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A METHOD FOR THE CALCULATION OF DEFECT EQUILIBRIUM IN ZnS:Cu:Al:Bi:Cl

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Abstract. A method for solving the system of quasichemical equations for the description of the high temperature equilibrium of defects is presented. This method enables to create a model of the high temperature equilibrium of defects for ZnS crystals doped with up to four types of foreign atoms.

Key words: binary compounds, defect equilibrium.

INTRODUCTION

The high temperature equilibrium of defects is described by a system of quasichemical reactions [1]. The system of equations for the description of the equilibrium contains linear balance equations for impurities and charges and nonlinear equations for connecting the defect concentrations via equilibrium constants [2, 3]. In this paper a method for the calculation of the defect equilibrium in ZnS:Cu:Al:Bi:Cl is proposed.

DESCRIPTION OF THE EQUILIBRIUM DEFECTS

At high temperatures the following defects exist in ZnS:Cu:Al:Bi:Cl: electrons, holes, native atomic imperfections, foreign atoms, and associates. The disorder can be described by the reactions of the formation and ionization of defects. The total concentrations for all types of foreign atoms are:

$$[Cu]_{TOT} = [Cu'_{Zn}] + [Cu^{\cdot}_{i}] + [Cu^{\times}_{Zn}] + [Cu^{\times}_{i}] + [(Cu_{Zn}V_S)^{\times}] +$$

$$+ [(Cu_{Zn}V_S)^{\cdot}] + [(Cu_iV_{Zn})^{\times}] + [(Cu_iV_{Zn})'] + 2[(Cu_{Zn}Cu_i)^{\times}] +$$

$$+[(Cu_{Zn}Zn_i)^{\times}]+[(Cu_{Zn}Zn_i)^{\cdot}]+[(Cu_{Zn}Al_{Zn})^{\times}]+[(Cu_iBi_S)^{\times}]+$$
$$+[(Cu_{Zn}Cl_S)^{\times}]+[(Cu_iCl_SV_{Zn})^{\times}]+[(Cu_{Zn}Zn_iV_{Zn})^{\times}]+$$
$$+2[((Cu_i)_2V_{Zn})^{\times}]+[(Cu_iAl_{Zn}V_{Zn})^{\times}]+[(Cu_{Zn}V_{Zn}V_S)^{'}]+$$
$$+[(Cu_{Zn}V_{Zn}V_S)^{\times}]+[(Cu_{Zn}Bi_SV_S)^{\times}]+[(Cu_{Zn}Zn_iV_{Zn})^{'}]+$$
$$+[(Cu_iV_{Zn}V_S)^{\cdot}]+[(Cu_iZn_iV_{Zn})^{\cdot}]+2[((Cu_{Zn})_2V_S)^{\times}]+$$
$$+2[((Cu_{Zn})_2Zn_i)^{\times}]+[(Cu_{Zn}Bi_SZn_i)^{\times}]+[(Cu_iZn_iV_{Zn})^{\times}]+$$
$$+[(Cu_iV_{Zn}V_S)^{\times}], \quad (1)$$

$$[Cl]_{TOT}=[Cl_S^{\cdot}]+[Cl_S^{\times}]+[(Cl_SV_{Zn})^{'}]+[(Cl_SV_{Zn})^{\times}]+$$
$$+[(Cu_{Zn}Cl_S)^{\times}]+[(Bi_SCl_S)^{\times}]+[(Cl_SZn_iV_{Zn})^{\times}]+[(Cl_SAl_{Zn}V_{Zn})^{\times}]+$$
$$+[(Cl_SV_{Zn}V_S)^{\times}]+[(Cu_iCl_SV_{Zn})^{\times}]+[(Cl_SV_{Zn}V_S)^{\cdot}]+$$
$$+2[((Cl_S)_2V_{Zn})^{\times}]+[(Cl_SZn_iV_{Zn})^{\cdot}], \quad (2)$$

$$[Al]_{TOT}=[Al_{Zn}^{\cdot}]+[Al_{Zn}^{\times}]+[(Al_{Zn}V_{Zn})^{\times}]+[(Al_{Zn}V_{Zn})^{'}]+$$
$$+[(Al_{Zn}Cu_{Zn})^{\times}]+[(Bi_SAl_{Zn})^{\times}]+[(Zn_iAl_{Zn}V_{Zn})^{\times}]+$$
$$+[(Zn_iAl_{Zn}V_{Zn})^{\cdot}]+2[((Al_{Zn})_2V_{Zn})^{\times}]+[(Al_{Zn}V_{Zn}V_S)^{\cdot}]+$$
$$+[(Al_{Zn}V_{Zn}V_S)^{\times}]+[(Cu_iAl_{Zn}V_{Zn})^{\times}]+[(Cl_SAl_{Zn}V_{Zn})^{\times}], \quad (3)$$

and

$$[Bi]_{TOT}=[Bi_S^{'}]+[Bi_S^{\times}]+[(Bi_SV_S)^{\cdot}]+[(Bi_SV_S)^{\times}]+[(Bi_SZn_i)^{\cdot}]+$$
$$+[(Bi_SZn_i)^{\times}]+[(Bi_SCu_i)^{\times}]+[(Bi_SCl_S)^{\times}]+[(Bi_SAl_{Zn})^{\times}]+$$
$$+[(Cu_{Zn}Bi_SV_S)^{\times}]+[(Zn_iBi_SV_{Zn})^{'}]+[(Zn_iBi_SV_{Zn})^{\times}]+$$
$$+2[((Bi_S)_2V_S)^{\times}]+[(Zn_iBi_SCu_{Zn})^{\times}]+[(Bi_SV_{Zn}V_S)^{'}]+$$
$$+[(Bi_SV_{Zn}V_S)^{\times}]+2[((Bi_S)_2Zn_i)^{\times}]. \quad (4)$$

All charged defects contribute to the electroneutrality condition.

THE SOLUTION OF THE SYSTEM OF EQUATIONS OF MATERIAL BALANCE

Now we find the dominating defect for each type of foreign atoms and express the material balance equations (1)–(4) through the dominating defect $x = [Cu'_{Zn}]$; $y = [Cl^{\cdot}_{S}]$; $z = [Al^{\cdot}_{Cu}]$; and $v = [Bi'_{S}]$. We obtain the following system of equations for material balance:

$$a_{1,1}x^2 + a_{1,2}xy + a_{1,3}xz + a_{1,4}xv + a_{1,5}x = a_{1,6}, \quad (5)$$

$$a_{2,1}y^2 + a_{2,2}xy + a_{2,3}yz + a_{2,4}yv + a_{2,5}y = a_{2,6}, \quad (6)$$

$$a_{3,1}z^2 + a_{3,2}xz + a_{3,3}yz + a_{3,4}zv + a_{3,5}z = a_{3,6}, \quad (7)$$

$$a_{4,1}v^2 + a_{4,2}xv + a_{4,3}yv + a_{4,4}zv + a_{4,5}v = a_{4,6}, \quad (8)$$

where $a_{i,1}$ – ($i = 1, 2, 3, 4$) the sum of the expressions for the description of the creation of defects containing two foreign atoms i via one dominating defect of this foreign atom;

$a_{i,j}$ – ($j = 2, 3, 4$) the sum of the expressions for the description of the creation of defects containing simultaneously a foreign atom i and a foreign atom j;

$a_{i,5}$ – the sum of the expressions for the description of the creation of defects containing one foreign atom and expressed via the dominating defect;

$a_{i,6}$ – the total concentration of foreign atoms of this type.

From (8) we find:

$$x = \frac{a_{4,6} - a_{4,1}v^2 - a_{4,3}yv - a_{4,4}zv - a_{4,5}v}{a_{4,2}v}. \quad (9)$$

Using this expression in (5), (6), and (7) we obtain a fourth order system of equations with three unknown concentrations:

$$b_{1,1}y^2v^2 + b_{1,2}yv^3 + b_{1,3}yv^2 + b_{1,4}yv + b_{1,5}yzv^2 + b_{1,6}z^2v^2 + b_{1,7}zv^3 +$$

$$+ b_{1,8}zv^2 + b_{1,9}zv + b_{1,10}v^4 + b_{1,11}v^3 + b_{1,12}v^2 + b_{1,13}v + b_{1,14} = 0, \quad (10)$$

$$b_{2,1}y^2v + b_{2,2}yv^2 + b_{2,3}yv + b_{2,4}yzv + b_{2,5}y + b_{2,6}v = 0, \quad (11)$$

$$b_{3,1}yzv + b_{3,2}z^2v + b_{3,3}zv^2 + b_{3,4}zv + b_{3,5}z + b_{3,6}v = 0. \quad (12)$$

The coefficient $b_{m,n}$ contains the sum of the expressions of the equilibrium constants and the concentrations of the defects derived from the initial equations (5)–(8).

From (12) we find:

$$y = \frac{-b_{3,6}v - b_{3,2}z^2v - b_{3,3}zv^2 - b_{3,4}zv - b_{3,5}z}{b_{3,1}zv} . \qquad (13)$$

Substituting this expression into (10) and (11) an eighth order system of equations with two unknown concentrations is obtained. This eighth order system of equations can be solved by the triple iteration method.

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ZnS:Cu:Al:Bi:Cl DEFEKTIDE TASAKAALU ARVUTAMISE MEETOD

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On esitatud kvaasikeemiliste võrrandite lahendusmeetod defektide kõrgtemperatuurse tasakaalu kirjeldamiseks. See meetod võimaldab luua defektide kõrgtemperatuurse tasakaalu mudeli kuni nelja lisandiga legeeritud kristallides.