Sol-Gel Synthesis of Fluorescent Materials Based on Tricalcium Aluminate

L. Selyunina, I. Mishenina, T. Belyaninova and T. Botvina
Faculty of Chemistry, Tomsk State University, 36 Lenina Street, Tomsk 634036, Russian Federation
E-mail: SelyuninaLA@mail.ru

Abstract. Calcium aluminate \( \text{Ca}_3\text{Al}_2\text{O}_6 \) and phosphors based on it were obtained by sol-gel method. Complex studies were used to identify the dynamics of phase and structural transformations in the synthesis of \( \text{Ca}_3\text{Al}_2\text{O}_6 \). We used thermal analysis, IR spectroscopy, X-ray phase analysis, scanning electron microscopy and micro-X-ray spectral analysis. Solid-phase interaction in the formation of \( \text{Ca}_3\text{Al}_2\text{O}_6 \) includes the steps of obtaining carbonate and calcium oxide at 700 °C, aluminates of composition \( \text{Ca}_5\text{Al}_6\text{O}_{14} \) (800 °C) and \( \text{CaAl}_2\text{O}_4 \) (900 °C). \( \text{Ca}_3\text{Al}_2\text{O}_6 \) is formed at 850 °C, single-phase cubic calcium aluminate is formed at 1000 °C. The degree of formation of the particles is increased with increasing synthesis temperature. Using the method of adsorption of Gamnet indicators we determined that the base Brensted centers predominate on the surface of calcium aluminate. The number of these centers decreases with an increase in the annealing temperature and with the introduction of the activator. The luminescent properties of the phosphors of the composition \( \text{Ca}_{3-x}\text{Eu}_x\text{Al}_2\text{O}_6 \) (\( x = 0.01 \text{–} 0.1 \)) were investigated by the method of spectrofluorimetry. The highest intensity of luminescence was achieved at \( x = 0.05 \). With a further increase in the content of europium, there was a concentration quenching of the luminescence.

1. Introduction
Phosphors are high-pure substances. They are widely applied in television, in fluorescent lighting, in the systems of light display of information. Lighting characteristics of devices, such as brightness, color of a luminescence, color rendition, visibility depend on quality of phosphors. Phosphors found application in medicine for health protection of people and prevention of diseases [1, 2].

Due to the extension of technical requirements and opportunities of practical using of phosphors based on aluminates of alkaline earth metals there is a needing for the solution of a number of the complex scientific and technical problems. One of such problems is bound to creation of phosphors with the increased brightness and duration of afterglow.

For receiving high-quality phosphors, it is necessary to consider all factors influencing their formation such as phase formation, surface properties and existence of the acid-base centers.

At present, the sol-gel method is widely used. It is one of the most effective methods for obtaining materials with different properties [3–7]. The main advantage of this method lies in the high degree of homogenization of the initial components. 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 [8–11].
The purpose of this work was to investigate the processes of formation of calcium aluminate with the composition of $\text{Ca}_3\text{Al}_2\text{O}_6$ and luminescent substances based on it, their structure and properties.

2. Experimental Part

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 $\text{Ca}_3\text{Al}_2\text{O}_6$. A molar ratio of Ca : Al : $\text{H}_4\text{Cit}$ was $3 : 2 : 5$. The luminescent materials based on calcium aluminate were obtained by introducing an ions of europium in an amount from 0.01 mol to 0.1 mol. A certain amount of $\text{Eu}_2\text{O}_3$ 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 hours using a magnetic stirrer. Yellowish solution was subjected to heat treatment at 130ºC in the SNOL 58/350 drying oven (Lithuania) for 5 hours. The resulting xerogel was ground and calcined in the SNOL 6/1300 muffle furnace (Lithuania) at different temperature (from 200 to 1200 ºC) for 3 hours. Scheme of the synthesis is shown in figure 1.

**Figure 1.** Flow chart for preparing of calcium aluminate $\text{Ca}_3\text{Al}_2\text{O}_6$ by sol-gel method.

For a research 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 ºC/min in air, the temperature range was from 25 to 1000 ºC;
- XRD was done using Rigaku MiniFlex 600 (Japan) (Cu Kα radiation $\lambda = 1.5406$Å) at room temperature with the range of angles 20 from 3 to 80º) at the scanning speed of 2 ºC/min. The phase identification was carried out using the literature [12–14] and PDF-2 database;
- 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 [10,13,17];
scanning electron microscopy (SEM) was done 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);  
X-ray microanalysis was done using Quantax 70 (Japan) instrument;  
the acid-base properties of the surface of calcium aluminate and a phosphor of the composition $\text{Ca}_{2.95}\text{Eu}_{0.05}\text{Al}_{2}\text{O}_{6}$ were studied by the adsorption of Gammel indicators;  
the luminescent properties were investigated using a spectrofluorometer Solar CM 2203 (Belarus).

3. Results 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.

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 (figure 2). They are superimposed on each other. This is evidenced by the energy effects on the DSC curve.

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 55.6 kJ/mol. It indicates the course of the physical process.

In the range of temperatures from 185 to 295 °C and from 305 to 395 °C, there is a sharp decrease of mass of the sample. The activation energies are 114.8 kJ/mol and 318 kJ/mol, respectively. 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 an exothermic effect. The activation energy is 448.1 kJ/mol.

In the range of temperatures from 650 to 750 °C formation of tricalcium aluminate begins. It is accompanied by a large value of the activation energy. The activation energy is 660.9 kJ/mol.

We received samples at a temperature of 130, 200, 300, 450, 500, 600, 700, 800, 850, 900, 1000, 1100, 1200 °C in order to describe in detail the processes that occur at each stage. We investigated the received samples using IR spectrometric and X-ray phase analyzes. We also investigated the initial solutions, sol and solutions in the course of the gel formation by an IR spectroscopy.

![Figure 2. TG, DTG and DSC curves of Ca$_3$Al$_2$O$_6$ precursor.](image-url)
In the process of drying the gel in the drying oven, the nitrate decomposition accompanied by the release of large quantities of brown gas. Therefore fluctuations –C‒NO\(_2\) bond in the IR spectra at 1350, 1550, 900 cm\(^{-1}\) are disappear above 300 °C. The released carbon dioxide forms carbonate ions with water vapor, whose presence is associated with oscillations at a frequency 1100 and 1500 cm\(^{-1}\). Fluctuations of tetrahedra [AlO\(_4\)] in the range 700–500 cm\(^{-1}\) and AlO\(_6\) in the range 808 и 798 cm\(^{-1}\) appear during the mixing of the solution. Intensity and resolution of the absorption bands which characteristic of communication Al–O–Al in calcium aluminate increase with increasing annealing temperature. The presence of these fluctuations says that the bond between the metal and oxygen is formed at the gel formation stage.

Using the data of X-ray and IR spectroscopic analyzes, we defined that the formation of calcium aluminate begins at a temperature of 500 °C. At this temperature, it is X-ray amorphous. At 700 °C, calcium carbonate is formed. Then it decomposes.

The crystalline tricalcium aluminate of the cubic modification is formed at a temperature of 850 °C. Together with it there are impurities of Ca\(_5\)Al\(_6\)O\(_{14}\) and CaO. A pure, single-phase product is formed at a temperature of 900 °C. X-ray phase analysis data are presented in table 1 and in figures 3, 4. Identification of the obtained samples was based on compliance of the diffraction pattern of the synthesized aluminates with reference compounds (ICDD (PDF-2) Release 2012) 00-032-0149 (Ca\(_3\)Al\(_2\)O\(_6\)), 00-011-0357 (Ca\(_5\)Al\(_6\)O\(_{14}\)) and 00-053-0191 (CaAl\(_2\)O\(_4\)).

Table 1. Composition of intermediate and final products of synthesis.

| Temperature, °C | Composition                  |
|----------------|------------------------------|
| 500            | amorphous                    |
| 600            | CaCO\(_3\)                   |
| 700            | CaO                          |
| 800            | Ca\(_5\)Al\(_6\)O\(_{14}\)   |
| 850            | Ca\(_5\)Al\(_6\)O\(_{14}\)   |
| 900            | Ca\(_5\)Al\(_6\)O\(_{14}\)   |
| 1000           | Ca\(_3\)Al\(_2\)O\(_6\)      |
| 1100           | Ca\(_3\)Al\(_2\)O\(_6\)      |
| 1200           | Ca\(_3\)Al\(_2\)O\(_6\)      |

According to the results of IR spectroscopic and X-ray phase analysis, we assumed that the formation of single-phase calcium aluminate proceeds as follows:

1. decomposition of citrate precursors, formation of calcium carbonate:
   \[\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2;\]
2. decomposition of calcium carbonate:
   \[5\text{CaO} + 3\text{Al}_2\text{O}_3 \rightarrow \text{Ca}_5\text{Al}_6\text{O}_{14};\]
3. formation of aluminates of different composition:
   \[\text{Ca}_5\text{Al}_6\text{O}_{14} \rightarrow 3\text{CaAl}_2\text{O}_4 + 2\text{CaO};\]
4. formation of single-phase aluminate \(\text{Ca}_3\text{Al}_2\text{O}_6\):
   \[\text{Ca}_5\text{Al}_6\text{O}_{14} + 4\text{CaO} \rightarrow 3\text{Ca}_3\text{Al}_2\text{O}_6.\]

The morphology of the surface of the obtained samples was investigated by scanning electron microscopy. An increase in the synthesis temperature leads to the formation of more formed particles. The greatest homogeneity of the sample is achieved at an annealing temperature of 1000 °C.
Figure 3. Results of X-ray diffraction analysis of samples obtained at different temperatures:

- a – 500 °C
- b – 600 °C
- c – 700 °C
- d – 800 °C
- e – 850 °C

* – Ca$_3$Al$_2$O$_6$

Figure 4. Results of X-ray diffraction analysis of samples obtained at different temperatures:

- a – 900 °C
- b – 1000 °C
- c – 1100 °C
- d – 1200 °C

The surface state has an effect on physical and chemical characteristics of calcium aluminate. Based on the study of the surface properties of the samples obtained at a temperature from 900 to 1200 °C, by the indicator method we established that with an increase in temperature the number of active sites on the surface decreases. It is due to the fact that the amount of defects become less.

At a temperature of 900 °C, the base sites of Lewis O$^-$ (pKa = −0.29) and the acid sites of Brensted CaOH$^+$, AlOH$^+$ (pKa = 0.8–6.4) are located on the surface. In the region of pKa from 7.15 to 13.1 a large number of the base sites of Brensted CaOH$^-$, AlOH$^-$ are observed on a surface. With increase in temperature, the quantity of active centers regularly decreases and their strength becomes smaller. The Lewis acid centers Al$^{3+}$, Ca$^{2+}$ are present at the region of pKa 16.8.

Using the results of the study, we obtained phosphors based on calcium aluminate Ca$_3$Al$_2$O$_6$, activated by europium(III) ions. The annealing temperature of the samples was 1000 °C.

According to X-ray phase analysis data (table 2), a mixture of aluminates Ca$_3$Al$_2$O$_6$ and Ca$_2$Al$_6$O$_{14}$ is formed by the addition of europium 0.01; 0.025; 0.075; 0.1 mol. A single-phase cubic aluminate Ca$_3$Al$_2$O$_6$ is formed at Eu content of 0.05 mol. As according to XRF data, no own phases of europium were found, it means that europium is embedded in the crystal lattice as replacement with the place of calcium.

| Sample          | Composition   |
|-----------------|---------------|
| Ca$_{2.99}$Eu$_{0.01}$Al$_2$O$_6$ | Ca$_3$Al$_2$O$_6$ |
|                 | Ca$_2$Al$_6$O$_{14}$ |
| Ca$_{2.975}$Eu$_{0.025}$Al$_2$O$_6$ | Ca$_3$Al$_2$O$_6$ |
|                 | Ca$_2$Al$_6$O$_{14}$ |
| Ca$_{2.95}$Eu$_{0.05}$Al$_2$O$_6$ | Ca$_3$Al$_2$O$_6$ |
| Ca$_{2.925}$Eu$_{0.075}$Al$_2$O$_6$ | Ca$_3$Al$_2$O$_6$ |
|                 | Ca$_2$Al$_6$O$_{14}$ |
| Ca$_{2.90}$Eu$_{0.1}$Al$_2$O$_6$ | Ca$_3$Al$_2$O$_6$ |
|                 | Ca$_2$Al$_6$O$_{14}$ |
We investigated the morphology of the surface of the obtained crystal phosphors by the method of scanning electron microscopy. All synthesized samples are the same in terms of particle size distribution. The particle size varies from 2 to 10 μm, they have enough regular shape with a clear facet. It indicates a well-formed crystalline structure.

To study the uniformity of the distribution of all elements, including the activator, on the surface of the sample, we made a micro-X-ray spectral analysis. Figure 5 shows the morphology of the sample surface with europium(III) content equal to 0.05 mol and the linear distribution profile of the elements. The analysis confirmed the presence of characteristic X-ray radiation of calcium, aluminum, oxygen and europium at each studied point (elements are equally distributed over the sample area). This allows us to conclude that these elements are present equally on the entire surface of the sample (figure 6). According to the quantitative analysis, the sample is homogeneous in composition and corresponds to the formula Ca$_{2.95}$Eu$_{0.05}$Al$_2$O$_6$.

The functional composition of the surfaces of phosphors and the nature of the active sites influences the luminescent properties of the studied materials [18]. The acid–base sites on the surfaces of phosphors samples were differentiated by means of Hammett indicator adsorption from aqueous media. Our studies were performed on an PE5400 VI/UV spectrophotometer (Russia) at a wavelength corresponding to the indicator solution absorption maximum. Our set of indicators allowed the detection of acid-base sites within a pKa range of –0.29 to +16.8. The obtained data were used as a basis for plotting the spectra of adsorption site distribution (ASD) on the surfaces of the studied compounds in the coordinates $q_{pK_a} = f(pK_a)$ [18, 19]. This method showed that the amount of active centers in calcium aluminate without RE ions are more than at a phosphorus. The main centers of Brønsted with pK$_a$ = 13.1 predominate on the sample surface. We can explain decrease of activity of a surface with the fact that ions of europium replace not only ions of calcium, but also fill vacancies on the surface of the aluminate. It reduces the number of defects on the surface. The surface active centers can reduce the luminescence intensity of phosphors due to nonradiative recombination of electrons on them. Thus, the decrease of the activity of a surface at a crystal phosphorus is a favorable factor for obtaining a material with high performance characteristics.

Figure 5. The surface morphology of sample. Figure 6. The distribution of elements on the surface of calcium aluminate.

We obtained excitation and photoluminescence spectra for samples with different content of europium in Ca$_3$Al$_2$O$_6$ (n(Eu$^{3+}$) = 0.01; 0.025; 0.05; 0.075; 0.01 mol) (figures 7, 8).

Studies have shown that phosphors can be efficiently excited by UV radiation in the visible region. They emit red light with a peak corresponding to a wavelength of 621 nm. It corresponds to a $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ ions. In the excitation spectrum of Ca$_3$Al$_2$O$_6$: Eu$^{3+}$ ($\lambda_{em} = 621$ nm) there is a wide, clear band at 254 nm.
Europium ions enter the lattice of calcium aluminate in the trivalent state ($\text{Eu}^{3+}$). We obtained emission bands of $\text{Eu}^{3+}$ in the red region of the spectrum under the influence of UV radiation with an excitation wavelength of 254 nm. They correspond to the characteristic transitions $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (orange) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$, (red) [15, 16]. The maximum intensity of visible radiation was obtained with a europium content of 0.05 mol. It was also found that an increase in the content of europium leads to quenching of luminescence.

**Figure 7.** Spectra of excitation of phosphors (λ<sub>em</sub> = 621 nm) (n(Eu<sup>3+</sup>), mol: a – 0.01; b – 0.025; c – 0.05; d – 0.075; e – 0.1).

**Figure 8.** Spectra of radiation of phosphors (λ<sub>ex</sub> = 254 nm) (n(Eu<sup>3+</sup>), mol: a – 0.01; b – 0.025; c – 0.05; d – 0.075; e – 0.1).

4. **Conclusion**

Tricalcium aluminate with the composition $\text{Ca}_3\text{Al}_2\text{O}_6$ and phosphors based on it, containing europium(III) from 0.01 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 $\text{Ca}_3\text{Al}_2\text{O}_6$ includes the steps of obtaining carbonate and calcium oxide at 700 °C, aluminates of composition $\text{Ca}_5\text{Al}_6\text{O}_{14}$ (800 °C) and $\text{CaAl}_2\text{O}_4$ (900 °C). $\text{Ca}_3\text{Al}_2\text{O}_6$ is formed at 850 °C, single-phase cubic calcium aluminate $\text{Ca}_3\text{Al}_2\text{O}_6$ is formed at 1000 °C.

The morphology of the surface and the distribution of elements along the surface of samples was investigated by the methods of scanning electron microscopy and micro-X-ray spectral analysis. The degree of formation of the particles is increased with increasing synthesis temperature. The distribution of calcium, aluminum, europium and oxygen is uniform.

Acid-base properties of the surface of calcium aluminate and a phosphor of the composition $\text{Ca}_{2.95}\text{Eu}_{0.05}\text{Al}_2\text{O}_6$ were investigated by the adsorption of Gammet indicators. It was determined that the base Brensted centers predominate on the surface (pK<sub>a</sub> = 9.45 and 13.1), the number of these centers decreases with an increase in the annealing temperature and with the introduction of the activator.

Luminescent properties of the phosphors of the composition $\text{Ca}_{3-x}\text{Eu}_x\text{Al}_2\text{O}_6$ (x = 0.01–0.1) 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 europium, there is a concentration quenching of the luminescence.

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