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Interdiffusion in Quasi-Ternary Semiconductor Systems of GeTe/SnTe/PbTe

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1. Introduction

Lead, tin and germanium tellurides are narrow-gap semiconductors; their solid solutions are applied for IR optoelectronics and as thermoelectric materials. To describe the diffusion/reaction path in a (Pb,Sn,Ge)Te quasi-ternary system the excess Gibbs energy and the diffusion behaviour in the quasibinary edge systems has to be known. The classical approach to the understanding of the diffusion properties of alloys considers the contribution of the thermodynamic interactions in the real solid solution, which are expressed by the thermodynamic factor *F*. It is calculated using the interaction parameters deduced from the phase diagram. This approach was applied for many metal systems, whereas for compound semiconductors, for which the stoichiometry control is critical, there are only several reports. Among binary alloys the interdiffussion coefficients are well known for (Pb,Sn)Te only. The present contribution is devoted to the interdiffusion study in the case of (Pb,Ge)Te and (Sn,Ge,Te). Besides the diffusion path in quasiternary alloy (Ge,Pb,Sn)Te is investigated.

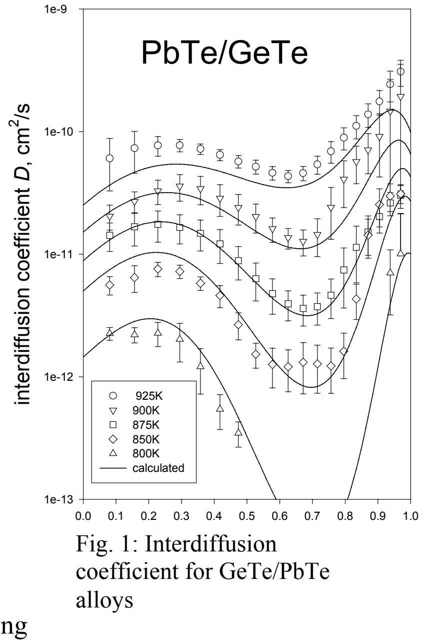

Fig. 1: Interdiffusion coefficient for GeTe/PbTe alloys

2. Diffusion in the quasibinary systems (Pb,Ge)Te and (Sn,Ge)Te

Because of the increasing difference between two metal radii in the sequence (Pb,Sn)Te-(Sn,Ge)Te-(Pb,Ge)Te the topology of the phase diagrams changes as follows [1,2]: complete solubility with almost ideal solid solution for (Pb,Sn)Te, complete solubility with minimum of melting temperature for (Sn,Ge)Te, complete solubility with minimum of melting temperature and spinodal demixing for (Pb,Ge)Te. It is well known that in an alloy with a spinodal miscibility gap the thermodynamic factor expresses the decrease of the interdiffusion coefficient if the conditions (temperature, composition) approach the critical value of spinodal demixing. For this reason the interdiffusion in (Pb,Ge)Te should be strongly influenced by thermodynamics.

Experimentally the diffusion behaviour was studied for couples composed of two single crystalline diffusion partners prepared with exact stoichiometry control. The couples were prepared by pressing together the polished surfaces of the crystals within a polycrystalline matrix. The polished cross-sections of the diffusion zones of annealed samples were investigated by EMPA. The diffusion coefficients were deduced by means of the Boltzmann-Matano method as modified by den Broeder.

The interdiffusion coefficient for the system (Pb,Ge)Te runs through a minimum near ≈70 mol. % GeTe. These minima are more pronouned at lower temperatures as shown in Fig.1. This behavior correlates well with the results of a calculation of the thermodynamic factor *F* from the interaction parameters on the basis of the phase diagram data.

For the (Sn,Ge)Te alloy the interdiffusion coefficients are higher than for (Pb,Ge)Te and slighly increase toward a higher GeTe mole fration. In a wide temperature range the compositional dependence is smooth. For Te-saturated alloys, the diffusion coefficients are essentially higher due to the higher concentration of cation vacancies. This fact confirms the supposition that the cation interdiffusion mechanism is mostly realised by means of vacancies.

3. Diffusion paths in the quasi-ternary system (Ge,Sn,Pb)Te

Diffusion paths at different temperatures in the range of 600-950K were measured between two points in the composition triangle using diffusion couples, composed of two quasibinary crystals. It was observed that the diffusion paths show only slight deviations from a linear behaviour which is best realized near the PbTe – GeTe edge.

4. Conclusion

Among the quasibinary alloys (Pb,Sn)Te, (Ge,Sn)Te and (Pb,Ge)Te the thermodynamic factor shows an influence on the interdiffusion coefficient only in the third system, where a broad region of spinodal demixing exists. This behaviour is similar to that in the Pb(S,Te) alloy [3]. For the (Ge,Sn)Te system, in general, the interdiffusion coefficients possess higher values due to lower melting temperature, higher vacancy concentration, and due to the absence of the thermodynamic influence. For Te-enriched alloys the vacancy diffusion mechanism seems to be most essential. In the case of the quasiternary system (Ge,Sn,Pb)Te the diffusion path shows only a slight deviation from a linear behaviour.

References

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