

FORMATION OF THE FINE-GRAIN STRUCTURE OF POLYCRYSTALLINE SHS ZINC SULFIDE

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UDC 536.46

ZnS luminophors have been synthesized by SHS. It is shown that addition of a fine-grain powder of the final product or a chlorine-base disperser to the initial mixture prepared in a batch may change the grain size. The materials synthesized are competitive in their inertial properties with etalon x-ray luminophors.

The majority of luminophors for the visible part of the spectrum are synthesized on the basis of ZnS. The traditional methods of obtaining ZnS are complicated and time consuming, and therefore the development of new ZnS synthesis methods is an urgent problem. In [1] the conditions are determined under which propagation of a stationary thermal wave in a Zn and S powder mixture, preliminarily prepared in a batch, may be realized. It is shown that polycrystalline ZnS and ZnS, activated by impurities, may be obtained in SHS by adding the impurities to the initial batch. The synthesized ZnS+Y, ZnS+Ba, ZnS+Cu, ZnS+Mn samples exhibit photo-, cathodo- x-ray-, and electroluminescence, and the last sample also shows triboluminescence [2].

After transit of a combustion wave a melt is formed, from which structurization proceeds. The combustion wave propagates along a cylindrical sample, whereas the crystallization mainly takes place in the radial direction from the side surface. The materials synthesized have a granular structure with a grain size of about 50 μm , consisting of three basic macrostructural zones typical for solidification occurring from a melt (Fig. 1). Anisotropy of the structure of the materials synthesized causes anisotropy of their physical properties (conductance, microhardness, phase composition, etc.) [3]. A decrease in the size of a structural grain causes a decrease in the anisotropy of the physical properties.

After grinding of the materials synthesized to micron sizes the intensity of the photoluminescence decreases abruptly. Mechanical stresses are probably released by grinding, thus healing the defects that cause intense photoluminescence. The present work is aimed at a search for synthesis conditions that allow synthesis of the materials with finer grains.

It is shown that when the final product is added in the form of a finely dispersed powder to the initial batch, the zone of pillar crystals diminishes substantially and the mean grain size decreases to $\sim 20 \mu\text{m}$. Furthermore, adding a chlorine-base disperser to the initial batch, one may change the crystallization mechanism and obtain ZnS powders with characteristic grain sizes of approximately 5 μm . These samples may be used as x-ray luminophors.

Experimental Technique. The samples synthesized were prepared from zinc and sulfur powders with addition of impurities. Then the mixture was compacted to attain a relative density of $\rho_{\text{rel}} = 0.85$. The compacted material was placed in a quartz beaker located in a high-pressure vessel. The vessel was filled with an inert gas. A synthesis wave was initiated by a local heat source and propagated along the sample. The pressure of the inert gas must be such that structurization of the final material ZnS+{pr} involves a melting stage. This ensures homogeneous mixing of the impurity with the basic material.

The samples synthesized were investigated on a setup using an x-ray microfocus source (Fig. 2). A portion of the powder was placed in a quartz cuvette. Luminescence was induced by incident x-ray radiation. A lead glass plate, nontransparent for x-ray radiation, and removable filters at $\lambda_1 = 510 \text{ nm}$ and $\lambda_2 = 460 \text{ nm}$ provided selective incidence of the induced radiation from a photomultiplier. The signal from the photomultiplier was recorded by an

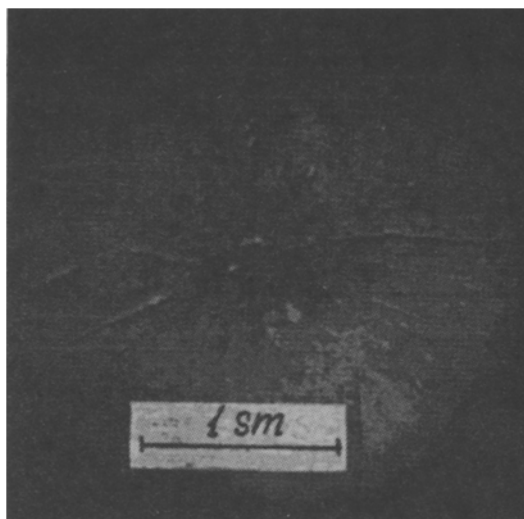


Fig. 1. Photograph of typical structural zones on the surface of the samples obtained. Magnification $\times 1.5$.

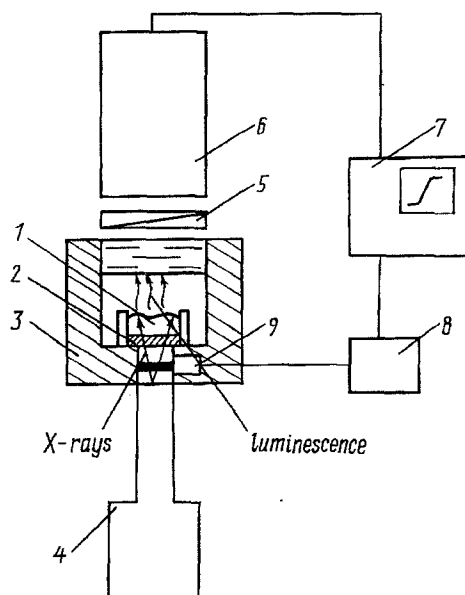


Fig. 2. Schematic of the experimental setup: 1) powder; 2) cell with a beryllium base; 3) chamber for the samples; 4) microfocus x-ray tube; 5) light filter; 6) photomultiplier; 7) storage oscilloscope; 8) synchrotronization unit; 9) shutter.

oscilloscope that was actuated in step with a shutter regulating the incidence of x-ray radiation onto the sample. This experimental setup allowed us not only to record the ratio $I_{\lambda_1}/I_{\lambda_2}$ but also to investigate afterluminescence of the material. For instance, the storage oscilloscope recorded the time diagram of appearance and disappearance of luminescence on excitation and cessation of x-ray radiation.

The stability of luminophors against temperature change was monitored with the ratio $I_{\lambda_1}/I_{\lambda_2}$ measured before and after annealing conducted in air and under vacuum conditions. After annealing, the phase composition of the samples synthesized was analyzed using a Bragg-Brentano x-ray diffractometer, operating with copper radiation at $\lambda = 1.54050 \text{ \AA}$ (K_{α_1}), and a graphite monochromator. In order to determine phases in the system, we singled out from the overall series of the d_{hkl} values obtained those typical of each phase. The size of a structural grain was fixed for samples with different content of the disperser using surface photographs obtained by a "Cameca" scanning electron microscope.

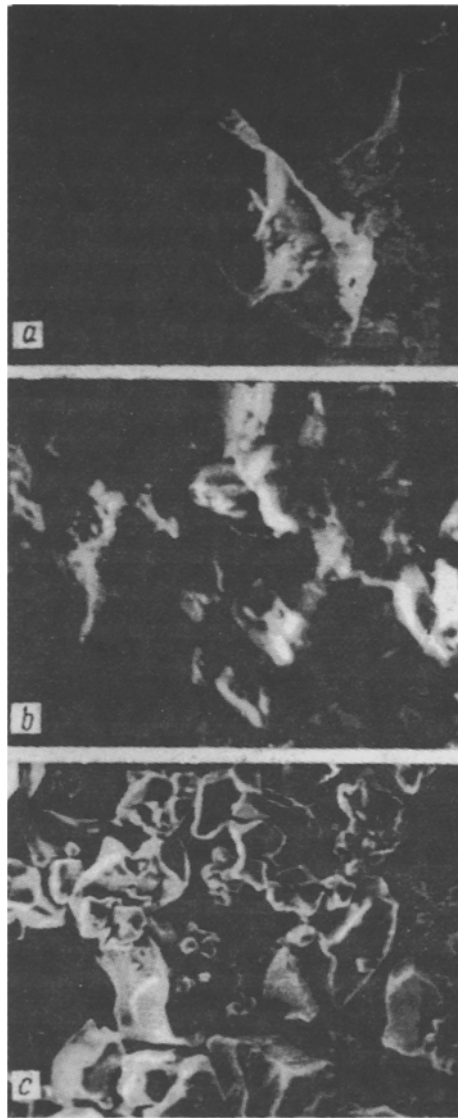


Fig. 3. Photographs of sample surfaces at different concentrations (c) of the disperser. a) $c = 0.1$ mole %; b) 0.15; c) 0.2 mole %. Magnification $\times 800$.

The first of the methods of changing the melt is addition of the final product to the initial mixture. The final product was added in a powdered state with dispersivity and weight concentrations being varied within wide limits. Addition of the ZnS powder caused almost complete disappearance of pillar crystals. The grain size became more than halved. This method of decreasing the grain size is based on increasing the number of their nucleation sites. On the other hand, additions of the final product cause a decrease in the mean temperature of the melt, thus leading to its solidification. Moreover, these additions decrease the temperature gradient to a value insufficient for formation of pillar crystals. The fine-grain structure prevents cracking of the samples. The phase of the final product consists of α -ZnS (wurtzite) and β -ZnS (zinc mixture). The luminescent properties of the samples differ slightly from the analogous samples without ZnS.

Addition of a disperser can be included among the mechanical methods of reducing the grain size. Such an impurity promotes intense gas liberation during formation of the ZnS-Zn-S melt. A rather effective method is mixing that leads to an increase in the number of nucleation sites and, therefore, to the formation of a finer-grain structure. We succeeded in choosing a chlorine-based disperser that possesses the properties both of a disperser and an optical activator. The concentration of the disperser (c) was changed from 0.1 to 0.2 mole %, whereas for concentrations lower than 0.1 mole % the final product preserved its form and the three characteristic microstructural zones. Structurization proceeded in the melt. The anisotropy of the structure was absolutely identical to that of

photoluminescence. The lifetime of the sample under consideration attained ~ 10 sec. However, the material synthesized was unstable; it was easily crushed even under weak mechanical action. An increase of the disperser concentration above 0.2 mole % disturbed the thermodynamic conditions of propagating the thermal wave of synthesis. At the disperser concentration 0.2 mole % the final product was synthesized in the form of a zinc sulfide powder activated with chlorine. The amount of heat released in the chemical reaction was insufficient to provide the conditions of self-sustained synthesis. The emergence of additional nucleation sites on addition of the impurity and, to a large extent, the dispersing effect revealed by the latter result in a change in the grains (Figs. 1 and 3). Rapid, as compared to monolith crystallization, structurization provides formation of just the high-temperature zinc sulfide modification, namely, wurtzite, in the final product.

The presence of chlorine favors the appearance of the luminescence peak at $\lambda = 460$ nm, with $I_{\lambda_2}/I_{\lambda_1} \approx 0.12 < 1$. On annealing of the sample (50-g batch) under vacuum conditions at $T = 800^\circ\text{C}$ for 30 min its phase composition does not change. Under the same annealing conditions but in air the phase composition changes from wurtzite to ZnO with the intensity $I_{\lambda_2}/I_{\lambda_1} > 1$ (see Fig. 1). Indeed, "blue" luminescence is weaker than "green." On vacuum annealing the ratio $I_{\lambda_2}/I_{\lambda_1}$ remains unchanged up to 800°C .

The data on the phase composition of the material make it possible to explain the luminescence stability in vacuum annealing and its instability in air annealing. According to the data of chemical analysis the ZnS synthesized contains no more than 0.3% ZnO and 0.3% ZnCl.

A comparison of the inertial properties of the ZnS+"Cl" luminophors with those of the etalon luminophors (Fig. 3) shows that the materials synthesized are competitive with the etalon x-ray luminophors.

Conclusion. It is shown that addition of a finely dispersed powder of the initial product or a chlorine-based disperser to the initial batch can change the grain size of ZnS-based SHS luminophors. This ensures the best luminescent characteristics of SHS ZnS luminophors. Use of the disperser makes it possible to obtain both monolithic and powdered samples. The disperser added leads to a change in the grain size in the structurization process. The fact that the disperser chosen combines the properties of the substance, whose decomposition is accompanied by extensive heat release, and the luminescence activator makes it possible to synthesize powdered ZnS luminophors. Such materials may be used as x-ray luminophors as well as for preparing luminescent emulsions.

NOTATION

ρ_{rel} , relative density; λ_1, λ_2 , wavelengths; I , intensity; pr, product.

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