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Thermodynamic Simulation of the Zn–S and Zn–Se Systems

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Abstract—The equilibrium composition and the thermodynamic characteristics of the Zn–Se and Zn–S semiconductor systems are studied. The temperature regions of the components of the condensed and gas phases that form when the ZnSe and ZnS compounds are heated in the temperature range 300–3000 K in an Ar atmosphere are revealed for a wide pressure range from 1 to 10^9 Pa. Equations are derived to describe the pressure dependence of the evaporation temperature. The effect of iron and chromium impurities on the equilibrium characteristics of the Zn–Se and Zn–S systems is studied. The enthalpy and the entropy of both systems are shown to increase linearly with the chromium and iron concentration. The results obtained are in good agreement with the experimental data on the dependence of the absorption coefficient and the effective generation of zinc selenide and sulfide on the impurity concentration.

Keywords: zinc selenide, zinc sulfide, thermodynamic simulation

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INTRODUCTION

II–VI semiconductor compounds are promising materials for creating unique devices for optics, optoelectronics, acoustoelectronics, nanoelectronics, laser engineering, and ionizing radiation detection [1–9]. For example, zinc selenide crystals are widely used in infrared, LED, and fiber-optic technologies as X-ray and elementary-particle detectors. Zinc sulfide ZnS is used for the production of infrared optics (ZnS lenses) operating in the range 8–13 μm. In addition, ZnS is used in infrared optical systems, which are usually aligned in the visible range. Zinc chalcogenide (ZnSe, ZnS) crystals doped with transition metal ions (Fe^{2+}, Co^{2+}, Cr^{2+}) are promising materials for creating active media for tunable solid-state lasers [6–9]. Zinc selenide doped with chromium is the most promising active medium material for generating radiation in the wavelength range 2–5 μm. Selective absorption bands in the transmission spectra of biological tissues and some gases are localized in this wavelength range [3, 10, 11].

From the point of view of industrial production, the most effective method for the production of large single crystals is growing from a melt [10]. The Bridgman technique is used for growing wide-gap II–VI semiconductors [12, 13]. This technique is based on the motion of an ampoule with a melt at a temperature gradient and gradual solidification at a temperature below the melting point of the material. To grow doped crystals, an appropriate amount of a doping component is added to a melt [13–15].

All technological processes are based on the knowledge of physical, chemical, thermodynamic, or electrochemical laws, which allow one to control the structural, electrical, mechanical, chemical, and other important properties of materials. As a result, the general physical laws that control the properties of materials or applied technological processes can be revealed and detected. Therefore, when developing and implementing promising technologies for producing new materials, it is necessary to conduct a large complex of physical, chemical and technological studies to obtain the desired results. Important information required for developing processes for growing crystals from a liquid phase is data on the properties of melts.

It should be noted that the physical and chemical properties of II–VI compounds and alloys are well studied in a solid state [1, 7, 10, 11, 16–21]. A number of articles are devoted to the properties of semiconductor systems, and the data obtained are included in handbooks and scientific literature (see, e.g., [22–26]). However, many properties of these materials require additional studies because of the great difficulties on working with these substances: high melting temperatures, high vapor pressures, chemical activity of a gas phase and melts, and toxicity.

Thus, to study the physical and chemical properties of ZnSe and ZnS remains a challenging problem. In addition, it is necessary to investigate the behavior of these materials under extreme conditions, in particular, in aggressive environment, at high or, conversely, cryogenic temperatures, and high pressures.

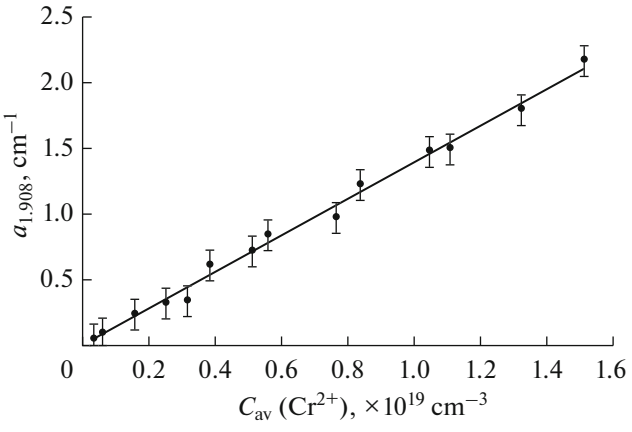

Fig. 5. Absorption coefficient in polycrystalline zinc selenide doped by a diffusion method at a wavelength of 1.908 μm vs. the average Cr^{2+} ion concentration [10].

tems. As the impurity content increases, the enthalpy and the entropy of the systems increase almost linearly. Therefore, the introduction of an impurity increases the heat content and disordering of the system, which significantly affects the physical and chemical properties of the compounds. As an example, we consider the effect of a chromium impurity on the absorption coefficient. Figure 5 shows the dependence of the absorption coefficient in polycrystalline zinc selenide doped by a diffusion method at a wavelength of 1.908 μm on the average concentration of Cr^{2+} ions [10].

The absorption coefficient depends linearly on the concentration of transition metal ions. Thus, a comparison of the results of thermodynamic simulation with the experimental data on the effect of chromium on the absorption coefficient demonstrates a good correlation between them.

CONCLUSIONS

The equilibrium compositions and the thermodynamic characteristics of the Zn–Se and Zn–S semiconductor systems were studied. The temperature regions of the condensed and gas phase components that form upon heating of the ZnSe and ZnS compounds the temperature range 300–3000 K in an Ar atmosphere in a wide pressure range from 1 to 10^9 Pa.

At atmospheric pressure $P = 10^5$ Pa, the mass fraction of the ZnS and ZnSe compounds in the condensed (solid and liquid) state changes weakly and is 0.99 in a wide temperature range (300–1800 K for ZnSe, 300–1600 for ZnS). Complete evaporation of ZnSe and ZnS, which is accompanied by an increase in the mass fraction of the gas phase from 0.01 to 1, occurs at 2150 and 2100 K, respectively.

The temperature at which active evaporation of ZnSe and ZnS begins increases with the pressure. Equations were derived to describe the pressure dependence of the evaporation temperature.

The temperature dependences of the thermodynamic characteristics of the Zn–Se and Zn–S systems were revealed not to be monotonic, and they contained inflection points to be explained by phase transitions in these systems.

The influence of iron and chromium impurities on the equilibrium characteristics of the Zn–Se and Zn–S systems was studied: when the chromium and iron concentrations increase, the enthalpy and entropy of both systems were shown to increase linearly. The introduction of an impurity increases the heat content and disordering of the system, which exerts a significant effect on the physical and chemical properties of the ZnSe and ZnS compounds. A comparison of the thermodynamic simulation results and the experimental data on the influence of chromium ions on the absorption coefficient of polycrystalline zinc selenide doped by a diffusion method demonstrates a qualitative agreement between them.

The results obtained allow us to estimate the composition of the condensed phase tat forms during equilibrium heating of the systems under study and to predict the behavior of materials under extreme conditions.

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