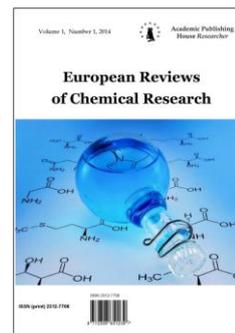


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Published in the Russian Federation
European Reviews of Chemical Research
Has been issued since 2014.
ISSN: 2312-7708
Vol. 2, No. 2, pp. 86-91, 2014

DOI: 10.13187/erchr.2014.2.86
www.ejournal14.com



UDC 546.816

Computer Simulation as a way to Determine the Conditions of Purposeful Synthesis of $Ag_xPb_{1-x}S$ Solid Solutions by Hydrochemical Deposition

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Abstract

In this paper authors have demonstrated the possibility of using aggregative growth model to search conditions of synthesis required composition $Ag_xPb_{1-x}S_{1-\delta}$ thin films. According to simulation results concentration areas of forming supersaturated solid solution components with a maximum of Ag_2S up to 12,8 mol.% have established. The experiment confirmed the adequacy of the model for the $PbS-Ag_2S$ system.

Keywords: computer simulating; hydrochemical deposition; lead sulfide; silver sulfide; solid solution.

Introduction

Sensitivity to optical radiation and physico-chemical effects allows to use thin films metal sulfides in many branches of engineering, in particular for creating on the basis of their selective chemical sensors to control the air toxic gases [1]. Efficacy of sensory cells based on thin films of lead sulfide to determine the nitrogen oxides presence in the air has shown by us earlier [2].

Forming solid solutions $Ag_xPb_{1-x}S$ based on lead sulfide can significantly extend the range of its electro and sensory properties, but according to the high-temperature phase diagram solubility limit Ag_2S in PbS is achieved at 970 K and no more than 0.4 mol. % [3], which corresponds to the solid solution $Ag_{0.008}Pb_{0.992}S$. So low rate explained by the fact that the individual silver and lead sulfides have different types of crystal lattices and space groups. Lead sulfide forms a simple cubic lattice (structure B1), and Ag_2S monoclinic or body-centered lattices

Despite the unsatisfactory conditions of isomorphic substitution, hydrochemical deposition method allows to extend the range of $Ag_xPb_{1-x}S$ solid solution of substitution, due to colloid-

chemical stage presence in the basis [4]. At this stage, there is a formation of metastable supersaturated solid solutions [5].

The greatest difficulty is the selection of purposeful conditions for producing a $\text{Ag}_x\text{Pb}_{1-x}\text{S}$ solid solution. One of perspective ways to create managed hydrochemical synthesis by co-precipitation of PbS and Ag_2S is a computer simulation. We have shown high efficiency of aggregative growth model to predict the composition of solid solution $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ and $\text{Cu}_x\text{Pb}_{1-x}\text{S}$ in their hydrochemical synthesis [6,7].

The purpose of this research was to use a computer model to find hydrochemical deposition conditions purposeful synthesis of $\text{Ag}_x\text{Pb}_{1-x}\text{S}$ substitutional solid solutions and their experimental verification.

Materials and Methods

Film formation and growth computer model $\text{Ag}_x\text{Pb}_{1-x}\text{S}$ is based on process of nucleus formation and primary clusters in reaction volume and further aggregative growth [8].

Regulations of rapid coagulation theory of Smolukhovskogho were used to set fundamental principle of solid phase formation, subject to stochastic nature of particles' motion.

To conduct calculation in acceptable time, volume of reaction mixture was conventionally divided into equal cubic "microvolumes", which is taken as pseudo-valid reactor with acceptable statistic deviations. Subsequently holistic picture of hydrochemical synthesis process was obtained by composition of descriptive status of "microvolumes". In reaction mixture balancing of reagent concentration in "microvolumes" was calculated by thermodynamic diffusion flows.

Second necessary criterion of the calculations in acceptable time is to set boundaries of concentration ranges per each of reagents. For the sake of this authors found concentration fields of individual metal sulfide co-formation. For revelation of sulphide formation PbS and Ag_2S collaborative area in temperature interval 298 – 343K analysis of ion equilibrium in multicomponent system was conducted, including lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2$, silver nitrate AgNO_3 , trisubstituted sodium citrate $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, ammonium hydroxide NH_4OH and thiocarbamide $\text{N}_2\text{H}_4\text{CS}$. Presence of citrate ions and thiocarbamide, binding in durable complex lead and silver respectively, in the reaction mixture prevents rapid emission of metal sulphide in settling.

An important feature of developed algorithm is simultaneous multithreaded control of all processes, coursed by synthesis in variety of reaction mixture micro-volumes.

In case of calculating of electronic structure, stability of lattices and interaction energy were used following approximations of quantum chemistry, necessary for solving Schrodinger equation: Born-Oppenheimer approximation, Hartree approximation, MO LCAO approximation (molecular orbital as a linear combination of atomic orbitals).

Calculations were made only on base of prior software with new source data, later were used its' average results. Quantum chemical calculations were conducted with application of "first principles" simulation program (the solution of first fundamental principles without additional empirical assumptions).

Density functional theory (DFT), which allows replacing many-electron wave function by electron density, using ab initio methods with given approaches and simplifications, enables to provide required calculations.

Simulating package houses major simplifications: valence approximation, approximation of local electron density (LDA+U); replacement of many-electron problem solution to the one-electron (with effective local potential); description of kinetic energy of electron movement by local approximation on the basis of free-electron theory; self-consistent field method.

For the purpose of determination of solid solution electron structure, were additionally used following approximations and calculation methods: generalized gradient approximations (GGA); self-interaction correction (SIC); optimized effective potential method; GW approximation (replacement of Coulomb potential in the Hartree-Fock approximation to the dynamically dispersive potential, furthermore exchange-correlation potential replaces by Green's function); full-potential method of linear muffin-tin orbitals (FP LMTO); pseudo potential method.

Discussion

The result of the simulation software is a description of the entire volume of the reactor to the level of detail for each atom, and in particular deposited onto a substrate material which is divided

into "clusters". Accordingly, the composition of the resulting solid solutions $\text{Ag}_x\text{Pb}_{1-x}\text{S}$ was defined internally developed software using the average value of a sequence of atomic conversion probability sample set of "clusters". Allowable error (statistical sampling error) was 4%.

Graphical interpretation of the calculation results in the coordinates "Content Ag_2S solid solution - function of the initial concentrations of the metal salts in the reaction mixture" is shown in Fig. 1.

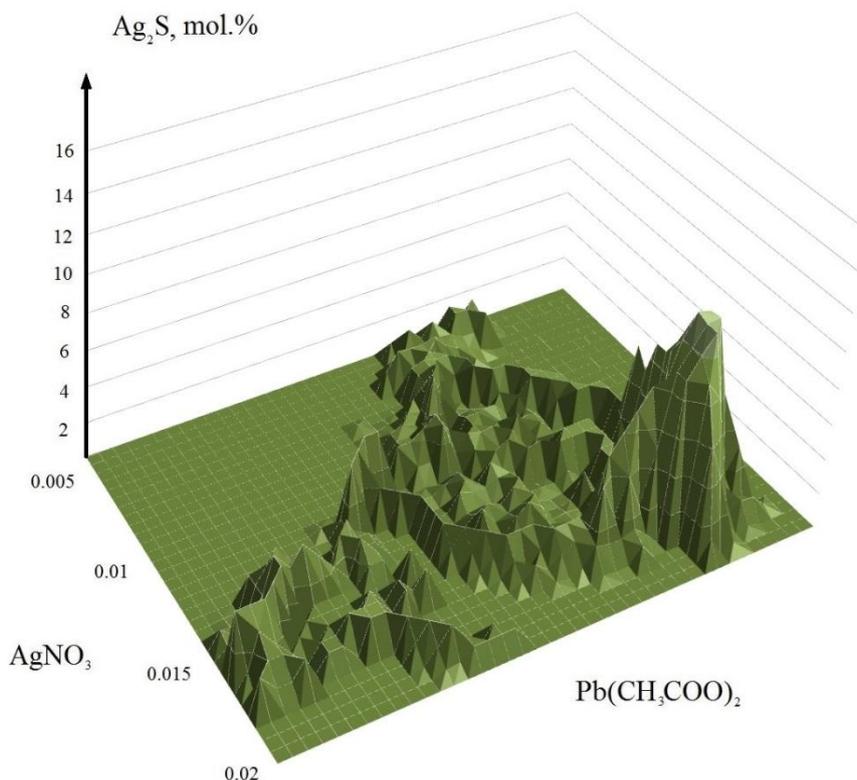


Fig. 1. The graphical interpretation of the results of computer simulation: the dependence of silver sulfide content in the solid solution $\text{Ag}_x\text{Pb}_{1-x}\text{S}$ from the initial concentration of metal salt in the reaction mixture

As in the case of computer modeling of the solid solutions in the deposition system PbS-CdS [6], the surface has pronounced local maximum. They substitute the appropriate content component in the solid solution $\text{Ag}_x\text{Pb}_{1-x}\text{S}$ in comparison with high phase diagram [3] greatly exceeds the limiting solubility of Ag_2S in the structure of PbS , which allows us to state of the formation of supersaturated solid solutions of substitution. Maximum content of Ag_2S in $\text{Ag}_x\text{Pb}_{1-x}\text{S}$ was 12.8 mol.%. However, apparently, we cannot clearly determine it as the absolute maximum.

Besides solid solution $\text{Ag}_x\text{Pb}_{1-x}\text{S}$, in "clusters" found a significant content of individual phases of silver sulfide, which introduces additional complexity in the interpretation of the data.

Fig. 2 shows the dependence of the substituting component by varying the initial concentration of the silver salt in the reaction mixture. It should be noted that it has an extreme character after reaching the maximum value of Ag_2S content in substitutional solid solution.

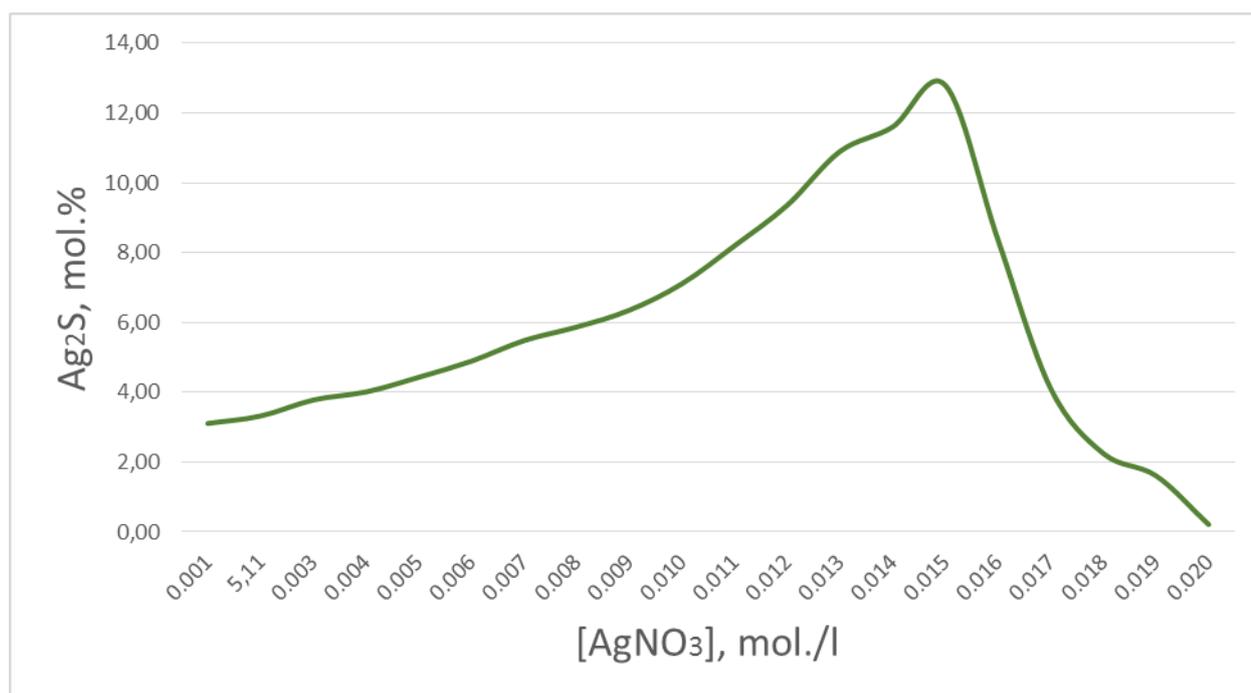


Fig. 2. Calculated concentration dependence substituting component by varying the concentration of the silver salt in the reaction mixture

We performed a series of experiments on hydrochemical deposition films $\text{Ag}_x\text{Pb}_{1-x}\text{S}$ by coprecipitation individual metal sulphide PbS and Ag_2S to test the adequacy of the results. Synthesis was carried out for 90 minutes at a temperature of 303 K during a change in the reaction mixture lead acetate content from 0.01 to 0.04 mol/l, and while varying the concentration of the silver salt in the range of $5,0 \times 10^{-5}$ – $1,2 \times 10^{-2}$ mol/l.

Analyzing the XRD patterns obtained films was observed the structure of cubic phase B1 only, the period of which is dependent on the film composition. Fig. 3 shows the X-ray films of lead sulfide and individual coprecipitating layers. We found that the period of the cubic phase of lead sulfide with increasing silver content in the reactor increased from 0.5934 to 0.5937 nm. It was interpreted as the formation of PbS by substitutional solid solutions $\text{Ag}_x\text{Pb}_{1-x}\text{S}$. In the formation of solid solution the lattice period increased due to replacement of lead ions (II) with a radius of 0.120 nm lattice PbS to larger silver Ag^+ ions with a radius of 0.126 nm.

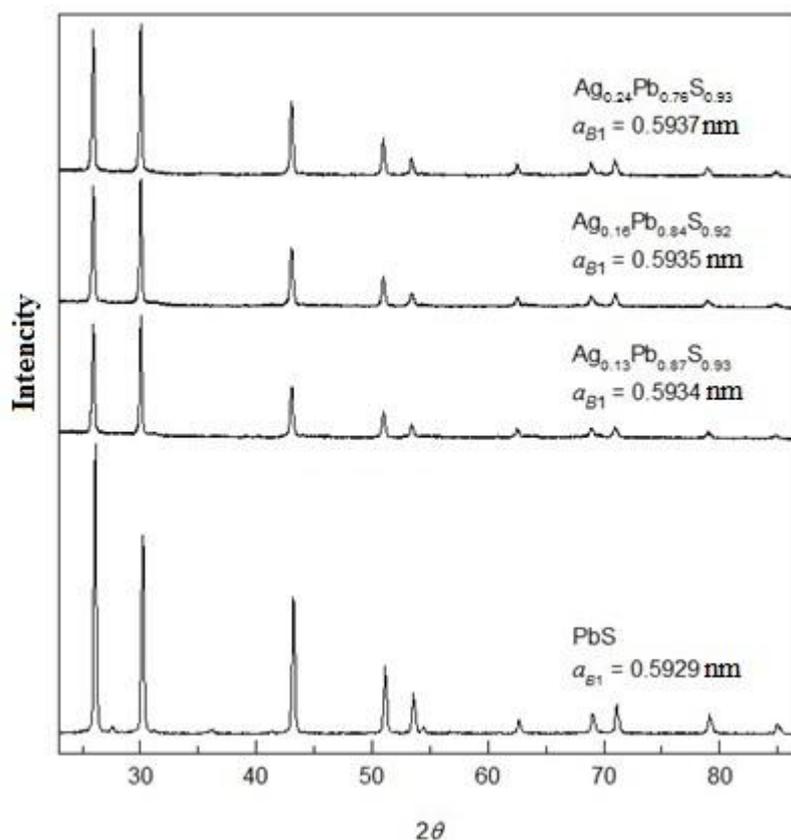


Fig. 3. XRD patterns PbS films and solid solutions $\text{Ag}_{0.13}\text{Pb}_{0.87}\text{S}_{0.93}$, $\text{Ag}_{0.16}\text{Pb}_{0.84}\text{S}_{0.92}$ and $\text{Ag}_{0.24}\text{Pb}_{0.76}\text{S}_{0.92}$ obtained by co-precipitation of sulfides of lead and silver at $T = 303 \text{ K}$

Elemental analysis of the films coprecipitated sulphide PbS and Ag_2S formed microanalyzer Superzond JCSA-733c on three points on the content of lead, silver and sulfur. We evaluated the number of elements in the films obtained by varying the composition of the reaction mixture.

Comparative results of calculations and experimental data are given in the table.

Table: The experimental data and computer simulations on the effect of synthesis conditions on the composition of hydrochemical coprecipitated solid solution films $\text{Ag}_x\text{Pb}_{1-x}\text{S}$.

Synthesis conditions	Formulaic composition of the $\text{Ag}_x\text{Pb}_{1-x}\text{S}_{1-\delta}$ solid solution (simulating result)	Formulaic composition of the $\text{Ag}_x\text{Pb}_{1-x}\text{S}_{1-\delta}$ solid solution (based on lattice period)
$[\text{AgNO}_3]$, мол/л		
0,001	$\text{Ag}_{0,07}\text{Pb}_{0,93}\text{S}_{0,96}$	$\text{Ag}_{0,08}\text{Pb}_{0,92}\text{S}_{0,96}$ ($a = 0,59319 \text{ nm}$)
0,002	$\text{Ag}_{0,11}\text{Pb}_{0,89}\text{S}_{0,95}$	$\text{Ag}_{0,10}\text{Pb}_{0,90}\text{S}_{0,95}$ ($a = 0,59324 \text{ nm}$)
0,005	$\text{Ag}_{0,15}\text{Pb}_{0,85}\text{S}_{0,93}$	$\text{Ag}_{0,13}\text{Pb}_{0,87}\text{S}_{0,93}$ ($a = 0,59338 \text{ nm}$)

0,010	$\text{Ag}_{0,16}\text{Pb}_{0,84}\text{S}_{0,92}$	–
0,012	$\text{Ag}_{0,17}\text{Pb}_{0,83}\text{S}_{0,92}$	$\text{Ag}_{0,16}\text{Pb}_{0,84}\text{S}_{0,92}$ ($a = 0,59348 \text{ nm}$)
0.0144	$\text{Ag}_{0,25}\text{Pb}_{0,75}\text{S}_{0,93}$	$\text{Ag}_{0,24}\text{Pb}_{0,76}\text{S}_{0,93}$ ($a = 0,59370 \text{ nm}$)

The table shows that with increasing concentration of silver salt in the reaction mixture in its solid phase content increases monotonously while reducing the lead. Among the samples studied Ag_2S maximum content in the $\text{Ag}_x\text{Pb}_{1-x}\text{S}$ solid solution was 8.5 mol.%. The discrepancy between the results of simulation and experiment does not exceed 14.4%, which is certainly acceptable. Noteworthy significant non-stoichiometry of sulfur in the composition of the solid solution. This occurrence may be explained by oxygen-containing metal phase in film, in particular, sodium hydroxide, lead, whose formation is confirmed by calculations of ionic equilibria. Detected non-stoichiometry on the sulfur content in the deposited solid solutions in general is reflected in the writing of their composition $\text{Ag}_x\text{Pb}_{1-x}\text{S}_{1-\delta}$.

Summary

Computer simulation of the $\text{Ag}_x\text{Pb}_{1-x}\text{S}_{1-\delta}$ solid solutions hydrochemical synthesis process was carried out. The potential conditions for the formation of supersaturated solid solutions with a replacement component, exceeding the solubility limit Ag_2S in PbS according to high temperature phase diagram were founded. Ag_2S concentration in solid solution has a number of local maximums on a calculated surface. Its absolute maximum of 12.8 mol.%.

The experimental results confirmed the adequacy of the simulation results. The maximum discrepancy between experiment and computer simulation results was 14.4%. Receipt of the solid solutions $\text{Ag}_x\text{Pb}_{1-x}\text{S}_{1-\delta}$ with the concentration of component replacement stated above the solubility limit in the areas calculated local maximum was confirmed.

The research was supported by the project of the Ministry of Education and Science by government contract No 4.1270.2014 / K "Development of physical and chemical bases and algorithm colloid-chemical synthesis of metal chalcogenides films for photonics and sensor technology".

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