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PHASE DIAGRAM OF THE $Tl_3TaS_{4-x}Se_x (0 \leqslant x \leqslant 4)$ SOLID SOLUTION SYSTEM

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ABSTRACT

Phase diagram of the $Tl_3TaS_{4-x}Se_x (0 \leqslant x \leqslant 4)$ system has been investigated by differential thermal analysis (DTA). Thermodynamical analysis of phase equilibrium has been carried out and a phase diagram plotted. The obtained results confirm the formation of a continuous series of solid solutions.

INTRODUCTION

In /1-3/ it is shown that the Tl_3TaS_4 and Tl_3TaSe_4 compounds possess interesting piezoelectric and semiconducting properties. Therefore the investigation of their solid solution properties is of some concern.

RESULTS AND DISCUSSION

The thermal differential analysis of the $Tl_3TaS_{4-x}Se_x$ system alloys, synthesized by direct alloying of the starting materials has been performed. The X-ray structural analysis supports the existence of a single-phase structure state in it with a $I\bar{4}3$ m cubic structure. The concentration dependence of the unit cell parameter agrees with Vegard's law.

The samples have been heated at the rate of 2-3 K/min. The temperature has been controlled by a Pt-Pt/Rh thermocouple, graduated by reference materials in the range from 373 to 1600 K with an accuracy of ± 1 K. The solidus and liquidus points have been determined using the heating curves. The DTA results testify to the congruent melting of all the system alloys. The melting temperatures of the starting compounds are 827 K for Tl_3TaS_4 and 899 K for Tl_3TaSe_4. The values of enthalpy and entropy of fusion of the compounds are determined to be ΔH_{fus} = 48.485 kJ/m ΔS_{fus} = 58.627 J/mol K for Tl_3TaS_4 and ΔH_{fus} = 85.555 kJ/mol,

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ΔS_{fus} =95.167 J/mol K for Tl_3TaSe_4. A phase equilibrium diagram of the Tl_3TaS_4-Tl_3TaSe_4 system solid solution has been plotted from the DTA data (Fig.1).

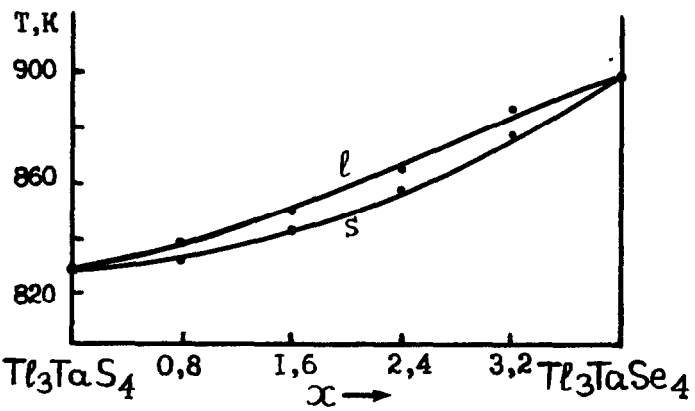

Fig.1

The points are the experimental results. In the same figure the phase diagram of the investigated system, calculated in approximation of the theory of regular solutions is given by solid curves. The calculation of the solidus and liquidus lines in the above mentioned approximation has been performed in terms of the equations:

$$\ln\frac{1-x^s}{1-x^l} = (x^l)^2\frac{k^l}{RT} - (x^s)^2\frac{k^s}{RT} - \frac{\Delta S_1}{R}\left(1 - \frac{T_1}{T}\right) \qquad (1)$$

$$\ln\frac{x^s}{x^l} = (1 - x^l)^2\frac{k^l}{RT} - (1 - x^s)^2\frac{k^s}{RT} - \frac{\Delta S_2}{R}\left(1 - \frac{T_2}{T}\right) \qquad (2)$$

where ΔS_1 and ΔS_2 are entropies of fusion of the compounds forming the system; T_1 and T_2 are the temperatures of melting. The interaction parameters calculated from (1) and (2) in the solid and liquid phase k^s and k^l for the investigated system prove to be equal to -0,84 kcal/mol and - 2.2 kcal/mol, respectively.

From the given figure it is seen that the solidus and liquidus lines of the Tl_3TaS_4-Tl_3TaSe_4 system of solid solu-

tions, calculated in the approximation of the theory of regular solutions, provide quite a good fit to the experimental data.

In accordance with the theory of regular solutions the heats of mixture in liquid and solid phases have been determined as the values proportional to the product of component concentrations: $\Delta H^{l}_{mix} = k^{l}x(1-x)$; $\Delta H^{s}_{mix} = k^{s}x(1-x)$. The variation of the heats of mixture depending on composition of the solid solution system is shown in Fig. 2.

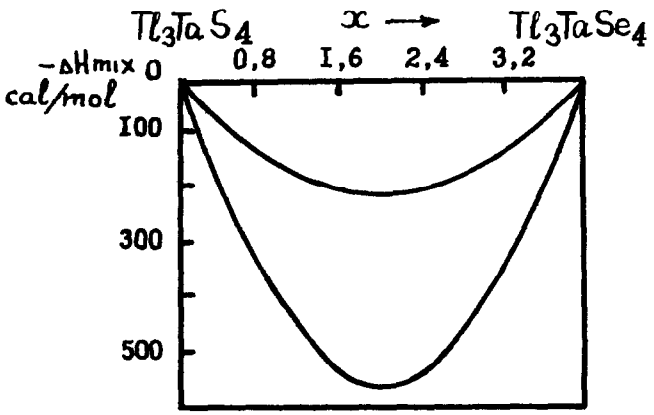

Fig. 2

In terms of the known interaction parameter values and using the relations

$$\ln\gamma_1^{l} = (k^{l}/RT)\, x_2^2$$
$$\ln\gamma_2^{l} = (k^{l}/RT)\cdot x_1^2 \qquad \text{for liquid phase}$$

$$\ln\gamma_1^{s} = (k^{s}/RT)\cdot x_2^2$$
$$\ln\gamma_2^{s} = (k^{s}/RT)\, x_1^2 \qquad \text{for solid phase}$$

the activity coefficients have been calculated. The concentra - tion dependences of the activities in solid and liquid state in

the $Tl_3TaS_{4-x}Se_x$ system are given in Fig. 3.

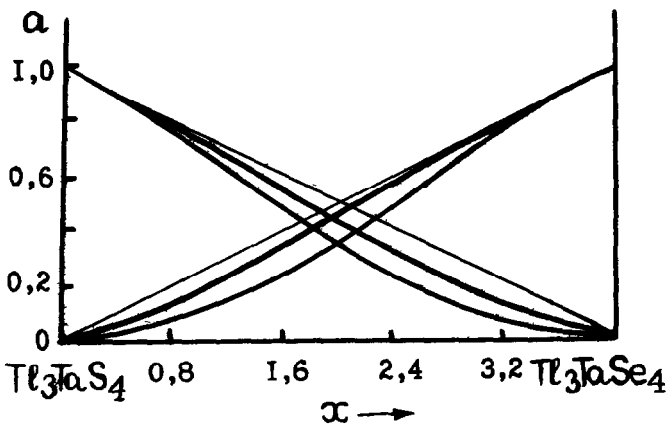

Fig.3

The negative shift of the activity trend from Raoult's law shows evidence for strong interaction between the heterogeneous atoms of sulphur and selenium.

Our study testifies to the formation of a continuous series of the $Tl_3TaS_{4-x}Se_x$ system solid solutions.

REFERENCES

1. A.A.Vaipolin, N.A.Goryunova, M.V.Orlov, V.I.Sokolova, E.V.Tsvetkova., Fizika. Kratkoe soderzhanie dokladov nauchnoi konferentsii LISI (1969)
2. K.Cermak., Ces. Cas. Fys. A 19(2), 149-152, 1969
3. T.J.Isaacs, R.W.Wenert, J. Electron. Mater., 5(1), 13-27, 1976.