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Effect of Mechanical Activation on the Phase Composition of Lanthanum Hexaboride Produced by SHS Method

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Abstract

Background/Objectives: The work considers the effect of mechanical activation of the charge on the phase composition of the final product based on lanthanum hexaboride produced by the method of self-propagating high-temperature synthesis. **Methods/Statistical analysis:** To study the influence of mechanical activation on the SHS process a mixture of the following reagents was taken: Lanthanum oxide La2O3 and amorphous boron in the mass fractions of 2 to 1 respectively. Mechanical activation was carried out on a planetary ball mill AGO-2S. **Findings:** The mechanical activation results in particle size reduction, but it has a "saturation threshold". Optimal parameters of mechanical activation are selected for the most complete conversion of the charge to the desired product of lanthanum hexaboride. It is established that mechanical activation has a "saturation threshold" after which further processing does not bring positive results, the sample either undergoes a thermo-mechanical destruction or the sample is converted to the finished product incompletely, so it is necessary to select the parameters of mechanical activation for each reagent mixture (charge). Optimal average particle size of the charge - 2.52 μm (activation mode with a frequency of 20 Hz and a processing time of 15 minutes) was defined experimentally at which the most complete conversion of the sample to the finished product occurs. **Applications/ Improvements:** Due to the development of accelerator equipment for various purposes, the main direction of the development of thermal cathodes is the provision of good emission characteristics in harsh environments.

Keywords: Accelerator Equipment, Effect of Mechanical Activation, Lanthanum Hexaboride, Phase Composition, SHS Method

1. Introduction

Due to the development of accelerator equipment for various purposes, the main direction of the development of thermal cathodes is the provision of good emission characteristics in harsh environments. These conditions include high and low temperatures, low and ultra-high vacuum, inert and corrosive environment, intensive ion and electron bombardment, various modes of exposure.

Hence, materials used in the production of thermionic cathodes must possess a number of desirable properties. Apart from thermionic characteristics (high current density and low electronic work function), the material must have a low electrical resistivity, thermal stability, low evaporation rate at the operating temperatures (not more than 10^{-8} g/cm^2-s at 1700°C)[1,2].

A variety of thermal cathodes production technologies has been evolved. Now there are many different types of thermal cathodes that differ in materials used, structure of the active layer, methods of heating and production. Characteristics of the most popular thermal cathodes are given in Table 1.

Metal compounds with boron of MeB_6 type are well studied and, due to their properties, have proven themselves as a material for thermal cathodes[3]. The emitters based on borides usually have higher operating temperature and a relatively low efficiency, but still are of practical interest because of the high performance and better state of knowledge of compounds based on hexaborides[4,5]. Among the hexaborides of rare earth metals, lanthanum hexaboride, characterized by low work function, is most promising and widely studied as

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a source of thermionic emission; it is most often used for the manufacture of cathodes[6].

Table 1. Comparison of thermal cathodes properties

Parameter	Material of thermal cathodes		
	W	LaB_6	ZrO/W(100)
Current density,A/cm^{2}at 200 kV	$5{\cdot}10^5$	$5{\cdot}10^6$	$5{\cdot}10^5$
Size of thermal cathodes, μm	50	10	0,1-1
Dispersion of electrons by energies, eV	2,3	1,5	0,6-0,8
Operating temperature, K	2800	1800	1800
Work function, eV	4,54	2,66	~4,00

It is difficult to realize the full potential of lanthanum hexaboride as the cathode material, because of its resource and energy consumption in the production of thermal cathodes based on it. There is a necessity to apply the methods of hot pressing, electro sintering due to high temperature of sintering, which is close to the melting point[6].

An alternative way is to get the finished product (cathode) by self-propagating high-temperature synthesis (SHS). SHS was discovered in 1967 by Merzhanov A.G., Borovinskaya I.P. and Shkiro V.M. SH-synthesis process is very simple: Synthesis reaction is selectively initiated in the initial mixture of oxidant and reductant. The reaction generates heat, which heats the adjacent cooler layers of material and excites the reaction in them. There occurs the process that self-propagates. A chemical reaction occurs in a narrow zone (combustion front), moving through the substance with a certain speed. For these processes, very high temperatures are needed that are close to the melting temperature of substances involved in the reaction. However, the fact that this high temperature occurs due to the energy released by the system itself makes a great advantage[7-8].

Synthesis of materials by SHS method includes the following steps:

- Mixing the original powdered reagents by the stereometrical calculation according to the corresponding equations of the reaction.
- Chargeprocessing.
- Pressing the initial charge of reactants in the cylindrical preforms of different diameters and heights, at the variation of density values of the material of the obtained original samples by modifying the compacting pressure.
- Implementation of the SHS process in a laboratory equipment and obtaining samples of the considered materials of the target application.
- Processing the finished sample after synthesis.
- Studying the possibility to use the obtained materials for the set goals: the definition of the phase composition, strength characteristics, physical properties.

Now, there are plenty of studies of the processes of SH-synthesis management. A number of ways are revealed that should be considered in relation to specific stages and variable settings.

2. Experimental

The method of influence on the phase composition of the product by changing the parameters of the original components of the charge, namely mechanical activation of the charge is considered in this paper.

Mechanical activation of the reactants is the process of transfer of mechanical energy to the sample with the purpose to deform and destroy the solid body by the accumulation of point defects and dislocations, which allows not only to receive the objects with linear sizes ranging from tens of micrometers to several nanometers, but also to accelerate the chemical reactions in the synthesis of solid-phase compounds.

To study the influence of mechanical activation on the SHS process a mixture of the following reagents was taken: lanthanum oxide La_2O_3 and amorphous boron in the mass fractions of 2 to 1 respectively. Mechanical activation was carried out on a planetary ball mill AGO-2S. Metal balls with a diameter of 6 mm were used as the grinding bodies.

During the experiment the following parameters were varied: Mill speed from 10 Hz to 40 Hz with the step of 10 Hz, and the activation time of the initial mixture of reactants in the mill from 5 to 60 minutes with the step of 5 minutes.

3. Result and Discussion

Because of mechanical activation, a more homogenous structure of the original mixture of reagents is achieved, the area of contact of the reacting particles is increased due to the particle size reduction, also, defects and

Table 2. Average particle size (μm)

Speed	Activation time				
	5 minutes	10 minutes	15 minutes	20 minutes	25 minutes
10 Hz	13,45	12,24	7,25	6,23	5,49
20 Hz	9,64	8,79	2,52	1,94	1,32
30 Hz	6,78	3,67	5,60	4,89	5,21
40 Hz	5,42	8,49	7,80	6,80	7,84

dislocations are accumulated, which are subject to relaxation under heat, thus increasing the energy in the reaction process. Table 2 shows the results of the study of the average particle size of the charge depending on the parameters of mechanical activation.

The table shows that during the mechanical activation average particle size is reduced both at the increase of the activation time, and at the increase of the speed of the mill. However, a "saturation threshold" of mechanical activation is observed, after which the average particle size starts to increase. This is due to the creation of large agglomerates, "riveting" of the particles on each other. The results of mechanical activation of more than 25 minutes were not considered, since in most cases thermomechanical destruction of the sample during the synthesis was observed. It can be explained by the increased specific power output of the ongoing reaction.

It is found out that when the average particle size is less than 2.52 microns thermomechanical destruction of the sample during synthesis is also observed.

The following pattern is observed: at low speed (10 Hz) mechanical activation reaches its maximum efficiency, longer than at higher frequencies (20-40 Hz).

X-ray phase analysis (XRFA) of the final product was carried out on X-ray diffractometer Shimadzu XRD 6000. Figures 1-3 show the radiographs obtained at an average rate of charge of 6.80 μm, 5.60 μm, 2.52 μm.

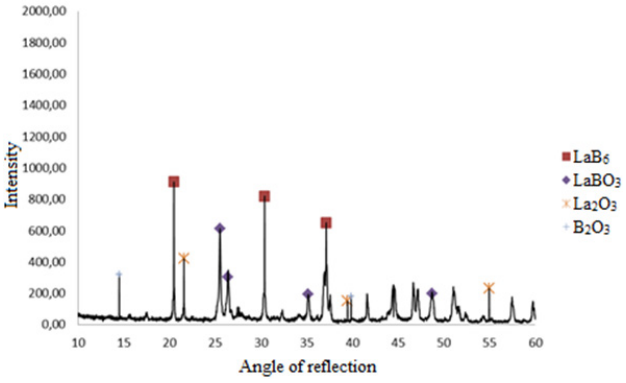

Figure 1. Phase composition of finished product at an average rate of particles of 6, 80 μm.

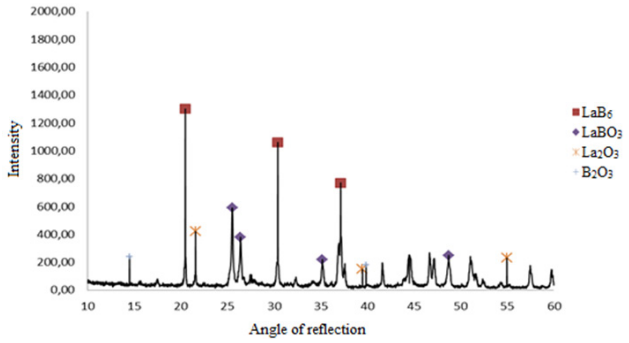

Figure 2. Phase composition of finished product at an average rate of particles of 5,60 μm.

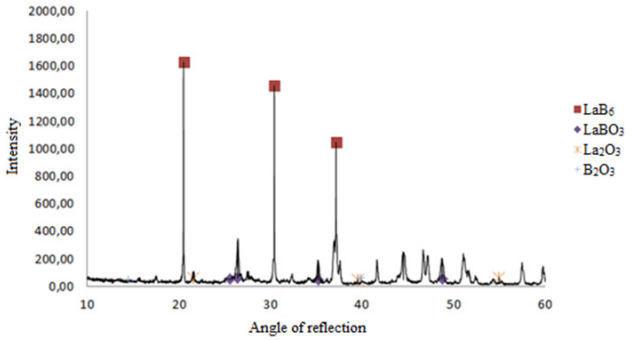

Figure 3. Phase composition of finished product at an average rate of particles of 2,52 μm.

Data analysis of the obtained samples by the phase composition showed that the final phase composition largely depends on the mode of preliminary mechanical activation of a mixture of the initial reagents, and, as a result, on the average particle size. Figure 1 shows that at the average particle size of 6.80 microns (activation mode at a frequency of 40 Hz and a processing time of 20 minutes), the sample reacted with the formation of LaB_6 45 % wt., but most of the sample did not react or remained in the intermediate phase (La_2O_3 and B_2O_3 7 % wt., $LaBO_3$ 28% wt.). When the average particle size was 5.60 microns, which is shown in Figure 2 (activation mode with a frequency of 30 Hz and a processing time of 15 minutes), the situation changed, the yield

percentage of LaB_6 61% wt. increased, but the proportion of intermediate phase and unreacted material remained high ($LaBO_3$ 18% wt., La_2O_3 and B_2O_3 2 %wt.). The best result was obtained with an average particle size of 2.52 microns, Figure 3 (activation mode with a frequency of 20 Hz and a processing time of 15 minutes), the content of the finished product of LaB_6 in the sample was 85 % wt., the proportion of impurities accounted 2% wt. for $LaBO_3$and1% wt. for La_2O_3.

4. Conclusions

In order to obtain high-quality and desirable materials, it is necessary to select the parameters of the preparation of the charge carefully, including those of the mechanical activation, which is only possible by experimentation. It is established that mechanical activation has a "saturation threshold" after which further processing does not bring positive results, the sample either undergoes a thermo-mechanical destruction or the sample is converted to the finished product incompletely, so it is necessary to select the parameters of mechanical activation for each reagent mixture (charge). Optimal average particle size of the charge - 2.52 μm (activation mode with a frequency of 20 Hz and a processing time of 15 minutes) was defined experimentally at which the most complete conversion of the sample to the finished product occurs.

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