Use of continuous solid-phase synthesis to obtain phosphors based on strontium aluminate

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Abstract. The effect of conditions of continuous solid-phase synthesis on particle size distribution of nanostructured powders of strontium aluminate was studied. It was shown that continuous solid-phase synthesis allows for: synthesis of strontium aluminate in the form of nanostructured powders with controlled particle size distribution directly during its synthesis; in the presence of a liquid phase strontium aluminate is synthesized with a high level of monophasity. It was shown that in order to optimize the illuminating parameters of phosphors based on strontium aluminate, it is advisable to use continuous solid-phase synthesis.

1. State-of-The-Art

One of the important areas of modern production actively using rare earth elements (REE) to solve their problems is the design and synthesis of phosphors. In this regard the materials that are of particular interest those that have not only the required illuminating elements, but also low-hazard effects on the human body, which in turn makes it possible to expand the scope of their application, and significantly reduces the cost of production as a whole. Such phosphors include phosphors based on strontium aluminates.

However, the optimization of the conditions of the synthesis of phosphors based on them is a rather complex technological problem [1-5], which is associated with:

- the criticality of chemical reactions in $SrO - Al_2O_3$ due to the rather large number of polymorphic transformations of starting reagents in the process of their heat treatment;
- the necessity of the introduction of activators and co-activators (Eu. Dy, etc.) in the crystal lattice of the phosphor base with the formation of a specific configuration of their order.

In this regard, the optimization of the probability of synthesis of phosphors based on strontium aluminates [6-10] is determined by the technological capabilities of the method of synthesis and depends, usually, on:

- the level of homogeneity achieved of the starting mechanical mixture of the synthesized strontium aluminate;
- the dispersion and the single-phase reagents used;
- the rate of synthesis of the desired material, as well as the controllability of technological factors governing the optimization of the processes.

Among the most common methods for the synthesis of phosphors based on strontium aluminates are classical solid-phase and sol-gel techniques. Less commonly used methods are combustion and induction heating. Solid-phase synthesis is usually accomplished in the range of sufficiently high temperatures of 1200 – 1400 ^{o}C for 4-6 hours using the inert or redox environment and the subsequent grinding of the desired product.

Virtually no method of synthesis provides a high level of monophasity of the desired material with a uniform distribution of REE in its entirety and, consequently, the maximum possible illuminating parameters. In this regard, the process procedure is a rather complex and multi-step regimen which, nevertheless, does not guarantee a sufficiently high level of repeatability of achievable parameters.

Recently, particular attention has been paid to solid-phase synthesis using strontium aluminate fluxing, i.e., in the presence of a liquid phase. This is due to the fact that the synthesis in the presence of a liquid phase usually occurs at a higher quality level, allowing in this regard for the significant reduction of the temperature of the synthesis. So, it should be noted that not every liquid phase provides the optimal solution to the problem, since in the process of heat treatment the liquid phase, coming into contact with the reagents of the starting mixture of the synthesized material, forms the intermediate phase and does not always promote the formation of the monophasity of the desired product.

It is known that solid-phase synthesis of inorganic photoluminophors is carried out with step calcination, in the final stage of which high temperatures and prolonged exposure cycles are conventionally used with the use of an inert or redox environment and the subsequent grinding of the desired product.

For example, yttrium aluminum garnet $(Y_3GdCe)3Al_5O_{12}$ is synthesized in three stages at a temperature at the finishing stage of 1520-1600 °C and a holding time of 8-10 hours, synthesis of strontium aluminate ($SrAl_2O_4$:Eu, Dy and $Sr_4Al_{14}O_{25}$:Eu, Dy) occurs in two stages to withstand temperatures at the finish of 1320 °C for 4-6 hours. In this regard, the achievement of homogeneous single-phase structures is not guaranteed, which ultimately has a negative effect on the brightness of stationary and spontaneous emission. Nevertheless, among the most common methods of synthesis of phosphors based on strontium aluminates are classical solid-phase and sol-gel techniques. Less commonly, the methods of combustion and induction heating are used. By virtue of the above reasons, almost no synthesis method used guarantees achievement of a high level of monophasity of the desired material with uniform distribution of REE in its entirety and, consequently, the maximum possible illuminating parameters. In this regard, the process procedure is a rather complex and multi-step regimen which, nevertheless, does not guarantee a sufficiently high level of repeatability of the achievable parameters.

Use of a liquid phase at the stage of synthesis allows the improvement of the quality of both phase composition and the powders of the synthesized materials. In this regard, the use of special purpose glasses (of the optimal composition with respect to the problem being solved) as a liquid phase allows, usually, achievement of a constructive compromise in solving the problems of general and special purpose, including in the case of synthesis in order to achieve monophasic strontium aluminate compounds and to enhance the illuminating parameters of the phosphors based on them.

In general, the use of such special purpose glasses allows for solid-phase synthesis in the presence of a minimum quantity of the liquid phase. The efficiency achieved in this regard is determined by the

probability of optimization of the balance of activity of the special purpose glass of the desired purpose with respect to the synthesized material, which ultimately allows ease of solid-phase synthesis to supplement the advantage of liquid phase synthesis, namely the acceleration of the transfer processes and increase the homogeneity of the desired product [12].

The complexity and ambiguity of the processes characterizing the luminescence properties of specific phosphors does not allow us today to talk about the priority of certain technological factors having a dominant influence on the formation of their illuminating parameters and forming, in particular, the nanostructured composition of the synthesized powders and their particle size distribution.

Generally, the effectiveness of the results achieved is associated with the development of the materials, including REE additives of various concentrations. The result of the research accomplished is the emergence of new materials and technologies possessing the maximum values of their functionally important parameters. In this regard, it should be understood that the involvement of the results achieved in the new research and development continually expands the use of REE and their role in the development of scientific and technological progress as a whole.

It is clear that the development of new materials is associated with existing technologies and especially with those whose capabilities most optimally meet the requirements of the problems being solved. In this sense, the technology of production of phosphors has a lot to do with the production technology of functional ceramics, particularly at the stage of solid-phase synthesis. Today, in the sphere of development of materials of different functionality, sufficiently large scientific, experimental and technological material has been accumulated to allow for the development of the most optimal algorithm for the new research. Obtaining of ultra- and nano-powders for the production of functional oxide ceramics with improved electrophysical, chemical and mechanical parameters is still one of the most urgent tasks of ceramic technology relating to the number of critical technologies of the federal level.

Nevertheless, the role of modern nanotechnologies in this matter clearly occupies a leading position. However, the fact that most of these technologies are of a laboratory character speaks to their constructive use at the stage of fundamental research of the tasks at hand, but does not provide rapid industrial implementation of the results obtained.

The practical solution of the problems of these critical technologies in the synthesis of high quality ultra- and nano-dispersed powders for the production of oxide ceramics with a stable chemical, phase and granulometric composition was found in the development of the technology of continuous solid-phase synthesis [13]. Conceptually, the continuity of solid-phase synthesis is associated with the transfer of the flow of solid phase reactions at the level of the individual granule of the starting homogeneous mechanical mixture introduced into the reaction chamber, preheated to the particular synthesis temperature of the oxide material. The thermal shock and temperature gradient emerging (at the initial time it reaches 8,000-100,000 deg/Mm.) so intensify the diffusion processes that the completion of the solid-phase synthesis is accomplished over a period of time measured in minutes rather than hours, as in classical solid-phase synthesis [13,14].

Research has shown that powders of oxide materials synthesized by solid-phase synthesis are a combination of nanostructured macro-objects formed from the nanophase by self-assembly (bottom-up) directly during synthesis. Thus, the nanostructured macro-object is not a single crystal formation, but is a plurality of discrete crystalline particles held within the scope of the macro-object by more significant forces than gravitational.

The purpose of this work was to study the effect of conditions of continuous solid-phase synthesis on the particle size distribution of nanostructured powders of strontium aluminate, because the issues of the effect the rate of synthesis, the composition of the gaseous medium, the particle size of the synthesized phase and minimizing of the defects of the precursor particles are being raised today by researchers of the synthesis of phosphors in general, and phosphors based on strontium aluminate in particular.

2. Experimental part and discussion of the results

Used for synthesis of strontium aluminate ($SrAl_2O_4$) were strontium carbonate ($SrCO_3$) and aluminum oxide (Al_2O_3) of chemically pure grade. Homogenization of the starting mechanical mixture was carried out with conventional ceramic technology by mixing the starting reagents using distilled water. Synthesis of strontium aluminates was carried out with the technology of continuous solid-phase synthesis at temperatures up to 1250^{o}C and a synthesis time of 30 min. The particle size distribution of the synthesized powders was determined by an Analysette 22 laser particle analyzer, X-Ray analysis on an ARL X'TRA diffractometer ($Cu_{k\alpha}$ radiation)

Figure 1 shows comparative data of particle size distribution of strontium aluminate synthesized by classical (CT) and continuous technologies. of solid-phase synthesis (SPS) using a batch process of the starting mechanical mixture (SMM) whose particle size distribution is as shown in Figure 1.

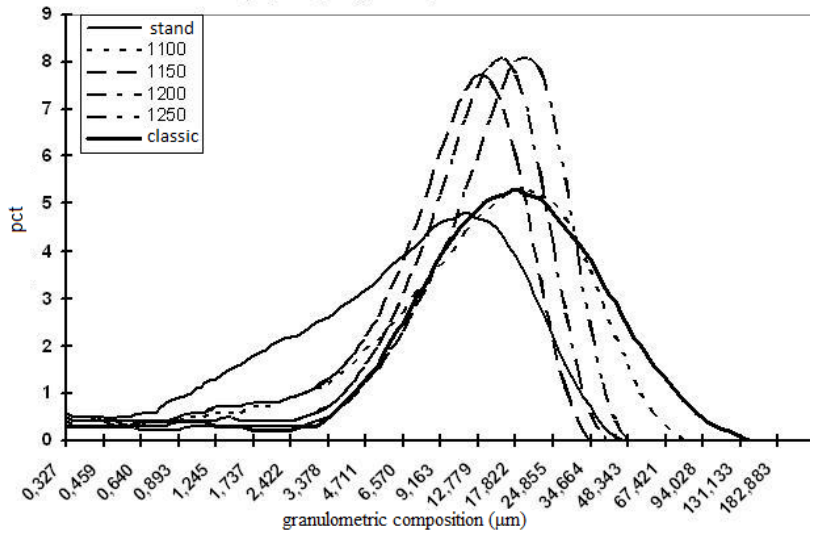

Figure 1. Particle size distribution $SrAl_2O_4$ (t=15minutes)

As can be seen, the particle size distribution of powders synthesized by the classical technology practically coincides with the particle size distribution of powders synthesized by solid-phase synthesis at a synthesis temperature of 1100^{o}C for 15 minutes.

According to a scanning microscope (ZEIZZ SUPRA – 25), the formation of particle size distribution of the synthesized oxide material is accomplished directly during the synthesis process by continuous self- optimization of its composition depending on the conditions of the synthesis. Thus, the prevalent influence on the optimization of the sizing of the nanostructured macro-objects formed is the synthesis temperature and the time duration of synthesis for the optimal ratio between them.

Analysis of the research showed that the process of formation of a growing nanostructured macro-object is accomplished by incorporating smaller macro-objects of varying complexity formed in turn from the initial nanoparticles sized in the order of 20-50 nm while obeying the conditions of self-optimization of the overall system.

This model is in good agreement with the results of the synthesis of strontium aluminate which follows from the analysis of particle size distribution of powders having a bias tending toward their increase at a synthesis temperature from 1150 to 1250 ^{o}C and maintaining a period of time of synthesis equal to 15 minutes.

Figure 2 shows the diffraction patterns of strontium aluminate synthesized in continuous and classical solid-phase techniques.

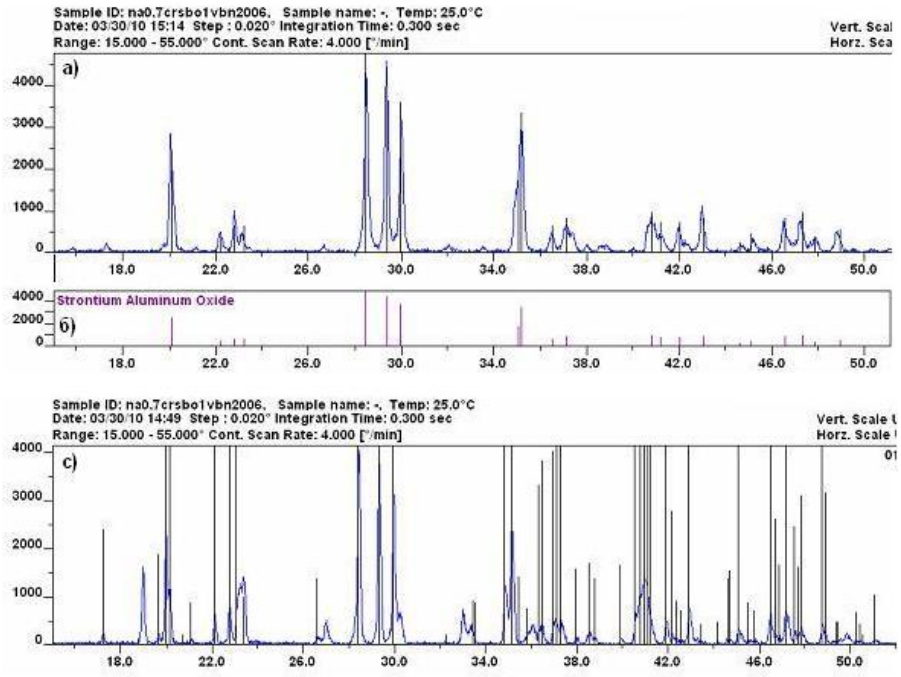

Figure 2. X-ray phase analysis of products of the synthesis of strontium aluminate by continuous (2a) and classical (2c) techniques, 2b – international standard bar chart

The results of research of the phase composition synthesized in conditions of continuous solid-phase synthesis in the presence of special purpose glass in an amount of 0.5-0.75% wt. (typically administered 2-8% wt.) showed that in the temperature interval of 1175-1225 ^{o}C and synthesis time 25-30 minutes, the monophasity of the synthesized strontium aluminate reaches 99±0.5 %.

Comparative analysis of these diffraction patterns from an international standard bar chart (Fig.2b) favors the monophasity of strontium aluminate synthesized by solid-phase technology in the presence of a liquid phase.

As can be seen from the data, the use of effective science-intensive technologies can solve not only general and special purpose problems at a higher level of quality, but also more actively promote the rapid filling of the internal market with high technology products.

The advantages of the proposed solution for technical, consumer and economic performance in comparison with known domestic analogs are shown in the table.

Technical Specifications	Classical Technology	Solid-Phase Synthesis Technology
Material	($SrAl_2O_4$):Eu,Dy,Y.	($SrAl_2O_4$):Eu,Dy,Y.
Temperature of synthesis, °C	1320	1225
Total time of synthesis, min.	≥ 1440	10-15
Particle fineness of synthesized material, μm.	Synthesized material, average grain size after grinding 15-20 μm	Sizes less than 25-50 nm, no further grinding required

3. Conclusions

1) Continuous solid-phase synthesis allows for the synthesis of strontium aluminate in the form of nanostructured powders with controlled particle size distribution directly during synthesis.

2) Continuous solid-phase synthesis in the presence of a liquid phase purpose allows for the synthesis of strontium aluminate with a high level of monophasity.

3) Continuous solid-phase synthesis is advisable to use to optimize illumination parameters of phosphors based on strontium aluminate.

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