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The systems Sr–Zn–{Si,Ge}: Phase equilibria and crystal structure of ternary phases

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ABSTRACT

Phase relations have been established by electron probe microanalysis (EPMA) and X-ray powder diffraction (XPD) for the Sr-poor part of the ternary systems Sr–Zn–Si at 800 °C and Sr–Zn–Ge at 700 °C. In the Sr–Zn–Si system one new ternary compound $SrZn_{2+x}Si_{2-x}$ ($0 \le x \le 0.45$) with $CeAl_2Ga_2$ structure and a statistical mixture of Zn/Si in the 4*e* site was found. Neither a type-I nor a type-IX clathrate phase was encountered. This system is characterized by formation of two further phases, i.e. $SrZn_{1-x}Si_{1+x}$ with ZrBeSi-type ($0.16 \le x \le 0.22$) and $SrZn_{1-x}Si_{1+x}$ with AlB_2-type ($0.35 \le x \le 0.65$) with a random distribution of Zn/Si atoms in the 2*c* site. For the Sr–Zn–Ge system, the homogeneity regions of the isotypic phases $SrZn_{1-x}Ge_{1+x}$ with ZrBeSi-type ($0 \le x \le 0.17$) and AlB_2-type ($0.32 \le x \le 0.56$), respectively, have been determined. Whereas the germanide $SrZn_{2+x}Ge_{2-x}$ ($CeAl_2Ga_2$-type) is characterized by a homogeneity region ($0 \le x \le 0.5$), the clathrate type-I phase $Sr_8Zn_8Ge_{38}$ shows a point composition.

1. Introduction

Semiconducting clathrates, in general, are promising candidates for new thermoelectric materials. Hitherto many systematic studies of phase relations, crystal structures and physical properties of ternary phases in the systems Ba–*M*–{Si,Ge} with *M*=Mn, Fe, Co, Ni, Cu, Zn, Pd, Ag, Cd, Pt, Au were carried out and showed the presence of thermoelectric clathrate-I phases essentially as solid solutions $Ba_8M_xGe_{46-x-y}\square_y$ of *M*-atoms in binary $Ba_8Ge_{43-x}\square_x$ [1–19]. Although transition metals are involved, the endpoint of the solid solutions coincides in most cases with the so-called Zintl limit near a metal to insulator transition [1–7,9,10]. However, the formation of clathrates in the homologous systems with strontium has hitherto been elucidated only in a few cases. Whereas a clathrate type I phase, $Sr_8Zn_8Ge_{38}$, was defined by neutron powder diffraction [20], no clathrate was encountered in the systems Sr–{Ni,Cu}–Si [21]. The results for $Ba_8M_xGe_{46-x-y}\square_y$ and $Ba_8M_xSi_{46-x}$ have demonstrated [1–19], that physical properties can be shifted from metallic-like to semiconducting behavior via the amount of substituted *M*-atoms. As detailed knowledge on the ternary phase diagrams including formation of ternary phases and their corresponding chemical compositions is required in order to define properly the presence and solubility range of clathrates, the authors will provide results of the investigations on the ternary systems Sr–Zn–Ge and Sr–Zn–Si in the compositional region of the type-I clathrate.

Although no complete phase diagram has been evaluated for the systems Sr–Zn–{Si,Ge} a series of isostructural compounds has been discovered. The crystal structure of SrZnSi was described as ZrBeSi-type [22] and later $SrZn_{1-x}Si_{1+x}$ with AlB_2 type was reported [21]. Similarly $SrZn_2Si_2$ has been determined with $CeAl_2Ga_2$ type [23] and SrZnGe with ZrBeSi-type [24]. However, for none of the aforementioned phases the homogeneity region was defined. In order to assess the formation and region of existence of clathrate-type I phases in the systems Sr–Zn–{Si,Ge}, we have investigated the Sr-poor part of the Sr–Zn–{Si,Ge} systems. The current paper will thus provide information on (i) the phase equilibria in the Sr–Zn–{Si,Ge} systems, (ii) on the crystal structures of ternary compounds in the Sr–Zn–Si system, and will provide (iii) a comparison of the investigated systems and explanations to some structural effects in the ternary phases.

2. Experimental

For sample preparation the following components were used—strontium rods with purity 99.5 mass%, zinc granules (Alfa Aesar, purity > 99.9 mass%; purified in quartz ampoules by heating below the Zn boiling point at 907 °C), germanium and silicon pieces with purity better than 99.999 mass%. Oxygen sensitive strontium was cleaned and weighed under cyclohexane.

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For sample preparation the appropriate amounts of Sr (excess of 3 mass% was used to compensate evaporation losses) and Si/Ge were melted in an electric arc-furnace under Ti-gettered argon with a non-consumable tungsten electrode on a water-cooled copper hearth for two times in order to achieve complete fusion and homogeneity. The obtained ingot was cracked into several pieces and with appropriate amounts of Zn was sealed in an evacuated quartz tube. Each ampoule was heated slowly at a rate of 2 °C/min to 950 °C and maintained at this temperature for 2 days to complete the reaction. After that, the temperature was reduced to 800 °C for Si-containing and 700 °C for Ge-containing samples, which were then annealed for 6 days. Finally the samples were water quenched without breaking the ampoules. Temperatures for the isothermal sections (800 °C for the Si-based and 700 °C for the Ge-based system) were selected close to the solidus in the respective binary boundary systems of Sr–Si and Sr–Ge at the nominal binary clathrate composition $Sr_8(Si,Ge)_{46}$.

X-ray powder diffraction data from the annealed specimens were collected with a Guinier–Huber image plate system (Cu$K\alpha_1$; $8^\circ \le 2\theta \le 100^\circ$). Precise lattice parameters were calculated by least-squares fits to indexed 2θ-values employing Ge (for Si-containing samples) or Si (for Ge-containing samples) as internal standards ($a_{Ge}=0.565791$ nm; $a_{Si}=0.543107$ nm) using the CSD program package [25]. For crystal structure refinements we used the FullProf Suite program [26] and the standardization procedure with program Structure Tidy [27]. The annealed samples were polished using standard procedures and were examined by electron probe microanalysis (EPMA). Chemical composition of phases were determined via a Zeiss Supra 55VP scanning electron microscope operated at 20 kV and equipped with an energy dispersive X-ray (EDX) spectrometer supported by the INCA software (Oxford Instruments). Standard deviations for the chemical compositions gained from EPMA were smaller than ± 1 at%.

3. Binary systems

Both equilibrium diagrams, Zn–Si and Zn–Ge are characterized by a complete insolubility of the components at 700 and 800 °C [28]. The liquid phase extends at 700 and 800 °C over most of the phase diagram Sr–Zn [28], sparing only the compound $SrZn_{13}$. A detailed investigation of the Sr–Si system revealed at 800 °C the existence of Sr_2Si, Sr_5Si_3, $SrSi_2$, and SrSi (α or β modifications depending on the cooling rate) [29].

For the Sr–Ge system at 700 °C [28] the formation of Sr_2Ge, SrGe, and $SrGe_2$ has been reported. Although information on the existence of a Sr_5Ge_3 compound was presented [30], no thermodynamic data were given.

4. Results and discussion

4.1. The ternary system Sr–Zn–Si at 800 °C

On the basis of X-ray analyses and EPMA of 17 samples, phase relations at 800 °C were derived in the isothermal section of the Sr–Zn–Si phase diagram (see Fig. 1). Phase equilibria are characterized by the formation of three ternary phases: τ_1-$SrZn_{2+x}Si_{2-x}$ ($CeAl_2Ga_2$-type), τ_2-$SrZn_{1-x}Si_{1+x}$ (ZrBeSi-type), and τ_3-$SrZn_{1-x}Si_{1+x}$ (AlB_2-type). Crystallographic data are listed in Table 1. Despite the insolubility of components in the binary Zn–Si system, all ternary phases are characterized by homogeneity regions with statistical mixtures of Si and Zn atoms in some of the crystallographic positions. Whereas the existence of the phase τ_3-$SrZn_{1-x}Si_{1+x}$ with AlB_2-type [21] was confirmed and the homogeneity region of $0.35 \le x \le 0.65$ was defined on the basis of EPMA and Rietveld

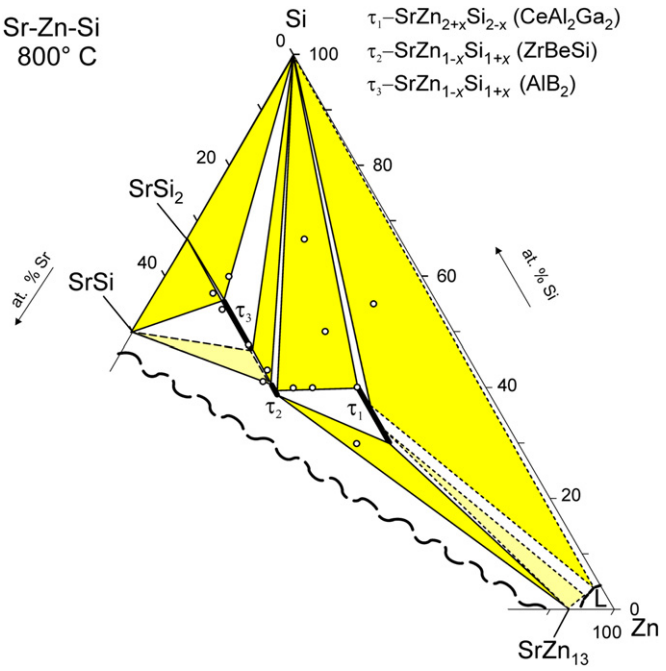

Fig. 1. Isothermal section of the Sr–Zn–Si diagram at 800 °C. Sample positions are indicated by open circles.

refinement data, the ternary phase τ_2-$SrZn_{1-x}Si_{1+x}$, reported at equiatomic composition with the ZrBeSi-type [22], appeared at 800 °C to be shifted along an Sr-isoconcentrate line in the direction of lower Zn content. This deviation from equiatomic composition was confirmed by EPMA and X-ray analysis of the bulk samples (Table 2). A small homogeneity range of $0.16 \le x \le 0.22$ exists at 800 °C, which, however, does not include the 1:1:1 stoichiometric composition SrZnSi earlier reported for a sample heated up to 1000 °C and slowly cooled to room temperature [22]. The phase appeared to be very brittle and rather air-sensitive as it decomposes completely in air within 2–3 days.

The τ_1-$SrZn_{2+x}Si_{2-x}$ phase [23], crystallizing in the $CeAl_2Ga_2$-type, extends within a homogeneity region ranging from $x=0$ to $x \le 0.45$. This phase appeared to be most stable against oxidation among all the ternary compounds in this system. Fig. 2 summarizes microstructures of selected alloys documenting the tie-line distribution at 800 °C for the ternary system Sr–Zn–Si. Interestingly, neither a ternary clathrate of type I ("$Sr_8(Zn,Si)_{46}$") nor of type IX ("$Sr_6(Zn,Si)_{25}$") have been encountered in alloys annealed at 800 °C.

4.2. The ternary system Sr–Zn–Ge at 700 °C

The isothermal section of the Sr–Zn–Ge phase diagram was constructed at 700 °C on the basis of X-ray and EPMA of 13 samples (Fig. 3). In comparison with the Sr–Zn–Si system, the annealing temperature was reduced to 700 °C to avoid liquid regions in the Ge-rich part of the binary and ternary phase diagram. Phase relations in the Sr–Zn–Ge system are characterized by the formation of four ternary phases: τ_1-$SrZn_{2+x}Ge_{2-x}$ ($CeAl_2Ga_2$-type), τ_2-$SrZn_{1-x}Ge_{1+x}$ (ZrBeSi-type), τ_3-$SrZn_{1-x}Ge_{1+x}$ (AlB_2-type) and τ_4-$Sr_8Zn_8Ge_{38}$ (clathrate type I). Crystallographic data are listed in Table 1; results of phase analyses and micrographs are shown in Table 3 and Fig. 4. Similar to the ternary Sr–Zn–Si compounds, all ternary phases with exception of the clathrate phase τ_4 are characterized by homogeneity regions at constant Sr-content but with statistical mixtures of Ge and Zn in