THERMODYNAMIC PROPERTIES MATERIALS FOR DEVELOPING SOLID PHASE CHEMICAL CURRENT SOURCES

A.S.Abbasov, J.Y.Aliyev, Z.J.Suleymanov, Y.R.Aliyeva

Institute of Physics, Azerbaijan National Academy of Sciences
33 H.Javid avenue, Baku, AZ1143, Azerbaijan
Fax: +(994-12) 447-04-56
E-mail: aa adilus@yahoo.com

ABSTRACT

Ternary compounds forming in S_m-J_n-S(Se,Te) systems are semiconductors materials and perspective in technique. The synthesis technology of their single crystals requires a knowledge of thermodynamic data which is also important for determination of stability of these materials, bond energies and for developing chemical current sources.

Keywords: ternary compound, semiconductor, crystal, solid phase, chemical current.

I. INTRODUCTION

Ternary compounds forming in S_m-J_n-S(Se,Te) systems are semiconductors. The technology of synthesis of these single crystals requires information on thermodynamic data, which important for determination of stability materials, bond energies and for developing chemical current sources.

II. EXPERIMENTAL

The elektromotiveforce method [1] based on measuring emt of electrochemical cells is widely used. Cells of the type

(-)Me, $\mid Me_1Cl_n$-(KCl-LiCl) $\mid$ Me_1 Me_2(+)

are studied, Me_1 being a pure metal and Me_1 , Me_2 an alloy of Me_1 with a nobler metal Me_2. These are concentration cells with respect to the electrodes. The potential – developing process in the cell corresponds to the transfer of Me_1 from the pure-metal electrode to the alloy electrode. The thermodynamic characteristics of this process are connected with the emfbeing measured by the following relationships:

$$\Delta\mu_i = -zFE, \quad (1)$$

$$\Delta\bar{S}_i = zF\frac{dE}{dT}, \quad (2)$$

$$\Delta\bar{H}_i = zF\left[\frac{dE}{dT}\cdot T - E\right] \quad (3)$$

where z is the charge of the Me_1 ion in the melt, F is the Faraday number equal to 23,062 cal/g.equiv.

A review of the work on the study of thermodynamic properties of metal alloys in the solid state, using the e.m.f method, is given in [1,2].

The formulation of the emf method may be extremely of the cells and in the use of various salt systems as electrolyte. In the majority of well-known cases however, an electrolyte consisting of a mixture of potassium and lithium chlorides of eutectic composition (47 mol% LiCl) has been used together with a slight trace of the chloride of the potential-developing ion. We must mention an inherent limitation of the emf method. It may be used to study alloys with components which are quite distinct in electrochemical nature, i.e., in the values of the standard electrode potentials. When the electrode potentials of Me_1 and Me_2 are close together, there may be a reaction

$$Me_2(\text{alloy}) + Me_1^{Z_1} \rightarrow Me_2^{Z_2} + Me_1(\text{alloy})$$

Reactions of this type alter the composition of the electrode and the electrolyte close to the surface of separation between electrode and electrolyte [3,4]. We have studied in range 300-460K thermodynamic properties of the Sm-Jn-S(Se,Te) semiconductors system perspective in technique. The design of the cells was very variegated. It was important to set up a cell witch would work in conditions of vacuum or inert medium in order to protect the electrodes and electrolyte from harmful effects of the atmosphere.

Alloys were prepared by fusing weighed portion in evacuated quartz ampoules x –ray phase analysis. The x – ray diffraction photographs were taken by the powder method with an RKD-57 camera in CuK_α-K_β radiation.

We obtained the parameters:

$SmJn_2S_4$: $a = 11{,}26\,\text{Å};\ b = 12{,}04\,\text{Å};\ c = 7{,}41\,\text{Å}$

$SmJn_4S_7$: $a = 10{,}33\,\text{Å};$

$SmJn_2Se_4$: $a = 12{,}11\,\text{Å};\ b = 11{,}96\,\text{Å};\ c = 6{,}14\,\text{Å}$

$SmJn_4Te_7$: $a = 11{,}64\,\text{Å};$

Experimental emf data belonging to the individual heterogeneous-phase regions, analyzed by the method of least squares are presented in the form of the equation E=A+B·T in table 1.

Table 1.

Phase region	E=f(T), Volt
$SmJn_4S_7$-Jn_2S_3	$(0{,}834-0{,}110\cdot T\cdot 10^{-3})\pm 3\cdot 10^{-3}$
$SmJn_2S_4$-$SmJn_4S_7$	$(0{,}643-0{,}092\cdot T\cdot 10^{-3})\pm 4\cdot 10^{-3}$
$SmJn_2Se_4$-Jn_2Se_3	$(0{,}763-0{,}095\cdot T\cdot 10^{-3})\pm 6\cdot 10^{-3}$
$SmJn_2Te_4$-Jn_2Te_3	$(0{,}699-0{,}089\cdot T\cdot 10^{-3})\pm 5\cdot 10^{-3}$

A combination of the equations E=f(T) enabled us to obtain equations ΔG=f(T) characterizing the change in the Gibbs energy for the reactions which form each of the four compounds from pure components at standard states [3,4].

The thermodynamic data are shown in table 2.

Table 2.

Phase	298K			
	$-\Delta H^0$	$-\Delta G^0$	$-\Delta H^a$	S^0
	kJ/g-at			J/g-at·K
$SmJn_2S_4$	4,9±0,3	4,6±0,1	59,4	6,4±0,2
$SmJn_2Se_4$	4,1±0,2	3,9±0,1	57,0	6,7±0,2
$SmJn_2Te_4$	3,8±0,3	3,6±0,1	55,3	7,2±0,3
$SmJn_4Te_7$	3,2±0,2	3,0±0,1	49,6	5,9±0,2

III. CONCLUSION

Thus, the total thermodynamic information about the bond energy in the ternary semi-conductors has been obtained.

REFERENCES

1. *A.S.Abbasov et all.* Dokl.Akad. Nauk SSSR. V.134(5) 726 1966 (in Russian).
2. *A.S.Abbasov.* Thermodynamic properties some semiconductors “Elm” Baku, 1981, 125p. (in Azeri).
3. *A.S.Abbasov et all.* Transaction of ANAS v.25,148 (2003) (in Azeri).
4. *F.M.Mustafayev, A.S.Abbasov*. Patent Solid phase chemical current sources. N19630, 2000 (in Azeri).