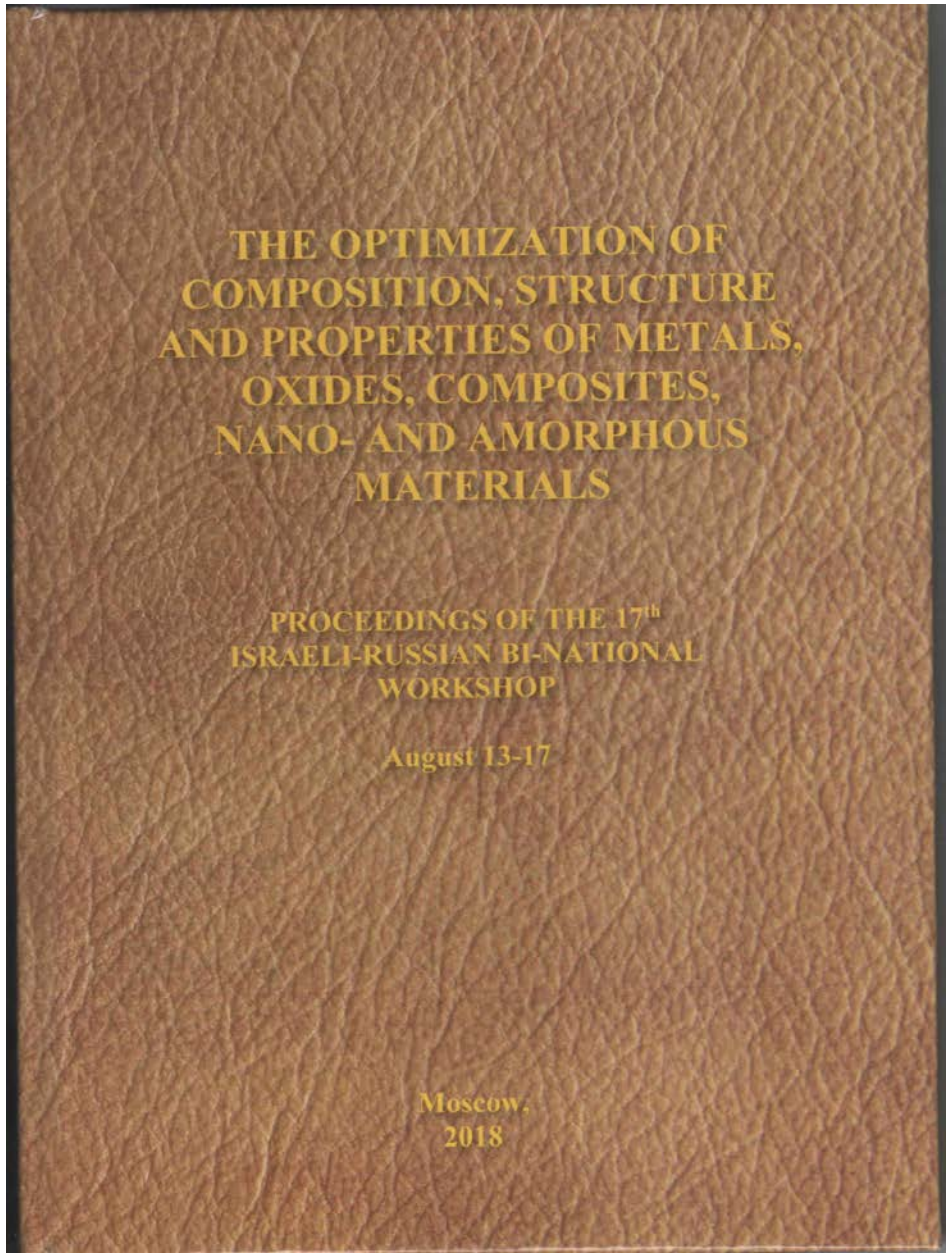
THE OPTIMIZATION OF COMPOSITION, STRUCTURE AND PROPERTIES OF METALS, OXIDES, COMPOSITES, NANO- AND AMORPHOUS MATERIALS
PROCEEDINGS OF THE 17th ISRAELI-RUSSIAN BI-NATIONAL WORKSHOP
August 13-17
Moscow,
2018

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Institute of Metallurgy of Ural Branch of RAS
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PREFACE

The common Bi – National Workshop Russia – Israel is organized in accordance with the Agreement of Scientific Co-operation between the Russian and Israeli Academies of Sciences. The following stages of the Workshop were carried out during the last thirteen years in Russia and Israel: 2002 - Moscow and Ekaterinburg, 2003 - Jerusalem and Tel-Aviv, 2004 - Saint-Petersburg, 2005 - Jerusalem, Tel-Aviv and Ariel), 2006 - Novosibirsk and Irkutsk, 2007 - Jerusalem, Ramat-Gan, Ariel, 2008 - Perm, 2009 - Jerusalem, Tel-Aviv, Ariel, 2010 - Belokurikha, 2011 - Jerusalem, Tel-Aviv and Ariel, 2012 - Chernogolovka, 2013 - Jerusalem, Tel-Aviv and Ariel, 2014 - Ekaterinburg, 2015 – Ariel and Tel-Aviv, 2016 – Ekaterinburg, 2017 - Ariel and Tel-Aviv, and 2018 – Moscow. Israeli and Russian scientists from different universities and research centers of science visited university laboratories and centers and industrial concerns and plants.

Some of the following joint activities were initiated: synthesis of the compact nanocrystal oxide materials and studying their structural, physical and chemical properties; thermodynamic and kinetic characteristics of metal and oxide; structure and properties of metal materials in solid state; thermal spray processes for surfacing; obtaining compact nanomaterials, investigating their structure and properties; mechanochemisty; plasma electrolytic oxidation; hardening of ferric and non-ferric metals by ultra-fine and nano- particles.

All of the papers scheduled for presentation are included in this book. In addition, the papers are also systematically placed on the conferences/workshops homepage (general gate: https://www.ariel.ac.il/sites/conf/mmt/index.htm).

The seventeen-year cooperation results induced an interest in both sides in expanding of collaboration themes. Support for continuing collaboration should be sought from the industry, and areas of practical application should be found for this purpose

Professor Michael Zinigrad	**Academician Leopold Leontiev**
Ariel University, Israel	Russian Academy of Science
Co-Chairman of the Workshop Organizing Committee	Co-Chairman of the Workshop Organizing Committee

THERMODYNAMIC MODELING OF Zn-S AND Zn-Se SYSTEMS

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Motivation

Semiconductor compounds of the A^2B^6 group are promising materials to creation of unique instruments of optics, optoelectronics, acoustoelectronics, nanoelectronics, laser technology, detecting ionizing radiations.

Chalcogenides of zinc, cadmium and mercury are included to compounds of the A^2B^6 type. Among them, sulphides, selenides and tellurides can be distinguished. This group does not include oxides of these metals [1 - 5]. A^2B^6 compounds crystallize in the structure of zinc blende of cubic (sphalerite) or hexagonal (wurtzite) type. The chemical bond has a mixed covalent ionic character. In the chalcogenides, the ionic component of the bond is strongly expressed, which is due to large differences in the electronegativities of the elements forming the compound. At high temperatures all A^2B^6 compounds decompose in accordance with the reaction:

$$2A^2B^6 \rightarrow 2A^2_{(gas)} + B^6_{6(gas)}.$$

The presence of AB molecules in the vapor phase is completely not excluded, but for most compounds their concentration is low and it can be assumed that the dissociation is complete. At the same time, the equilibrium vapor pressure of volatile components strongly depends on temperature. An important feature of type A^2B^6 semiconductors is that many of them exhibit electrical conductivity of only one type, regardless of the conditions of production and the nature of the crystal doping. The conductivity of compounds of the A^2B^6 type can be significantly, by several orders of magnitude, changed by heat treatment in the vapor of the intrinsic components.

Zinc sulphide ZnS is used for the production of infrared IR optics (ZnS windows and ZnS lenses) operating in the range of 8-13

μm. In addition, the ZnS material is used in optical systems of the infrared range, the alignment of which, as a rule, is performed in the visible range.

The range of application of ZnSe is very wide. For example, zinc selenide crystals are increasingly applied in the infrared, LED, and fiber optic technology as the detectors of X-rays and elementary particles. Crystals of zinc chalcogenides (ZnSe and ZnS) doped with ions of transition metals (Fe^{2+}, Co^{2+}, Cr^{2+}) are promising materials for creating active media of tunable solid-state lasers.

All technological processes based on the knowledge of physical, chemical, thermodynamic or electrochemical regularities that allow controlling structural, electrical, mechanical, chemical and other important properties of materials. This makes it possible to identify and determine the general physical laws governing the properties of materials or applied technological processes.

Therefore, when developing and implementing promising technologies for obtaining new materials, it is necessary to carry out a large complex of physical, chemical and technological studies to obtain the desired results.

Nowadays, thermodynamic methods are widely used to study the production processes, as well as properties of semiconductor materials. Thermodynamic studies make it possible to predict a number of properties of materials obtained in real conditions, that is, they are the basis of a technology for controlled synthesis of semiconductor and other electronic engineering materials for the creation of electronic structures on their basis.

In addition, the problem of studying the behavior of these materials under extreme conditions, in particular, in corrosive environments, at high or, conversely, cryogenic temperatures, elevated pressures, etc., is also topical.

Presented work is devoted to investigation of thermodynamic characteristics and equilibrium composition of the condensed and gas phases formed during the equilibrium heating of ZnSe and ZnS in a wide range of temperatures and pressures.

Method of investigation

Thermodynamic modeling was performed using TERRA software [6] and thermodynamic modeling method [7].

The modeling of thermal decomposition of ZnSe, ZnS was carried out in the initial argon atmosphere over a wide range of temperatures (300-3000 K) at the different pressures (1, 10, 10^2, 10^3, 10^4, 10^5, 10^6, 10^7, 10^8, 10^9Pa) Pa and temperatures up 300 K to 3000 K. The melt structure was described by the model of ideal solutions of interaction products (ISIP) [7-8]. Modeling system consists of condensed phase and gas phase above it. The content of components is determined by equilibrium state of the all system.

Thermochemical properties of elements, compounds and ions were taken into account in modeling: gaseous Ar, Zn, Se, Se_2, Se_3, Se_4, Se_5, Se_6, Se_7,Se_8, Se^-, Zn^+, ZnS, S, S_2, S_3, S_4,S_5, S_6,S_7, S_8, S^-, S_2^-, S_3^-, e^-, Cd, Cd^+, Cd_2,CdS; condensed Zn, S, Se, ZnSe, ZnS. The properties of all substances are taken from the database TERRA. props.

Results

The thermodynamic characteristics and equilibrium composition of the condensed and gas phases formed during the equilibrium heating of ZnSe and ZnS in a wide range of temperatures (300-3000 K) at the common pressure of P = 1, 10, 10^2, 10^3, 10^4, 10^5, 10^6, 10^7, 10^8, 10^9 Pa in an argon atmosphere were studied.

As an example the temperature dependences of content of ZnSe (c) in condensed phase at the different pressures are presented at the Fig.1.

As can be seen from Fig.1, at the atmospheric pressure of P = 10^5 Pa, with increasing temperature from 300 to 1050 K, the mass fraction of ZnSe in the condensed phase practically does not change and is equal to 0.99 mass fractions. With the increasing of temperature from 1050 to 1800 K, an insignificant decrease in the ZnSe content occurs, and with a further increasing of temperature, a sharp decrease in the condensed phase is observed, which is due to evaporation. At T = 2150 K, the condensed phase disappears, complete evaporation of ZnSe takes place, accompanied by an increase in the mass fraction of the gas phase from 0.01 to 1.

When the pressure changes more or less from the atmospheric pressure, the behavior of the components of the condensed and gas phases changes. As can be seen from Fig.1, the evaporation temperature of ZnSe increases with increasing of pressure.

The similar dependencies are obtained for ZnS.

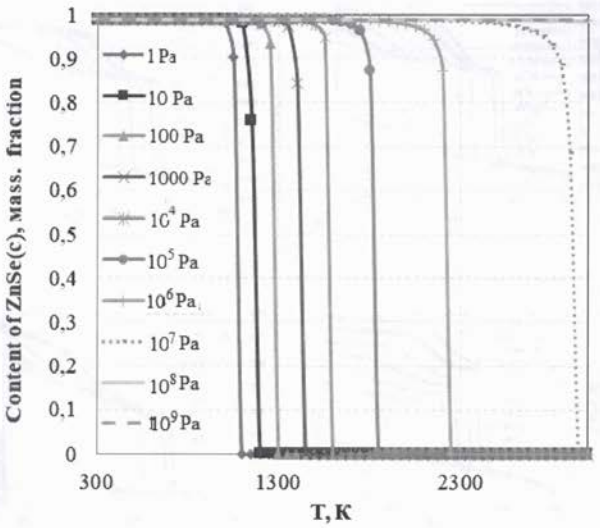

Fig.1. Temperature dependences of ZnSe(c) content at the different pressures.

The dependence of the evaporation temperature on the pressure $T_v(P)$ is not linear, but it can be divided into two intervals in which $T_v(P)$ varies linearly:

P=1-10^5Па, $T_v = 61.181\ ln(P) + 911.9$, K;
P=10^5-10^7Па: $T_v = 206.29\ ln(P) - 766.67$, K.

Fig.2 shows the temperature dependences of the enthalpy, entropy, internal energy and sound velocity of the ZnSe + Ar system. As can be seen from Fig.2, the temperature dependences of the thermodynamic characteristics are not monotonic. The breaks in these graphs can be explained by phase transitions.

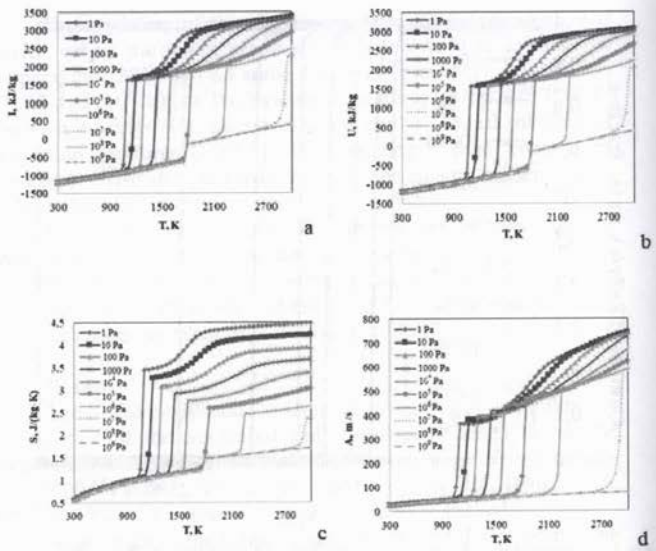

Fig.2. Temperature dependences of enthalpy (a), internal energy (b) entropy (c) and sound velocity (d) at the different pressures.

It is known that zinc chalcogenides doped with transition metals (Cr, Fe) are now attracting the attention of researchers developing medium-IR lasers. Thus, zinc selenide doped with chromium is the most promising material of the active medium for generating radiation in the wavelength range from 2 to 5 μm. In this region of wavelengths, selective absorption bands are localized in the transmission spectra of biological tissues and some gases.

In the present work, the influence of chromium and iron impurities on the composition and equilibrium characteristics of the Zn-Se and Zn-S system was studied. The simulation was performed in an argon atmosphere at T = 293 K and total pressure P = 10_5 Pa.

Fig.3 shows the dependences of enthalpy and entropy on the content of chromium and iron impurities in the simulated systems.

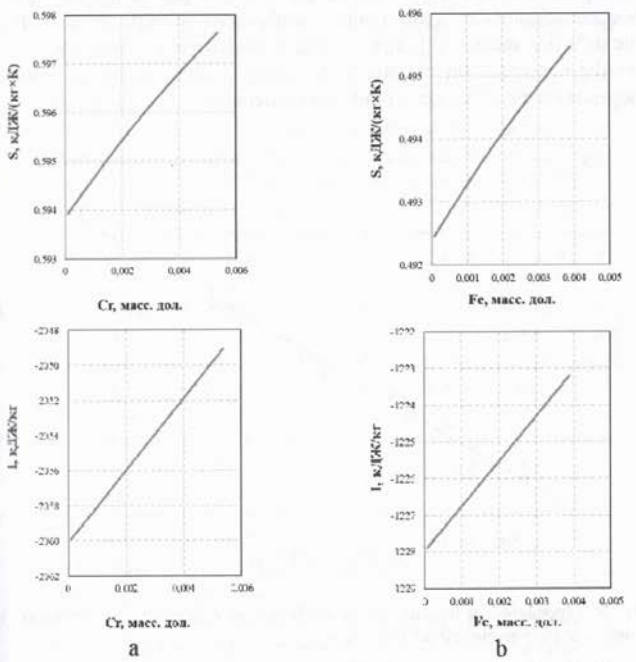

Fig. 3. Dependences of the entropy and enthalpy in the ZnSe (ZnS) + Cr (a) and ZnSe (ZnS) + Fe (b) systems on the Cr and Fe impurity content.

As can be seen from Fig.3, with increasing impurity content, the enthalpy and entropy of all systems under investigation increase practically linearly. Thus, it can be concluded that the introduction of an impurity increases the heat content and disorder of the system, which has a significant effect on the physical and chemical properties of these compounds.

As an example, let us consider the effect of chromium impurity

on the absorption coefficient. Fig.4 shows the dependence of the absorption coefficient at a wavelength of 1.908 μm on the average concentration of Cr^{2+} ions in polycrystalline zinc selenide doped with the diffusion method [9]. The absorption coefficient depends linearly on the concentration of ions of transition metals, which, in turn, depends on the efficiency of radiation generation.

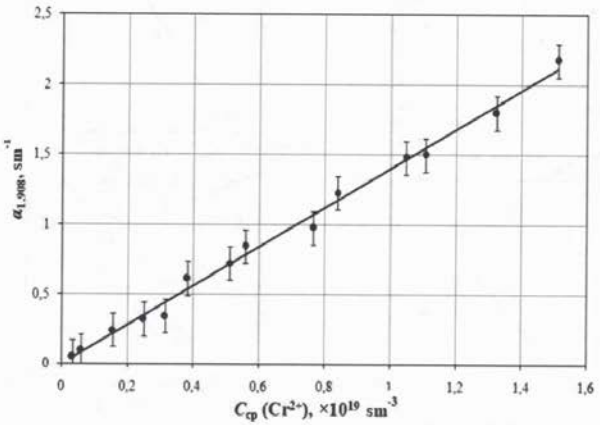

Fig.4. Dependence of the absorption coefficient of ZnS on the iron impurity content at the wavelength of 1.908 μm

Thus, a comparison of the results of thermodynamic modeling and experimental data on the effect of chromium on the absorption coefficient shows that there is a good correlation between them.

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