8	814.8	820	820	820	820	Al–OH end
691	675	669	700	654	681.8	Al–OH
567.8	567.8	564.6	561.5	570	571.5	Al–O
			-	443	437	[AlO ₄]

To determine the dynamics of phase transitions, the dried gel was subjected to heat treatment in the temperature range from 100 to 1100 °C.

X-ray analysis of synthetic intermediates defined by the results of thermal analysis, allowed to follow the dynamics of structure of barium aluminate (Fig. 3). The obtained diffraction patterns can be seen that the samples up to 800°C are X-ray amorphous, so determine the phase composition of the product by this method is not possible. However, the appearance of the intense peak corresponding BaAl₂O₄ phase indicates nucleation of main phase already at 650°C. Formation of hexagonal barium aluminate occurs at 800°C. A small amount of barium carbonate impurities present in the sample at that temperature. It disappears with further increase in temperature. Increasing the annealing temperature is accompanied by an increase in the crystallite size. Under different conditions of drying the gel is formed hexagonal barium aluminate, but the change in the method of drying the gel leads to a different space groups. In the case of heat treatment in the oven is produced a product with a spatial group P6₃, but in the case of using microwaves is obtained barium aluminate with space group R6₃22 (Table 2).

The degree of formation of the crystal and the surface morphology of the barium aluminate has a great influence on the intensity of the luminescence. According to the scanning electron microscope, it is seen that the method of treatment of the gel affects particle size. The product obtained by heat treatment of the gel in an oven is a crystalline powder, which consists of large particle agglomerates. The use of microwave radiation leads to coarsening of the particles up to 350–550 nm (Fig. 4). Microprobe analysis revealed a uniform distribution of all elements on the surface of the obtained sample. The quantitative content of the elements corresponds to the composition of barium monoaluminate.

TABLE 2. Data X-ray diffraction

Temperature, °C	I,%		d,Å		Parameters cell, Å		Region of coherent scattering, Å	
	Micro-wave	130°C	Micro-wave	130°C	Micro-wave	130°C	Micro-wave	130°C
800	100	100	3.15	3.15	a = 5.22	a = 10.45	289	309
	42	45	2.61	2.61	c = 8.80	c = 8.79		
	38	37	4.52	4.52				
900	100	100	3.15	3.15	a = 5.22	a = 10.45	365	327
	41	43	2.61	2.61	c = 8.80	c = 8.79		
	38	33	4.51	4.52				
1000	100	100	3.15	3.15	a = 5.22	a = 10.45	454	372
	42	43	2.61	2.61	c = 8.80	c = 8.79		
	35	37	4.52	4.51				
1100	100	100	3.15	3.15	a = 5.22	a = 10.45	463	566
	41	45	2.61	2.61	c = 8.80	c = 8.79		
	34	31	4.51	4.52				

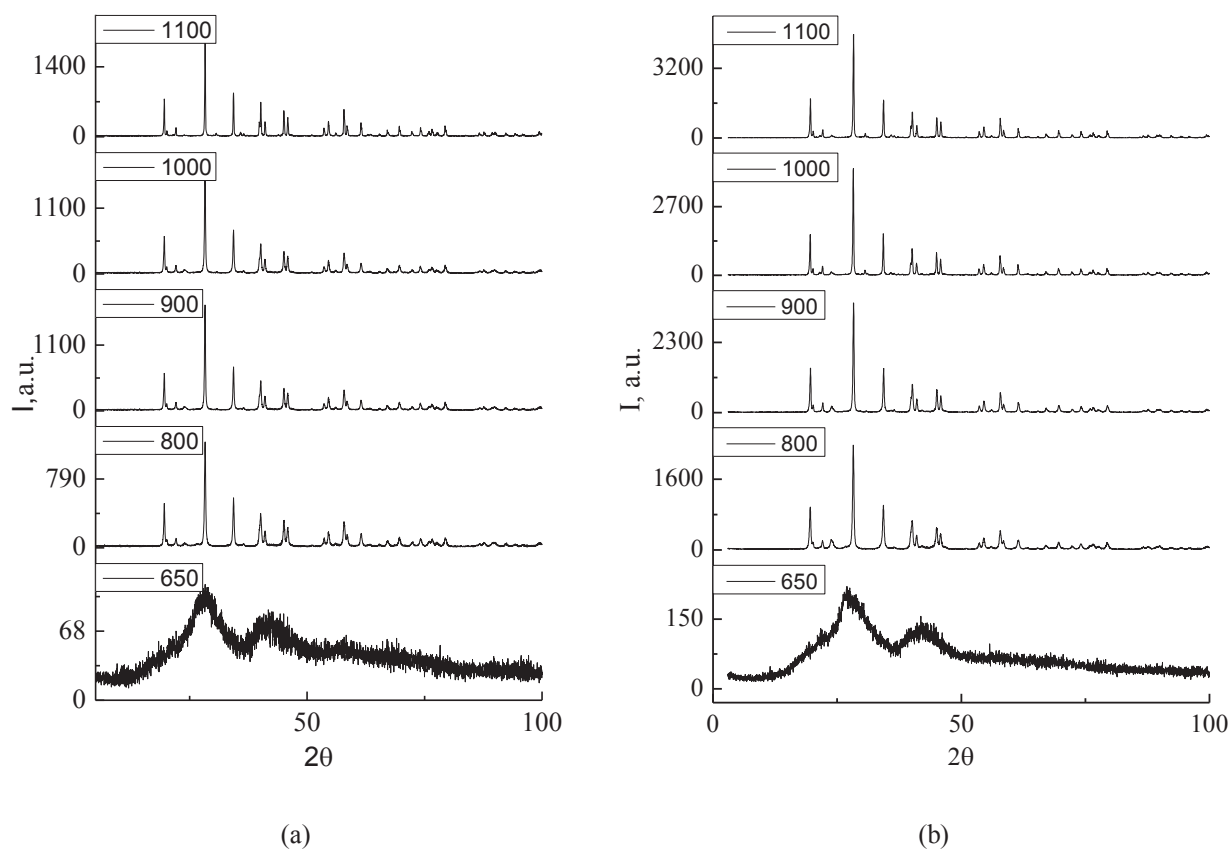


FIGURE 3. XRD data of samples, obtained: (a) – using heat treatment at 130°C in the oven, (b) - using microwave radiation

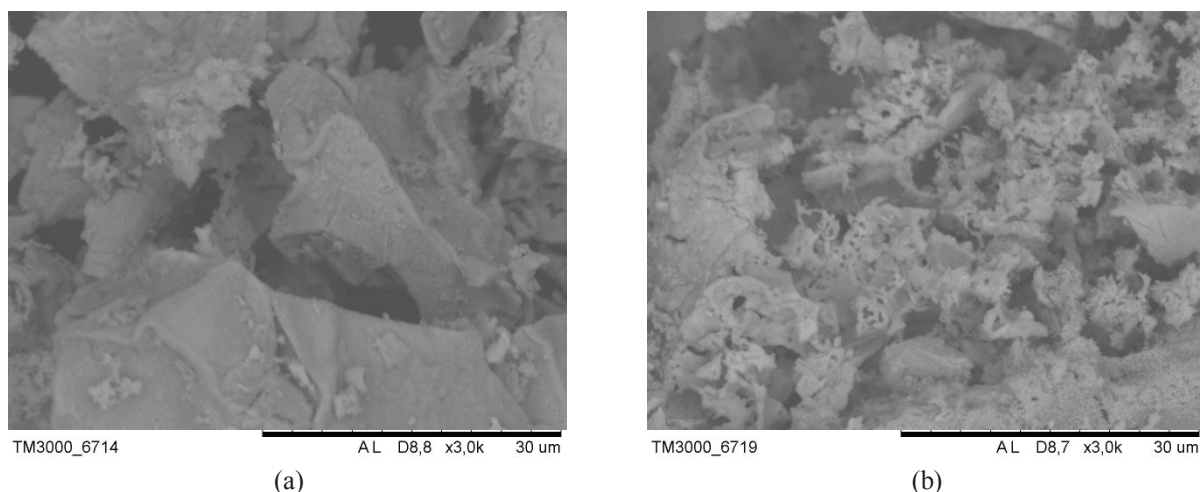


FIGURE 4. Morphology of the surface of $\text{Ba}_{0.9}\text{Eu}_{0.1}\text{Al}_2\text{O}_4$, obtained: (a) – using heat treatment at 130°C in the oven, (b) - using microwave radiation

The luminescence spectrum (Fig. 5) consists of characteristic narrow lines of emission of ion Eu^{3+} , corresponding to transitions of electrons within the 4f-shell. Forced electric dipole transition ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ with a peak with wavelength of 617 nm is more intense than the magnetic dipole transition ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ due to lack inversion ions Eu^{3+} . In the spectrum of the luminescence of $\text{BaAl}_2\text{O}_4:\text{Eu}^{3+}$ synthesized at temperatures of 1100°C , there are following lines: ${}^5\text{D}_0\text{--}{}^7\text{F}_3$ (651.5 nm), ${}^5\text{D}_0\text{--}{}^7\text{F}_4$ (703.7 nm). The concentration of the rare earth ion in the sample greatly affects the intensity of the luminescence. Therefore, as a result of the research necessary to find the optimum concentration of luminescent centers and get the greatest light intensity [12].

Increasing the content of europium leads to an increase in the symmetry of environment of europium ions. Magnetic dipole transition ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ becomes more intense transition. It suggests that the lattice becomes more "correct". In case of using microwave treatment intensity of luminescent is increased up to content of Eu^{3+} equal of 0.75 mol. Further increase of concentration leads to concentration quenching, which leads to a decrease in the quantum yield of luminescence due to increased nonradiative processes. In case of heat treatment of the gel the maximum of luminescence is observed when the content of Eu^{3+} is 0,1 mol. It is known that ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ - forced electric dipole transition and ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ - a magnetic dipole transition. Although the intensity of a magnetic dipole transition is largely independent of the environment of the Eu^{3+} ion, the ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ transition directly reflects the crystal-field splitting of the ${}^7\text{F}_1$ level. In the emission spectra of the phosphor obtained based on the barium aluminate using microwave radiation the split of ${}^7\text{F}_1$ -level is observed, while using a heat treatment of the gel in an oven split is not observed. The ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ transition is a so-called "hypersensitive transition", which means that its intensity is much more influenced by the local symmetry of the Eu^{3+} ion than the intensities of the other transitions. The ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ transition is responsible for the typical red luminescence observed in europium(III) phosphors. The ratio of the intensities of these transitions depends on the symmetry of the environment of the rare earth ion Eu^{3+} .

The spectrum of luminescence excitation of powder $\text{BaAl}_2\text{O}_4:\text{Eu}^{3+}$ for forced electric dipole transition ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ with a maximum $\lambda_{em} = 617$ nm is shown in Fig. 5. The spectrum consists of a broad band and a few narrow lines at longer wavelengths. A broad band with a maximum around 254 nm may correspond to charge transfer from oxygen atoms to the central atom of aluminum. On the other hand, the band can be explained by the charge transfer between Eu^{3+} and O^{2-} , with the electron orbitals of oxygen ($2p^6$) moves to the orbital Europium $4f^6$. Thus, we can conclude that a broad band in the ultraviolet region of the spectrum is related to the overlap of the absorption of AlO_4^- - group and charge transfer between Eu^{3+} and O^{2-} . The narrow lines in the spectrum of excitation associated with typical transitions in Eu^{3+} ion.

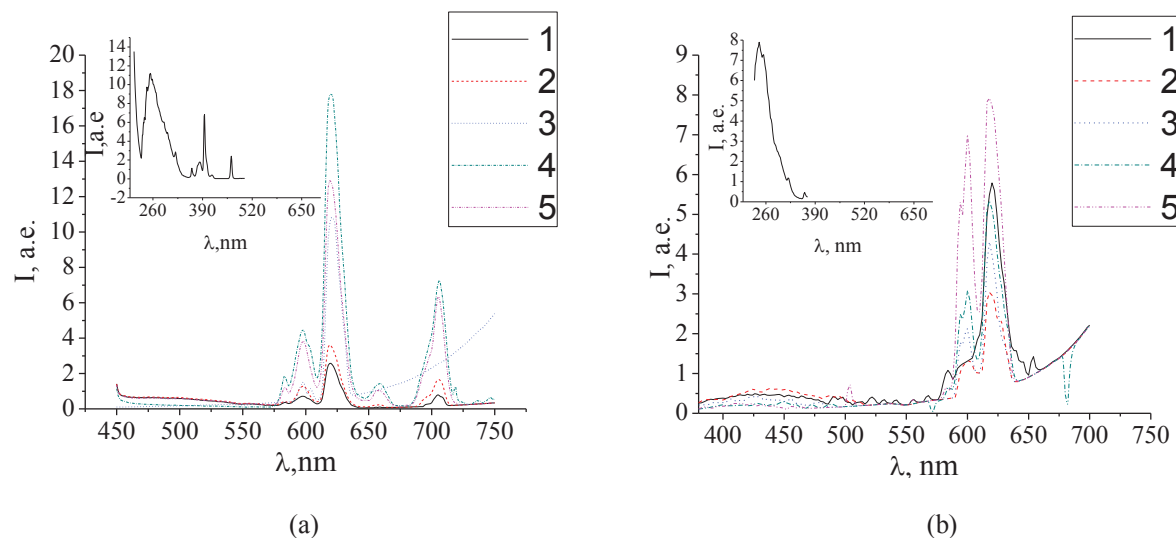


FIGURE 5. The luminescence spectra aluminate phosphors $Ba_{1-x}Eu_xAl_2O_4$, obtained: (a) – using heat treatment at 130°C in the oven, (b) - using microwave radiation

CONCLUSION

Thus, during operation was obtained hexagonal barium aluminate and the phosphors composition $Ba_{1-x}Eu_xAl_2O_4$. The best result was achieved using a microwave exposure of capacity of 360 watts. Under different conditions of drying the gel is formed hexagonal barium aluminate, but the change in the method of drying the gel leads to a different space groups. In the case of heat treatment in the oven is produced a product with a spatial group $P6_3$, but in the case of using microwaves is obtained barium aluminate with space group $R6_32_2$. Microwave exposure leads to enlargement of the spherical granules to 350–550 nm. Increasing the content of europium leads to growth environment symmetry europium ions in a sample obtained under microwave irradiation treatment and increase the luminescence intensity. The maximum of luminescent intensity is achieved when the content of Eu^{3+} is 0.75 mol. A further increase in the content of the activator leads to concentration quenching of luminescence. When using heat treatment of the gel the symmetry growth is less intense, and the maximum emission is observed when the content of Eu^{3+} is 0.1 mol.

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