

The phase diagram of the quasiternary system $\text{Ga}_{2k}\text{Hg}_{3-3k}\text{Se}_{3l}\text{Te}_{3-3l}$

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Received 30 July 2004; accepted 25 August 2004

Abstract

The quasiternary system $\text{Ga}_{2k}\text{Hg}_{3-3k}\text{Se}_{3l}\text{Te}_{3-3l}$ was investigated by X-ray phase analysis and electron microprobe analysis. The system yields both ordered regions and spinodal miscibility gaps. Along the quasibinary edges, extended regions of solid solutions occur. The phase diagram can be modeled by a Gibbs energy function for a sub-regular system with ordering tendencies.

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Subject classification: Ga_2Se_3 ; Ga_2Te_3 ; HgSe; HgTe

Keywords: Quasiternary systems; Thermodynamics; Ordering processes; Solid solutions; Lattice constants; Chalcogenides

1. Introduction

The quasiternary system $\text{Ga}_{2k}\text{Hg}_{3-3k}\text{Se}_{3l}\text{Te}_{3-3l}$ seems to be very simple because all four binary components HgSe, HgTe, Ga_2Te_3 and Ga_2Se_3 crystallize, at least at high temperatures, in the cubic zinc-blende structure. Moreover, the quasibinary edge systems $\text{Hg}(\text{Se}_l\text{Te}_{1-l})$ [1] and $\text{Ga}_2(\text{Se}_l\text{Te}_{1-l})_3$ [2] show complete solid solubility. But, considering the stoichiometry of the Ga chalcogenides, the situation will become more complicated because of the structural vacancies in their cationic sublattice, i.e. only two-thirds of the cation sites of the zinc-blende lattice are occupied by Ga. Including these structural vacancies as V into the formulas, the two quasibinary edge systems with a mixed cation sublattice have to be written as $(\text{Ga}_{2k}\text{V}_k\text{Hg}_{3-3k})\text{Se}_3$ [3] and $(\text{Ga}_{2k}\text{V}_k\text{Hg}_{3-3k})\text{Te}_3$ [4].

From the investigation of these two systems, we know that the structural vacancies cause a tendency towards ordering near $k = 3/8$ and $3/4$. The super structures at $k = 3/8$ occur only at lower temperatures ($T < 800$ K), where the annealing times for equilibration are very long. Therefore, we restricted the experiments to $T = 900$ K. At this temperature, as a consequence of the ordering tendencies, only the chalcopyrite

structure around $k = 3/4$ should be formed. Thus, it is to be expected that, at 900 K the field of complete solid solubility in the phase diagram is intersected by a super structure phase with the stoichiometry $\text{Ga}_2\text{VHg}(\text{Se}_l\text{Te}_{1-l})_4$ that is neighbored on both sides by miscibility gaps.

2. X-ray measurements

The experimental data for the phase diagram were gathered by X-ray diffraction phase analysis (XRD) and electron microprobe analysis (EMA). Fig. 1 shows the overall compositions of all quasiternary samples that were prepared from the binary components to detect the one- and two-phase regions. The methods of preparation are described in [2–4].

The X-ray experiments at samples with $k = 3/4$ show that, in contrast to the expectation, there is no complete solid solubility between $\text{HgGa}_2\text{VSe}_4$ and $\text{HgGa}_2\text{VTe}_4$. The telluride-rich chalcopyrite phase extends only from $l = 0$ up to $l \approx 0.3$ and the selenide-rich one from $l = 1$ down to $l \approx 0.9$ (cf. Fig. 1).

2.1. The experimental determination of lattice constants

The homogeneous one-phase samples were used to determine the structures and their lattice parameters. Besides

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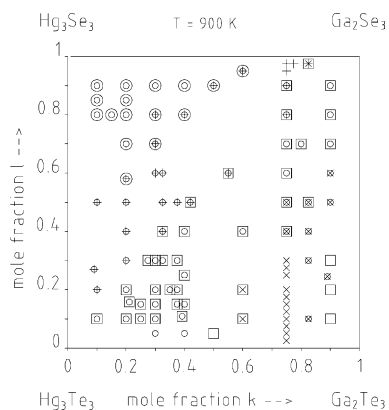


Fig. 1. The phase square with the samples investigated by X-ray diffraction. The sites of the following symbols correspond to the overall compositions of samples that were either homogeneous or heterogeneous after equilibration, with a cubic set of reflections for Hg chalcogenide-rich samples (\circ , \odot) and for Ga chalcogenide-rich samples (\square), with a tetragonal set of reflections for selenide-rich samples (+) and for telluride-rich samples (\times). The superpositions of two or three of these symbols at one site indicate two-phase or three-phase samples; the superpositions of two cubic symbols indicate a spinodal demixing.

the cubic zinc-blende structure, only the tetragonal structure of the defect chalcopyrite could be detected. As this is a superstructure of the zinc-blende lattice, a so-called pseudo-cubic lattice constant, defined by $a^* = (a^2c/2)^{1/3}$, will be attributed to this lattice. Considering the composition dependences of the lattice constants for the quasibinary edge systems $\text{Ga}_2\text{VSe}_3/\text{Te}_{3-3l}$ [2], $\text{Hg}_{3-3k}\text{Ga}_{2k}\text{V}_k\text{Se}_3$ [3], $\text{Hg}_{3-3k}\text{Ga}_{2k}\text{V}_k\text{Te}_3$ [4], $\text{Hg}(\text{Se}/\text{Te}_{1-l})$ [5] and including the cubic and pseudo-cubic lattice constants of the quasiternary samples, as determined for the present paper, the composition dependence of the lattice constant in the quasiternary system can be described by

$$a(k, l)/\text{pm} = 645.94 - 57.16k - 8.03k^2 + 9.62k^3 - 10.72kl + 14.30k^2l - 11.36k^3l - 37.44l. \quad (1)$$

The highest deviations of the values calculated by use of Eq. (1) from the above-mentioned literature data for the quasibinary edge systems and from the X-ray data for the quasiternary samples do not exceed ± 0.4 pm. Fig. 2 shows a net of 'iso lattice constant lines' in steps of 5 pm calculated from Eq. (1).

2.2. The domain structure

The homogeneous one-phase samples with $k = 3/4$ that were annealed at 900 K show, in addition to the reflections of the normal chalcopyrite structure, many sharp reflections with rather low intensity. Corresponding X-ray patterns can also be observed when Hg is substituted by Cd [6].

It is very astonishing that after quenching to room temperature, homogeneous samples that were annealed at high

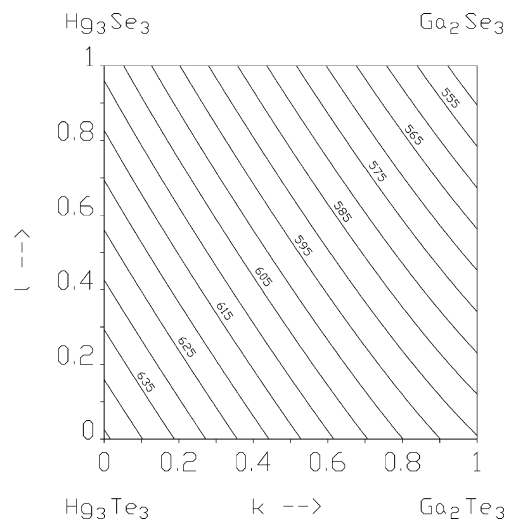


Fig. 2. Projection of lines with constant values of the cubic or pseudo-cubic lattice constant, $a^*(k, l) = \text{const}$, onto the square of the quasiternary system; the 'iso lattice constant lines' are plotted in steps of 5 pm.

temperatures (900 K) yield X-ray patterns with much more reflections than belonging to the chalcopyrite structure that is realized when the same samples are annealed at lower temperatures. Though ordering should decrease with increasing temperature, the high temperature pattern looks like one of a higher ordered lattice, but no single superstructure of the zinc-blende lattice could be found that allows explaining all reflections.

As at high enough temperatures the energy difference between similar superstructures gets more and more negligible, it seems to be possible that at such high temperatures domains of several different superstructures of the zinc-blende lattice could exist simultaneously because of energy fluctuations. We think that by quenching from the high annealing temperature (900 K) down to room temperature, big enough domains of some of such superstructures are preserved in addition to the energetically most favorable chalcopyrite structure. Practically, each of the observed additional reflections can be assigned to one of these possible superstructures. Therefore, we call the structure yielding this reflection-rich X-ray pattern the 'domain structure'.

Using only the reflections belonging to the tetragonal chalcopyrite structure we calculated the lattice constants of this phase in dependence on the mole fraction l . Fig. 3a shows that the lattice constant a changes linearly with l , whereas c (Fig. 3b) at first is constant and then decreases linearly for $l > 0.08$. The c/a -ratio (Fig. 3c) starts at $l = 0$ with the ideal value of two.

This means that the lattice of the pure $\text{HgGa}_2\text{VTe}_4$ is undistorted, whereas the lattice becomes more and more distorted when Te is successively substituted by Se. This distortion is connected with a splitting of characteristic reflections (e.g. (0 0 4), (0 2 4), (1 1 6)) of the undistorted tetragonal chalcopyrite structure into doublets. According to Gastaldi [7], the increasing lattice distortion of the Ga-containing chalcopyrite structure leads to a splitting of the reflections into doublets.

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