



Phase formation and luminescent properties of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}:\text{Eu}, \text{Nd}$ prepared by sol-gel method

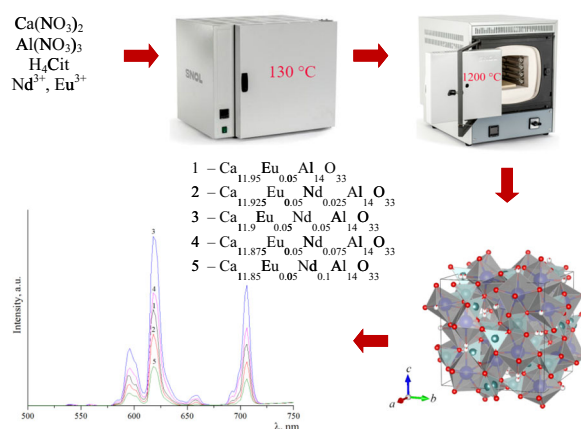
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Abstract

Calcium aluminate $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and phosphors based on it were obtained using sol-gel technology. Complex studies were used to identify the dynamics of phase and structural transformations in the synthesis of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. The main stages of the calcium aluminate formation were determined using thermal analysis, IR spectroscopy and X-ray phase analysis. Solid-phase interaction in the formation of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ includes the steps of obtaining calcium carbonate and amorphous alumina (800 °C), aluminates of composition $\text{Ca}_3\text{Al}_2\text{O}_6$ and CaAl_2O_4 (900–1000 °C), and $\text{Ca}_5\text{Al}_6\text{O}_{14}$ and $\text{Ca}_4\text{Al}_6\text{O}_{13}$ (1000–1100 °C). $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ begins to form at 1100 °C. The graphic image of the structure was constructed according to the obtained atomic coordinates using the ReX Powder diffraction program. Luminescent properties of the phosphors of the composition $\text{Ca}_{12-(0.05+x)}\text{Al}_{14}\text{O}_{33}:\text{Nd}_x\text{Eu}_{0.05}$ ($x = 0.025-0.1$) were investigated. It was determined that the highest intensity of luminescence is achieved at $x = 0.05$. With a further increase in the content of neodymium, there was a concentration quenching of the luminescence.

Graphical Abstract



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Highlights

- Calcium aluminate $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and phosphors based on it was obtained using sol–gel technology.
- Based on thermal analysis, IR spectroscopy and X-ray phase analysis, scheme of intermediate products transformation during synthesis was proposed.
- The highest intensity of luminescent was reached at a neodymium(III) content of 0.05 mol.

Keywords Calcium aluminate · Sol–gel · Phosphors · Europium · Neodymium.

1 Introduction

Until now, white LEDs, which were obtained by combining a blue LED chip and a yellow phosphor based on an yttrium aluminum garnet, had been popular. In recent years, there has been a tendency to replace them with LEDs made on the basis of a combination of ultraviolet LED chips and trichromatic crystal phosphors. Red phosphor shows lower luminescence efficiency compared with blue and green phosphor among trichromatic phosphors. Therefore, at present, the development of red phosphors, which have good photoluminescent characteristics, high thermal and chemical stability, are efficiently excited by UV radiation is important today [1–3].

Alkaline earth metal aluminates have a diverse chemical composition and numerous crystalline structures [4–8]. They are used as matrices for obtaining effective crystal phosphors. Ions of trivalent europium are used as an activator ion. They emit an intense red light corresponding to the transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ when they are in a non-centrosymmetric environment [9]. The phase composition, crystal structure, and surface morphology of the luminescent matrix strongly depend on the calcination temperature and the ratio of $\text{Ca}^{2+}:\text{Al}^{3+}$ in the initial reaction mixture. This has a significant effect on the properties of the final product. It is known that phosphors based on alkaline earth metal aluminates, with the same $\text{M}^{2+}:\text{Al}^{3+}$ ratio in equivalent structures, have a radiation intensity that increases in the series $\text{Ca} \rightarrow \text{Ba} \rightarrow \text{Sr} \rightarrow \text{Mg}$ -containing phosphors [10, 11].

One of the most promising substances for obtaining effective red phosphors are cubic calcium aluminates of the composition $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, activated by europium (III) ions [12–16]. The crystal structure of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ consists of hollow formations with the inclusion of free oxygen ions. It is prompting suggestions that intensity of the emission of the europium ion will increase as a result of co-activation of neodymium (III) ions [17].

There are many ways to obtain aluminate systems, including the method of solid-phase synthesis, the method of chemical coprecipitation, the method of combustion, sol–gel method. At present sol–gel method is widely used. It is one of the most effective methods for obtaining materials with different properties [18–21]. Sol–gel method mainly differs from the others, it provides a homogeneous mixing

of the starting components at the molecular level. It is achieved by dissolving of salts and oxides of the starting substances. This method allows us to achieve a reduction in energy costs. The product turns out high degree of purity at all stages of synthesis. Products are characterized by monophasic crystalline structure, strictly stoichiometric composition, absence of extraneous phases [22–26].

The purpose of the work was to study the phase formation and the formation of the structure of calcium aluminate of the composition $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and the preparation of phosphors based on it activated by europium (III) and neodymium (III) ions.

2 Experimental

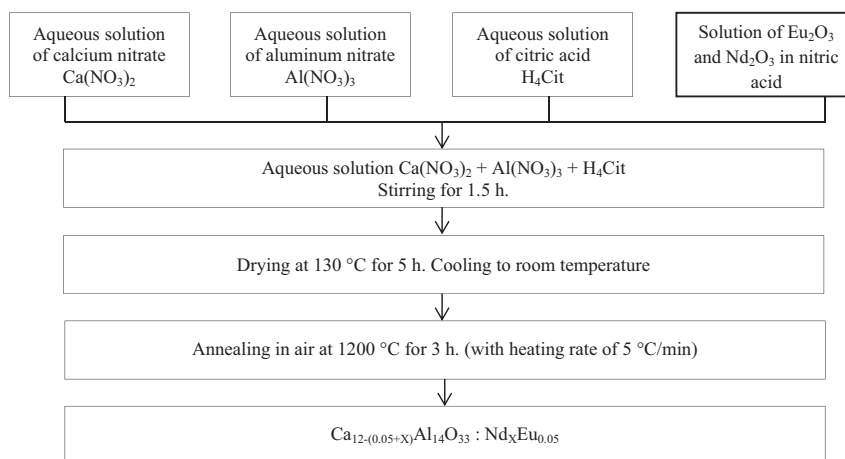
2.1 Materials preparation

Calcium nitrate tetrahydrate (Vekton, Russia), aluminum nitrate nonahydrate (LLC “NPF Nevsky chemist”, Russia) and citric acid monohydrate (LLC “CITROBEL”, Russia) was used as initial materials to synthesize $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. A molar ratio of $\text{Ca}:\text{Al}:\text{H}_4\text{Cit}$ was 12:14:26. The luminescent materials $\text{Ca}_{12-(0.05+x)}\text{Al}_{14}\text{O}_{33}:\text{Nd}_x\text{Eu}_{0.05}$ were obtained by introducing an ions of europium and neodymium. The molar ratio of the initial reagents is shown in Table 1. A certain amount of Eu_2O_3 and Nd_2O_3 was dissolved in the nitric acid (BIOMEDHIM, Russia). Salts were dissolved in the minimum amount of distilled water. The resulting clear solutions were mixed together and stirred for 1.5 h using a magnetic stirrer. Yellowish solution was subjected to heat treatment at 130 °C in the drying oven (SNOL 58/350, Lithuania) for 5 h. The resulting xerogel was ground

Table 1 The molar ratio of the initial reagents

Sample	Amount of reagents, mol				
	Nd^{3+}	Ca^{2+}	Eu^{3+}	Al^{3+}	$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$
1	0	11.95	0.5	14	26
2	0.025	11.925	0.5	14	26
3	0.05	11.90	0.5	14	26
4	0.075	11.875	0.5	14	26
5	0.1	11.85	0.5	14	26

Fig. 1 Flow chart for preparing of calcium aluminate $\text{Ca}_{12-(0.05+x)}\text{Al}_{14}\text{O}_{33}:\text{Nd}_x\text{Eu}_{0.05}$ by sol-gel method



and calcined in the muffle furnace (SNOL 6/1300, Lithuania) at different temperature (from 200 to 1200 °C) for 3 h. Scheme of the synthesis is shown in Fig. 1.

2.2 Materials characterization

For researching of processes which proceed at calcium aluminate formation we used a complex of physical and chemical research techniques:

thermal analysis 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;

XRD was done using Rigaku MiniFlex 600 (Japan) (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 PDF-2 database. The structure refinement was made by the Rietveld method using the ReX Powder diffraction program [27–29];

the crystal structure model is constructed using the VESTA program [30];

IR spectroscopy was done by IR spectrometer Agilent Technologies Cary 600 Series FTIR Spectrometer (made in USA). Decoding of IR spectra was carried out according to the literature [8, 12, 31, 32];

the luminescent properties were investigated using a spectrofluorometer Solar CM 2203 (Belarus).

3 Result and discussion

We defined the main stages of the synthesis process, the structure of prepared powders and the nature of the bonding using Thermal analysis, XRD and IR spectroscopy.

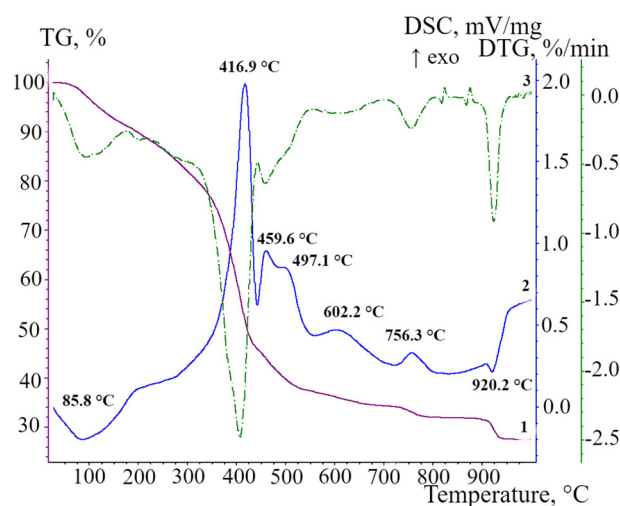


Fig. 2 TG (1), DTG (2), and DSC (3) curves of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ precursor

Analysis of TG and DSC curves allowed to see the main stages of formation of calcium aluminate in the temperature range from 25 to 1000 °C (Fig. 2).

The thermogram shows that some processes overlap each other. At the first stage there is a solvent remove from the surface of the sample, it is accompanied by a small endothermic effect and a small value of activation energy. The activation energy of this process is 58 kJ/mol. It indicates the course of the physical process. Activation energy calculated by Metzger–Horowitz method [25].

At the temperature ranges from 205 to 450 °C there is a sharp decrease of mass of the sample. It is accompanied by a large exothermic effect. The activation energy is 195 kJ/mol. It indicates the course of chemical processes, such as the decomposition of the organic framework. At further temperature increase there is a decomposition of a polymeric complex and oxidation of organic matters. It is accompanied by some exothermic effects.

At temperatures above 700, aluminates are formed. These processes are accompanied by high values of activation energy. The activation energy is about 700 kJ/mol.

We received samples at a temperature of 130, 300, 450, 600, 800, 900, 1000, 1100, and 1200 °C in order to describe in detail the processes that occur at each stage and investigated the received samples using IR spectrometric and X-ray phase analyzes.

Figure 3 shows the IR spectra of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ precursors. According to the data of IR spectroscopy, we can say that all the M–O bonds are formed during the maturation process of the solution. In the future, we observe only the growth of the polymer.

At low temperatures from 130 to 300 °C in the regions from 1410 to 1340 cm^{-1} and from 860 to 800 cm^{-1} , there are characteristic bands belonging to the nitrate ion. In

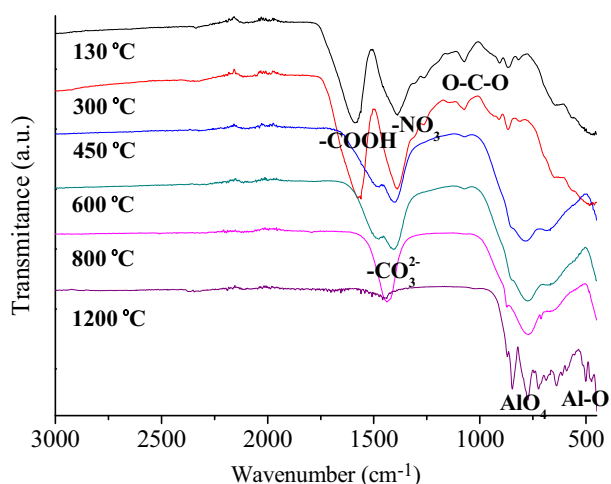


Fig. 3 IR spectra of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ precursors

samples obtained up to 500 °C, there are bands in the range from 1610 to 1550 cm^{-1} . They are associated with stretching vibrations of the carboxyl group in citrate complexes. With increasing the temperature, the vibrations of the carboxyl group and the vibrations of the C–O bond in the carboxyl group disappear. It indicates the decomposition of citrate complexes.

When the initial solution passes into the gel, there is characteristic fluctuation of the O–C–O in 1074 cm^{-1} . It is due to the polycondensation process. At temperatures above 900, we can see bands in the low-frequency region from 900 to 500 cm^{-1} related to vibrations of the Ca–O–Al bond. This bond forms the basis of the calcium aluminate crystal lattice.

In the samples obtained during annealing in the temperature range from 600 to 800 °C there are bands in the region of 1450–1410 cm^{-1} , corresponding to the carbonate ion. X-ray phase data confirm the presence of CaCO_3 in the samples.

The strong broad band absorptions at around 800 cm^{-1} are attributed to $[\text{AlO}_4]$ tetrahedra stretching vibration, which are composed by two absorption peaks at 850 cm^{-1} for “condensed” AlO_4 and at 773 cm^{-1} for “isolated” AlO_4 tetrahedra [33]. Those results demonstrate there are two $[\text{AlO}_4]$ tetrahedral structures in the lattice, which is accordance with the obtained structure in the $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ unit cell [34]. The peaks located 617 cm^{-1} and 574 cm^{-1} should derive from characteristic vibration absorption of Al–O bonds.

X-ray phase analysis data of the $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ precursors calcined at 800–1200 °C are presented in Table 2 and in Figs. 4 and 5.

Table 2 X-ray phase analysis data

Synthesis temperature, °C	Crystalline phases	Space group	ICDD (PDF-2/Release 2012)	Quantitative content, % (mass.)
800	CaCO_3	$R\bar{3}c$	01-086-2341	100
900	$\text{Ca}_3\text{Al}_2\text{O}_6$	$\text{Pa}\bar{3}$	00-038-1429	50.7
	CaAl_2O_4	$\text{P}2_1/n$	00-053-0191	49.3
1000	$\text{Ca}_3\text{Al}_2\text{O}_6$	$\text{Pa}\bar{3}$	00-038-1429	34.0
	$\text{Ca}_5\text{Al}_6\text{O}_{14}$	$\text{Cmc}2_1$	01-070-0801	26.3
	$\text{Ca}_4\text{Al}_6\text{O}_{13}$	$\text{I}4\bar{3}m$	01-072-0755	20.1
	CaAl_2O_4	$\text{P}2_1/n$	00-053-0191	19.6
1100	$\text{Ca}_5\text{Al}_6\text{O}_{14}$	$\text{Cmc}2_1$	01-070-0801	79.2
	$\text{Ca}_4\text{Al}_6\text{O}_{13}$	$\text{I}4\bar{3}m$	01-072-0755	6.2
	$\text{Ca}_3\text{Al}_2\text{O}_6$	$\text{Pa}\bar{3}$	00-038-1429	7.2
	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	$\text{I}4\bar{3}d$	01-078-2976	7.4
1200	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	$\text{I}4\bar{3}d$	01-078-2976	97.0
	$\text{Ca}_5\text{Al}_6\text{O}_{14}$	$\text{Cmc}2_1$	01-070-0801	2.7
	$\text{Ca}_4\text{Al}_6\text{O}_{13}$	$\text{I}4\bar{3}m$	01-072-0755	0.3

Until the temperature of 700 °C, the samples are X-ray amorphous. Heating the precursors at 800 °C for 3 h produces a mixture of crystalline calcium carbonate and amorphous alumina. Noncrystalline alumina is undetect by diffraction methods, therefore evidence of its existence is indirect. Heating at 900 °C gives a mixture of $\text{Ca}_3\text{Al}_2\text{O}_6$ and CaAl_2O_4 . Mass ratio of aluminates is practically equal. Increasing calcination temperature to 1000 °C, the content of the phases $\text{Ca}_3\text{Al}_2\text{O}_6$ and CaAl_2O_4 significantly decreases. New phases $\text{Ca}_5\text{Al}_6\text{O}_{14}$ and $\text{Ca}_4\text{Al}_6\text{O}_{13}$ appear. The peaks of these aluminates are clearly visible on X-ray diffraction patterns. $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ begins to form at 1100 °C, but the main phase is $\text{Ca}_5\text{Al}_6\text{O}_{14}$. The content of $\text{Ca}_4\text{Al}_6\text{O}_{13}$ and $\text{Ca}_3\text{Al}_2\text{O}_6$ at this temperature significantly decreases. At 1200 °C, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ becomes the main phase. An insignificant content of $\text{Ca}_5\text{Al}_6\text{O}_{14}$ and $\text{Ca}_4\text{Al}_6\text{O}_{13}$ is also observed. These intermediates of the synthesis also have been discovered by other researchers [25]. Based on the

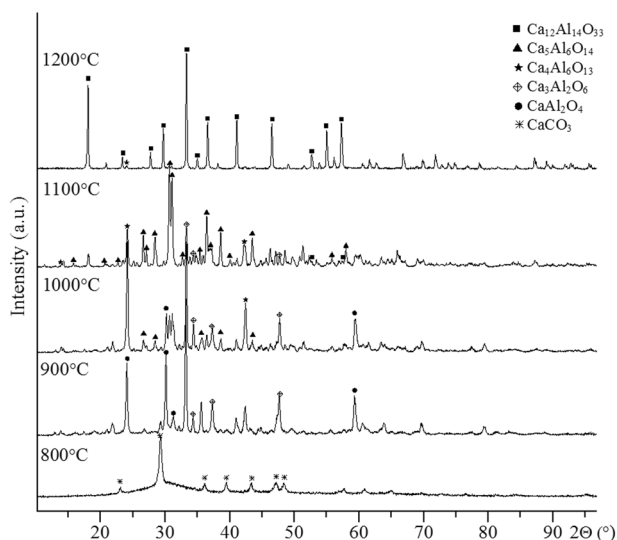
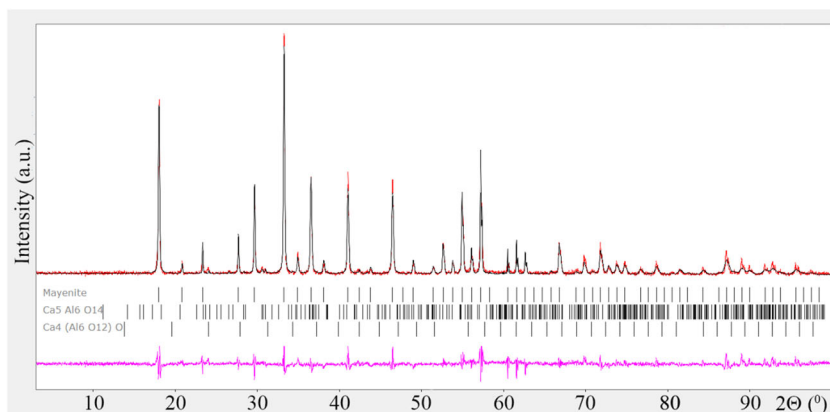


Fig. 4 XRD patterns of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ precursors calcined at various temperature

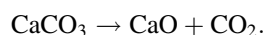
Fig. 5 Graphic representation of the results of structure refinement using the Rietveld method for a sample obtained at 1200 °C



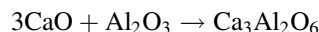
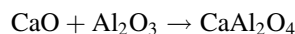
experiment, the following transformation scheme was proposed:

(1) The precursors decompose to CaCO_3 and Al_2O_3 .

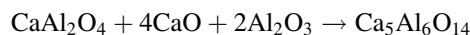
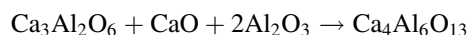
(2) Calcium carbonate is decomposed to CaO and CO_2 . It is confirmed by the results of thermal analysis (we can see endothermic effect on the DSC curve and mass reduction on the TG curve):



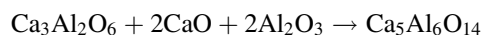
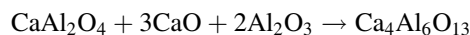
(3) At 900 °C, monoaluminate and tricalcium aluminate are formed:



(4) At 1000 °C, monoaluminate and tricalcium aluminate are converted to $\text{Ca}_5\text{Al}_6\text{O}_{14}$ and $\text{Ca}_4\text{Al}_6\text{O}_{13}$. The following transformations are possible:



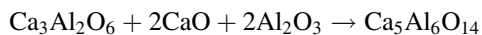
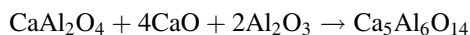
The formation of these aluminates is most likely due to the similarity of the structures $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_4\text{Al}_6\text{O}_{13}$, and CaAl_2O_4 and $\text{Ca}_5\text{Al}_6\text{O}_{14}$. Although it is possible that other aluminates are formed:



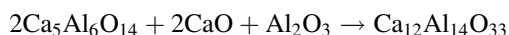
(5) At 1100 °C, $\text{Ca}_5\text{Al}_6\text{O}_{14}$ becomes the main phase:



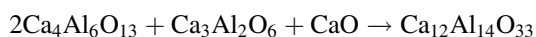
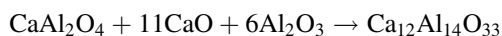
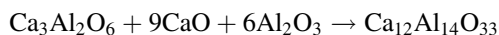
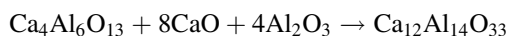
It is possibly:



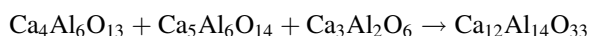
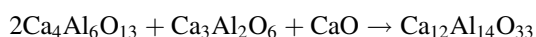
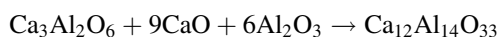
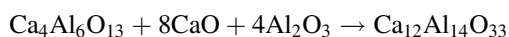
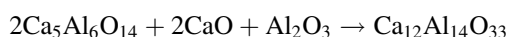
The main product begins to form:



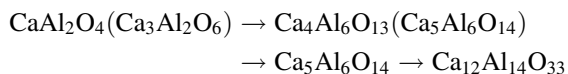
It is possibly:



(6) At 1200 °C, cubic $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is formed.



With increasing synthesis temperature, the following scheme is implemented:



The structure refinement was made by the Rietveld method using the ReX Powder diffraction program. The calculation results showed that the space group $I\bar{4}3d$, $a = 12.043 \text{ \AA}$, $R_p = 0.168136$, $R_{exp} = 0.168202$, and $R_{wp} = 0.223990$. The graphic image of the structure was constructed according to the obtained atomic coordinates.

$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ has a complex structure composed of hollow spheres (Fig. 6). It possesses a framework composed of aluminum-oxygen tetrahedra $[\text{AlO}_4]$. Tetrahedra are interconnected through oxygen atoms and partially through bridging calcium cations, forming eight-membered rings. The structure includes one type of calcium atoms (Ca1), two types of aluminum atoms (Al1 and Al2) in a tetrahedral environment of oxygen and three types of oxygen (O1, O2, and O3). They are distinguished by their surroundings. O1 are coordinated by the aluminum atom Al2; O1 and O2 are

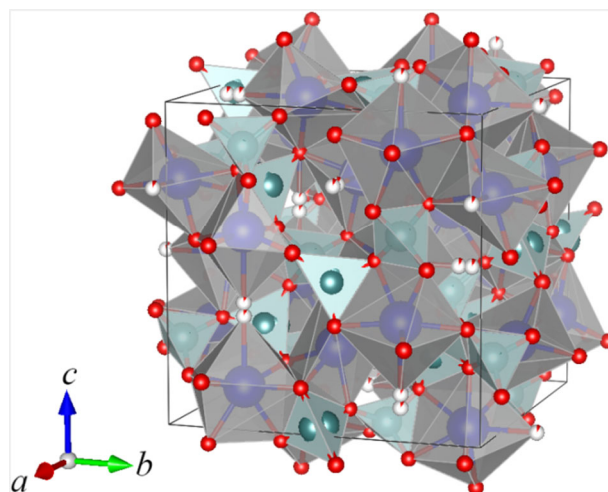


Fig. 6 The crystal structure of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (the blue ones are Ca atoms, the green ones are Al atoms, the red ones are bound O atoms, the white ones are unbound O atoms)

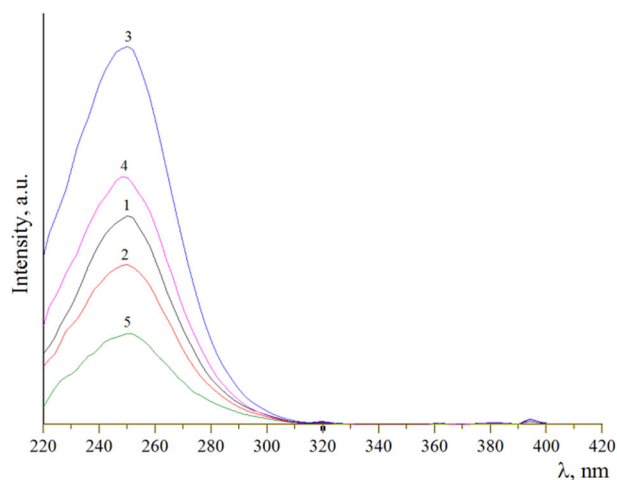


Fig. 7 Spectra of excitation of phosphors $\text{Ca}_{12-(0.05+x)}\text{Al}_{14}\text{O}_{33}:\text{Nd}_x\text{Eu}_{0.05}$ ($\lambda_{em} = 618 \text{ nm}$) ($n(\text{Nd}^{3+})$, mol: 1—0; 2—0.025; 3—0.05; 4—0.075; 5—0.1)

coordinated by the aluminum atom Al1. They form aluminum-oxygen tetrahedra, herewith tetrahedron containing O2 is distorted. O3 form anions of unbound oxygen. Such anions O^{2-} are located inside hollow spheres.

Phosphors based on $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, activated by europium (III) and neodymium (III) ions were obtained at a temperature of 1200 °C.

We obtained excitation (Fig. 7) and photoluminescence (Fig. 8) spectra for samples with different content of neodymium in $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ($n(\text{Nd}^{3+})$: 1—0; 2—0.025; 3—0.05; 4—0.075; 5—0.1 mol).

An intense band with $\lambda_{max} = 250\text{--}260 \text{ nm}$ is observed in the short-wave region of the excitation spectrum. It indicates the transfer of excitation energy from the O^{2-} ion to

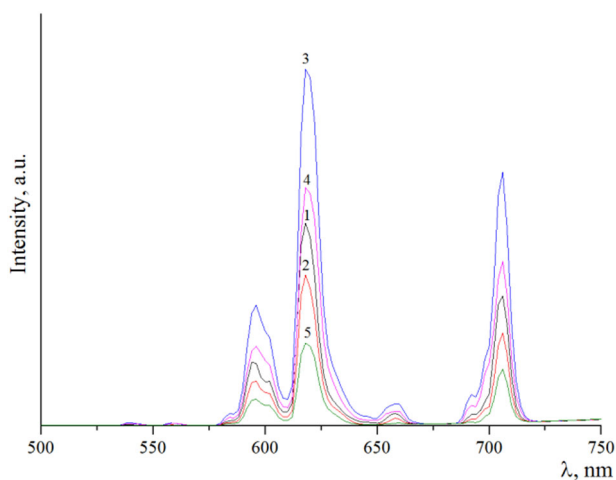


Fig. 8 Spectra of radiation of phosphors $\text{Ca}_{12-(0.05+x)}\text{Al}_{14}\text{O}_{33}:\text{Nd},\text{Eu}_{0.05}$ ($\lambda_{\text{ex}} = 254 \text{ nm}$) ($n(\text{Nd}^{3+})$, mol: 1—0; 2—0.025; 3—0.05; 4—0.075; 5—0.1

the Eu^{3+} ion. Therefore, we used an excitation wavelength of 254 nm in obtaining luminescence spectra. In the luminescence spectra of phosphors containing europium(III) and neodymium(III) ions, several narrow bands with a wavelength of 618 nm are observed. It corresponds to the red region of the spectrum and indicates the occurrence of europium(III) ion in the structure of calcium aluminate in the trivalent state. The luminescence spectrum consists of characteristic narrow emission lines of the Eu^{3+} ion, corresponding to the transitions of electrons inside the 4f shell. The most intense is the induced electric dipole transition ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ with a maximum at a wavelength of 618 nm, then ${}^5\text{D}_0\text{--}{}^7\text{F}_4$ with a wavelength of 704 nm. The magnetic dipole transition ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ has the lowest intensity ($\lambda_{\text{max}} = 595 \text{ nm}$) [17].

The presence of neodymium(III) ions in the structure of calcium aluminate affects the radiation intensity of luminescence centers, which include europium(III). The highest intensity is reached at a neodymium content of 0.05 mol. With increasing concentration of the Nd^{3+} ion, concentration quenching occurs and the radiation intensity decreases.

4 Conclusion

Calcium aluminate with the composition $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and phosphors based on it, containing europium(III) (0.05 mol) and neodymium(III) (from 0.025 to 0.1 mol) were obtained using sol–gel technology.

The main stages of the formation of calcium aluminate were determined using thermal analysis, IR spectroscopy and X-ray phase analysis. Solid-phase interaction in the formation of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ includes the steps of obtaining calcium carbonate and amorphous alumina (800 °C),

aluminates of composition $\text{Ca}_3\text{Al}_2\text{O}_6$ and CaAl_2O_4 (900–1000 °C), and $\text{Ca}_5\text{Al}_6\text{O}_{14}$ and $\text{Ca}_4\text{Al}_6\text{O}_{13}$ (1000–1100 °C). $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ begins to form at 1100 °C.

The graphic image of the structure was constructed according to the obtained atomic coordinates using the ReX Powder diffraction program.

Luminescent properties of the phosphors of the composition $\text{Ca}_{12-(0.05+x)}\text{Al}_{14}\text{O}_{33}:\text{Nd}_x\text{Eu}_{0.05}$ ($x = 0.025\text{--}0.1$) were investigated. It was determined that the highest intensity of luminescence is achieved at $x = 0.05$. With a further increase in the content of neodymium there is a concentration quenching of the luminescence.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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