

Electrical and optical properties of semiconducting ZnS and ZnMnS ceramics prepared by Self-Propagating High Temperature Synthesis

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Bulk ceramic specimen of pure and Mn-doped ZnS were prepared by the SPHTS technique (Self-Propagating High Temperature Synthesis: based on the exothermic interaction of the components of the stoichiometric powder mixture in a high-pressure vessel). The samples were studied using optical microscopy, electric impedance measurements and Micro Raman light scattering. The results show that during the heat wave propagation and the subsequent short high temperature period, micro crystals of ZnS are formed, surrounded by liquid sulfur. They exhibit a dynamic interaction leading to an anisotropic distribution and thus to dielectric and electric anisotropy of the material. The phonon spectrum of most of the crystals found by the Micro Raman technique is about the same as that for regular ZnS. However, some of the crystals present a Raman spectrum with additional sharp features corresponding to modes activated by strain. In Mn-doped crystals the main phonon lines present a red shift indicating the presence of a negative strain. On the basis of our results, we could consider the SPHTS as a quick and cheap technology for producing high-quality semiconductor micro crystals.

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I. INTRODUCTION

The so-called Self-Propagating High Temperature Synthesis (SPHTS, see, for example, [1]) as a technique for quick creation of various solid (ceramic) materials has been known for about 20 years, but it is still rarely used and not much investigated. In applications to semiconductors, it is known to produce materials in a highly non-equilibrium state. The object of this work was to make a detailed investigation of one of the SPHTS-semiconductors, to study the features resulting from the specific kinetics of the process, and to analyze its possibilities in technical applications. We found that this process could produce high quality micro crystals not much different from those made by the traditional technologies.

II. EXPERIMENTAL

Self-propagating high temperature synthesis of ceramic samples. A mixture of fine powders of the

components (Zn, S) was compressed under pressure from 6 to 12 Mpa and placed in a special vessel (1 in Fig.1) filled with Ar or N and designed to stand both high temperature and pressure. The reacting components (3, Fig.1) fill the quartz ampoule 2; to start the synthesis reaction, the mixture was heated from one side by passing current through a wire (6, Fig.1). In the melted zone so formed, the exothermic interaction of the components takes place leading to the formation of micro crystals of ZnS; the energetic balance of the interaction is such that the neighbor zone would also be melted. In such a way, a burning wave with a thickness around 10 mm propagates through the whole vessel forming a solid sample of about 1 Lt in volume in approximately 1 min (for details see Refs. [1-5]). The temperature was monitored with a thermocouple (4, Fig. 1); its value in the reaction zone was ca. 2000 K, which approximately corresponds to the ZnS melting temperature. The reactor has a window (5, Fig. 1)

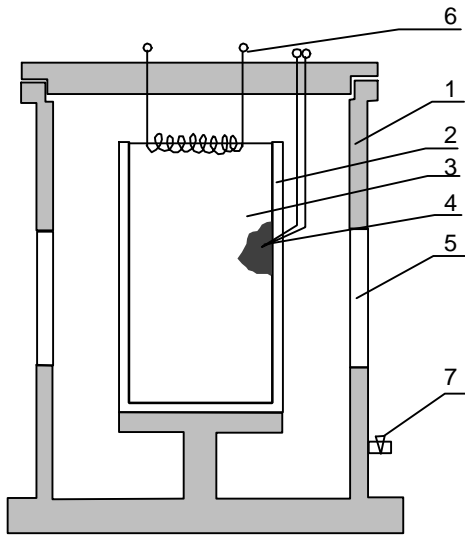


Fig. 1. Scheme of the reactor for SPHTS (see text)

used for visual and photographic control; the valve (7) is used for pressure changes. Fig.2 shows how the pressure influences the percentage of the material transformed from the powder into the solid form.

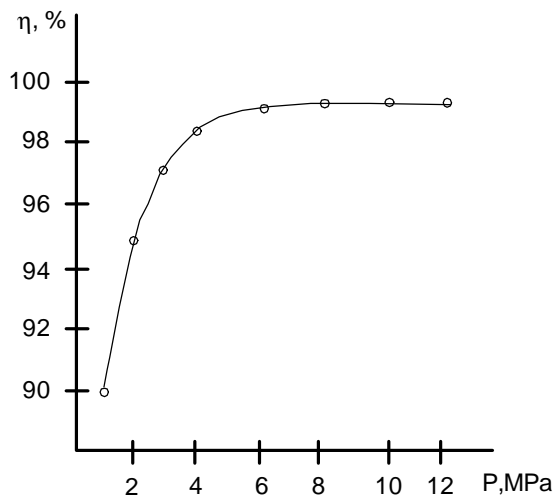


Fig. 2. Dependence of the effectiveness of the reaction upon the pressure in the reactor

To increase both the speed of the synthesis reaction and the amount of the material transformed into solid form, up to 10% of ammonium chloride was added to the initial mixture: in the high temperature reaction zone it disintegrates into gaseous components NH_4^+ and Cl^- which actively interacts with Zn and S powders mixing and dispersing the grains and forming short-living

components interacting with each other. After melting and subsequent cooling of the active zone, no NH_4Cl is left in the solid formed, and the coefficient of transformation is about 98% (without ammonium chloride it is around 90%).

To obtain the Mn-doped ceramics, Mn powder was included into the initial mixture.

Experimental equipment. To measure the a.c. electrical parameters of the material, a standard electric bridge for impedance measurements was used with a working frequency of 1 MHz. For the determination of the conductivity at higher frequencies, we used a standard Q-meter detecting the variation of the quality (ΔQ) in a resonance circuit composed of inductance and capacitance, caused by the introduction of a sample inside the capacitor. The sample's specific conductivity was calculated after the formula

$$\sigma = \Delta Q \pi \epsilon \epsilon_0 \nu / Q^2$$

which follows from a definition of the quality parameter Q (ϵ being the relative dielectric constant of material, ν – the frequency, and ϵ_0 – the dielectric constant of vacuum).

The Raman spectra of the individual crystallites were obtained with a Micro Raman system having a 632.8-nm laser as the excitation source with typical power densities of 10 W/cm^2 . The size of the illuminated spot was about $1 \mu\text{m}$ in diameter.

III. RESULTS AND DISCUSSION

Sample's microstructure. It can be expected that the ceramic material formed during this very quick and practically uncontrollable process will be strained, non-uniform and anisotropic. The microscopic analysis (see Fig.3) shows, in general, an anisotropic distribution of the micro crystallites within the specimen: only in the central part micro crystals are found with similar dimensions for all directions (Fig.3a). In the major part of the sample, elongated crystallites were formed (Fig.3b) with sizes from 1 to $100 \mu\text{m}$ orientated, as a rule, along the radius of the specimen (i.e. normal to the axis of the vessel); sometimes they formed aggregates of spherical shape (Fig.3c).

Electrical properties. The d.c. conductivity of our samples is practically zero; for a.c. conductivity, in the frequency range around 1 MHz it is measurable, and increases with frequency increments (see Fig.4a). Fig.4b shows the results of studying the distribution of the electrical characteristics along the radius of a sample cut normally to the axis of the vessel. It is seen that the conductivity (order of magnitude $10^{-5}(\Omega\text{cm})^{-1}$) decreases with the distance

from the vessel axis. The dielectric losses, scaled

agrees well with the observations made above about the electrical properties of the samples.

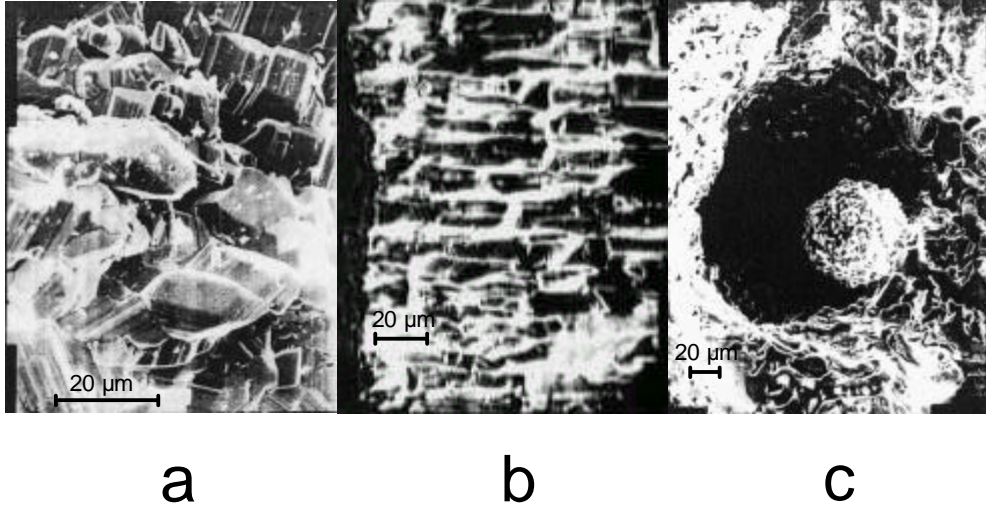


Fig. 3. Micro photograph of the SPHTS made ZnS
c – with 10 w.% of NH_4Cl); the 20 μm length is

(a,b – with 5 w.% of NH_4Cl in the initial mixture, indicated in the photographs

according to the factor $\text{tg } d$, have the same behavior, which is expected, since

$$\text{tg } d = \frac{s}{2pnee_o}$$

Moreover, Fig.4b contains the radial dependence of the measured dielectric constant; as well as two other dependencies, it shows the decrease of the corresponding value with an increase in the distance from the axis. All these data indicate that in the ceramic so obtained, the semiconducting crystallites are surrounded by insulating material; this explains the zero d.c. conductivity and the rest of the results on electric parameters: micro crystals orientated along the radius have higher density near the axis than at the periphery of the sample. This causes a decrease of the conductivity along the radius. The dielectric constant is determined by the volume fraction of insulator, which should have a smaller value of ϵ ; an increase of this fraction with the distance from the axis would explain the observed $\epsilon(r)$ dependence.

Micro Raman investigations. The study of the substance separating the crystallites from each other indicates the presence of phonon lines at 151, 218 and 474 cm^{-1} , typical of sulfur. Since sulfur is an insulator with a value of $\epsilon = 4$ (for ZnS $\epsilon = 5$), it

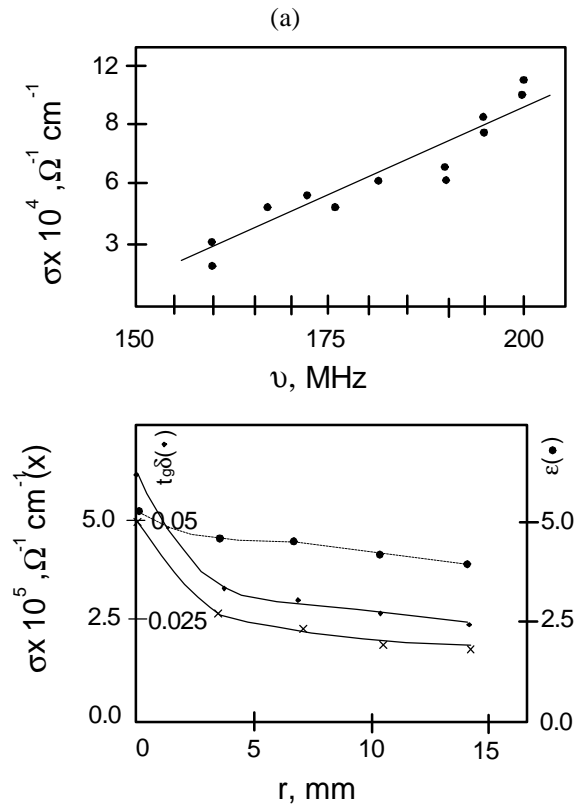


Fig. 4. Frequency dependence of the specific conductivity σ (a); radial change of σ , ϵ , $\text{tg } \delta$ (b).

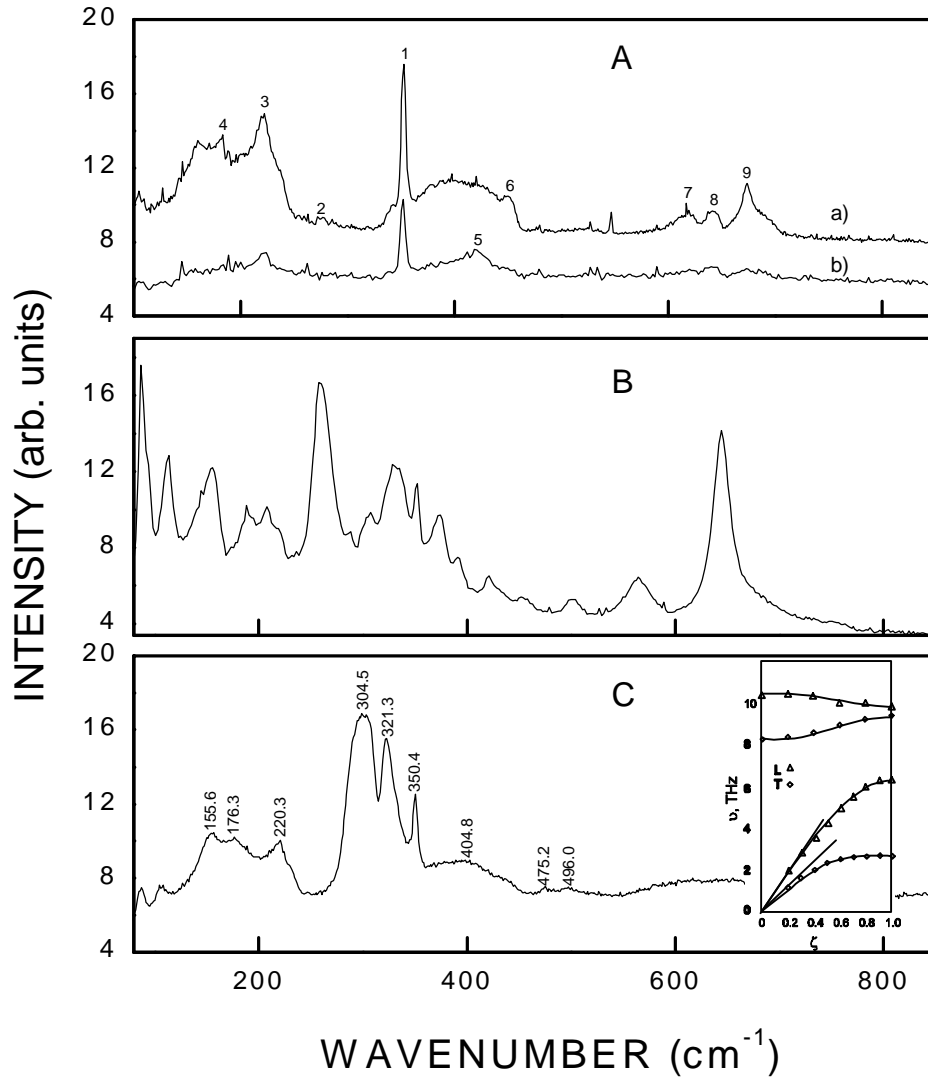


Fig. 5. A – Raman spectra of ZnS micro crystals for spectrum of a ZnS strained micro crystal. C - Raman

parallel (a) and crossed (b) polarizations. B - Raman spectrum of a Mn-doped ZnS crystal. The insert shows the ZnS phonon dispersion curves along the

The majority of ZnS micro crystals studied (about 98% of them) have their Raman spectra with the typical features [6-9] for this material when obtained by the traditional methods. This was an unexpected result considering the high probability of strain following from the characteristics of the technology (see Fig.5, curves *a,b* for two different polarization configurations). Line 1 around 352 cm^{-1} belongs to LO-phonons, line 2 (273 cm^{-1}) – to the TO modes, both with wave vector close to zero (Γ -point of the Brillouin's zone); lines 3 and 4 (221 and 179 cm^{-1} , correspondingly) are second-order modes (2LA and 2TA, point X). The rest of the lines are assigned to:

#5 (420 cm^{-1}) – TO + LA; #6 (448 cm^{-1}) – LO + TA (X); #7 (615 cm^{-1}) – 2TO (X); #8 (640 cm^{-1}) – TO + LO (X, L); #9 (671 cm^{-1}) – 2 LO, see [7-9].

According to the observation made in [7], the ratio of intensities of the LO to TO lines is an indication of the crystal modification: the higher is the ratio, the larger is the volume with hexagonal structure. In our case this ratio is around 25 which means that we have mainly hexagonal crystals.

Less than 2% of the crystals studied have the spectrum essentially different from that normal to ZnS, an example is shown in Fig.5B. One can see that here the lines 2 and 8 are dominating (TO and TO + LO lines). It is generally accepted [8-10] that in Raman spectra the longitudinal optical modes are usually dominant over the transversal ones. So, an unusual spectrum with the dominating role of the transversal phonons may be connected with internal strain and deformation of the corresponding micro crystals causing the enhancement of the influence of

the transversal waves upon the crystal polarizability [10].

The relatively small amount of such strained crystals suggests that the substance among the crystals is softer than the crystals themselves. The known mechanical and thermal properties of ZnS and S [11] agree with this conclusion: ZnS has a hardness of 3.5 – 4 and a melting point of 1700° C for wurtzite, and 1020° C for spheralite. S has a hardness of 1.5 – 2.5, and a melting point of 119° C. During the sample's formation, the crystallites, as a rule, are created within liquid surroundings and after cooling and solidification, the softer substance relieves the deformation. $Zn_{0.95}Mn_{0.05}S$ (Fig.5C) has a Raman spectrum which again coincides in the main features with that of traditionally made ZnS(Mn) [12]. It is seen that the normal LO, 2LA and 2TA lines are observed; the rest originates from resonance modes induced by the Mn impurity. A detailed comparison of our spectrum to that analyzed in [12] shows that the line observed at 321.3 cm^{-1} is essentially red shifted (in fact, the phonon density of normal ZnS has a gap at this point). The analysis of the stress influence upon the phonon spectra presented in [12] leads us to the conclusion that the Mn-doped crystallites have a negative strain, in addition to the fact that the majority of the undoped crystals have no strain at all. This negative strain could be understood if we compare the ionic radii of the Zn and Mn ions: entering the substitution position, Mn has a smaller radius than Zn (0.80 and 0.88 Å correspondingly, see [11]). For the low levels of doping used in [12], this effect could be negligible, but it becomes noticeable in our case.

Possible reasons for micro crystals aggregation and orientation. On the basis of the above results it is possible to conclude that the ZnS micro crystals are formed in a liquid sulfur environment, and remain in this environment during a large part of the cooling process (from 1700 to 119° C). This process is accompanied by thermal shrinking (usually, larger for the liquid than for the solid) of the system. During the process, the relative position of crystals will be changing. The physical reason for this would be their elastic interaction with the liquid leading to an appearance of the corresponding forces pushing crystals towards each other. Thus, the drift of the crystallites towards each other would accompany the cooling process; after their contact, the rotational torque would appear orientating crystallites parallel to each other. These effects of dynamic attraction of crystallites in the liquid

surrounding should, in general, produce a parallel orientation and aggregation.

IV. CONCLUSIONS

The zinc sulfide ceramic obtained by the self-propagating high temperature synthesis (SPHTS) contains micro crystals, mainly with hexagonal structure, which are often arranged in approximately axial or spherical symmetry. These micro crystals are semiconducting, the substance separating them from each other is insulating. Therefore the material possesses spatial non-uniformity and anisotropy of the electric conductivity and dielectric constant; the former increasing with an increase in the frequency. The above mentioned ordering of the crystallites is achieved during the cooling process of the system as a consequence of the different temperature of solidification of ZnS and the excess S, and the dynamic interaction between the crystallites in a liquid environment. The major part of the crystallites is not deformed and, in general, their characteristics are not much different from the material obtained by traditional methods. Therefore, the SPHTS may be estimated as a cheap and quick technology of production of good quality semiconducting ZnS micro crystals.

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