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DEVELOPMENT OF ZnSxSe1-x NANOCRYSTALS WITH IMPROVED PHYSICAL AND OPTICAL PROPERTIES OBTAINED BY THE COMBUSTION SYNTHESIS METHOD

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Abstract. *All compounds of ZnS_xSe_{1-x} nanocrystals were created by combustion synthesis method. The obtained samples were discovered to have diameters of 55 ± 5 nm and to have a heterogeneous crystalline structure. The fraction of the cubic phase grew in the appropriate ratios as the x value increased, but the fraction of the hexagonal phase in nanocrystals declined from 65 ± 5% to 30 ± 5%. According to XRD data, Mn^{2+} impurity ions are not mixed in the immediate environment despite the creation of ZnS_xSe_{1-x} solid solutions. The Mn^{2+} ions were surrounded by sulfur ions at a value of $0.2 < x \leq 1$ and selenium ions were at a value of $x \leq 0.2$.*

Keywords: *ZnSxSe1-x nanocrystals, combustion synthesis, X-ray diffraction analysis, crystal structure, EPR spectra.*

Introduction

Due to their unique physical characteristics, ZnS_xSe_{1-x} solid solutions stand out among semiconductor compounds of the A_2B_6 type. Such materials, which have an energy bandgap in the range of 2.7–3.7 eV depending on the value of x, can be used to create short-wave radiation photosensitive devices, light-emitting diodes, and lasers in the blue spectral band [1]. The widespread utilization of A_2B_6 type nanocrystals (NC) chemicals in different optoelectronic-radiating structures has recently drawn more attention to these substances. As a result, high-performance technologies are being developed to produce NC with predictable and regulated qualities.

In comparison to other techniques, the combustion synthesis (CS) (self-propagating high-temperature synthesis) has a number of benefits for producing NC of the A_2B_6 type. This approach stands out for its high rate of NC production, ability to generate huge quantities, low cost and energy consumption per unit, simplicity of the used equipment, and environmental friendliness [2]. By using a straightforward high-temperature reaction of a fine powder mixture of Zn, S, and Se, the CS approach enables the production of doped NC during the synthesis by adding the appropriate doping materials to the charge.

Analysis of publications

It should be mentioned that prior CS results were obtained for ZnS NC, ZnS:Mn, and ZnSe polycrystals [3,4]. However, according to our sources, this approach has not yet been used to synthesis ZnS_xSe_{1-x} and ZnS_xSe_{1-x}:Mn NC. The features of ZnS_xSe_{1-x} and ZnS_xSe_{1-x}:Mn NC obtained by the CS method, as well as the research findings of their crystal frameworks and EPR spectra, are examined in this paper.

Results and discussion

In a quartz ampoule positioned inside a sealed steel reactor, solid solutions of ZnS_xSe_{1-x} and ZnS_xSe_{1-x}:Mn were synthesized. Zn, S, and Se powders that had been physically combined and placed into the ampoule in the proper ratios. Ethyl alcohol was added to the charge prior to premixing in order to facilitate better mixing. The x_p parameter describes the S to Se ratio in the charge. After the

mixture had dried, a thermal impulse from the nickel-chromium coil in the reactor's upper section was used to start the synthesis reaction. Atmospheric pressure in the air was used for the synthesis. The x parameter, which was later shown to differ from the x_p parameter, was responsible for determining the S and Se ratio in the resulting ZnS_xSe_{1-x} NC. The $MnCl_2$ salt was added to the ZnS_xSe_{1-x} NC in order to dope it with Mn^{2+} ions, 10^{-2} weight percent of the initial charge.

Utilizing Co-K radiation, XRD examination of the produced NC was carried out on a DRON-2 diffractometer. Utilizing the Radiopan SE/X-2543 radiospectrometer, the EPR spectrum was investigated. Using a REMMA-102-02 scanning electron microscope, the images of the nanoparticles were captured.

The shape of the powder made up of the ZnS_xSe_{1-x} NC crystals produced by CS According to the XRD results, this powder was made up of polycrystals with a heterogeneous crystal framework that ranged in size from 1 to 5 μm and contained NC. The Scherrer method was used to measure their diameters, which were within 55 ± 5 nm. The ZnS_xSe_{1-x} NC's minimum and maximum dimensions were unique to the compound with an x value of 0.2 and 1, respectively.

The proportion of the hexagonal phase in the ZnS NC was ~ (65 ± 5)%, the cubic phase ~ (35 ± 5)%, the $ZnS_{0.8}Se_{0.2}$ NC (60 ± 5)% and (40 ± 5)%, the $ZnS_{0.8}Se_{0.2}$ NC (50 ± 5)% and (50 ± 5)%, and the ZnSe NC (30 ± 5)% and (70 ± 5)%. As a result, the proportion of the cubic phase in the ZnS_xSe_{1-x} NC rose as the x parameter decreased. It is notable that a significant portion of the hexagonal phase, which is not unique to ZnSe bulk crystals, was found in the ZnSe NC. The ZnS_xSe_{1-x} solid solution's cubic phase's NC crystal lattice parameters ranged from a = 5.386 (for x = 1) to a = 5.633 (for x = 0). These values found determined to be less than the ZnS_xSe_{1-x} solid solution single crystal lattice parameters, which range from a = 5.4093 (for x = 1) to a = 5.6687 (for x = 0) [5]. This further demonstrates the strain pressures unique to NC. The ZnS_xSe_{1-x} ($\Delta a/a$) NC crystal lattice has microdeformations ranging from $5 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$. The compounds with x = 1 and x = 0.9 had the smallest degree of microdeformations, whereas the compound with x = 0.2 had the largest. From $5 \cdot 10^{10}$ to $1 \cdot 10^{12}$, the dislocation densities were observed. Specific compounds with x = 1 and x = 0 had the lowest dislocation density, and compounds with x = 0.1 and x = 0.2 had the highest dislocation density. The results indicate that the compound with x = 0.2 undergoes a significant rearrangement of the ZnS_xSe_{1-x} NC crystal structure.

During the ZnS_xSe_{1-x} NC's CS reactions at $x_p \leq 0.9$, a sediment made of selenium oxides precipitated out on the reactor walls. This fact enables us to assume that the S and Se ratio in the charge prepared for CS is determined by the x_p parameter, not the x parameter in the ZnS_xSe_{1-x} NC. Using Vegard's law—a linear modification of the crystal lattice parameters when the S and Se ratio is changed—we were able to calculate the x parameter in the ZnS_xSe_{1-x} NC according to XRD data. This law only applies to ZnS_xSe_{1-x} solid solution crystals. It was discovered as a result that the parameter x considerably differs from the x_p parameter in the synthesized ZnS_xSe_{1-x} NC.

Up until the compound with x = 0, no more crystalline phases are seen in the produced solid solutions, according to the XRD data. Only in the ZnSe NC did we find evidence of the Se_2O_5 phase traces, which makes sense given that NC is often synthesized in the atmosphere.

An analysis of the ZnS_xSe_{1-x} NC of solid solutions EPR spectra revealed that all compounds include a hyperfine structure made up of six evenly spaced lines peculiar to the Mn^{2+} paramagnetic centers, even in the NC undoped by manganese. These lines appeared to be doubled in the compound where x = 1, indicating the overlap of two EPR spectra. One of them is a member of the Mn^{2+} ions that are found in a hexagonal local environment and has the hyperfine structural constant A = 7.15 mT. Mn^{2+} ions found in a cubic environment are linked to another spectrum with a hyperfine structure constant A = 6.88 mT.

Conclusions

The results demonstrate that it is feasible to synthesize NC of ZnS_xSe_{1-x} mixed compounds using the CS approach, as well as to dope them with a manganese admixture during the synthesis. NC is a mixed crystal framework in all substances. According to the EPR findings, the local environment of

the Mn^{2+} ions is not mixed in the compounds with $0.2 < x \leq 1$. Sulfur ions surround the Mn^{2+} ions in these NC. Selenium ions surround the Mn^{2+} ions in compounds where $x \leq 0.2$.

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