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Phase equilibria, crystal chemistry, electronic structure and physical properties of Ag–Ba–Ge clathrates

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Abstract

In the Ag–Ba–Ge system the clathrate type-I solid solution, $Ba_8Ag_xGe_{46-x-y}\square_y$, extends at 800 °C from binary $Ba_8Ge_{43}\square_3$ (□ is a vacancy) to $Ba_8Ag_{5.3}Ge_{40.7}$. For the clathrate phase ($1 \leqslant x \leqslant 5.3$) the cubic space group $Pm\bar{3}n$ was established by X-ray powder diffraction and confirmed by X-ray single-crystal analyses of the samples $Ba_8Ag_{2.3}Ge_{41.9}\square_{1.8}$ and $Ba_8Ag_{4.4}Ge_{41.3}\square_{0.3}$. Increasing the concentration of Ag causes the lattice parameters of the solid solution to increase linearly from a value of $a = 1.0656$ ($x = 0$, $y = 3$) to $a = 1.0842$ ($x = 4.8$, $y = 0$) nm. Site preference determination using X-ray refinement reveals that Ag atoms preferentially occupy the 6d site randomly mixed with Ge and vacancies, which become filled in the compound $Ba_8Ag_{4.8}Ge_{41.2}$ when the Ag content increases. At 600 °C the phase region of the clathrate solution $Ba_8Ag_xGe_{46-x-y}\square_y$ becomes separated from the Ba–Ge boundary and extends from 6.6 to 9.8 at.% Ag. The compound Ba_6Ge_{25} (clathrate type-IX) dissolves at 800 °C a maximum of 1.5 at.% Ag. The homogeneity regions of the two ternary compounds $BaAg_{2-x}Ge_{2+x}$ ($ThCr_2Si_2$-type, $0.2 \leqslant x \leqslant 0.7$) and $Ba(Ag_{1-x}Ge_x)_2$ (AlB_2-type, $0.65 \leqslant x \leqslant 0.75$) were established at 800 °C. Studies of transport properties for the series of $Ba_8Ag_xGe_{46-x-y}\square_y$ compounds evidenced that electrons are the predominant charge carriers with the Fermi energy close to a gap. Its position can be fine-tuned by the substitution of Ge by Ag atoms and by mechanical processing of the starting material, Ba_8Ge_{43}. The proximity of the electronic structure at Fermi energy of $Ba_8Ag_xGe_{46-x-y}\square_y$ to a gap is also corroborated by density functional theory calculations. This gap near the Fermi energy gives rise to distinct features of the temperature-dependent electrical resistivity and the Seebeck effect is in very good agreement with the experiment findings.

Keywords: Clathrate; Transport properties; Phase diagram; Electronic structure; *n*-Type

1. Introduction

The promising thermoelectric properties observed in clathrates have initiated a large number of studies in recent years [1]. A comprehensive review of the different clathrate types and crystal structures can be found in Ref. [2].

Although several investigations have already dealt with compounds of the Ag–Ba–Ge system, little is known about the phase equilibria in the ternary system and about the solubility range of ternary phases at a defined temperature. Beside the type-I clathrate $Ba_8Ag_6Ge_{40}$, for which perfect atomic ordering has been elucidated from an X-ray single-crystal study [3] and for which thermoelectric properties have been described (p-type material) [4], two more ternary compounds have been evaluated in the literature, namely (i) $BaAg_{0.8}Ge_{1.2}$ with the AlB_2 structure type and a small undefined homogeneity region at 550 °C [5]; and (ii) $BaAg_2Ge_2$ with the $ThCr_2Si_2$ structure type [6].

The aim of the present study is: (i) to provide consistent information on the phase relations in isothermal sections at

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800 and 600 °C for the region with less than 33 at.% Ba; (ii) to obtain details on the homogeneity regions of binary and ternary compounds in combination with atomic ordering in the corresponding crystal structures; (iii) to acquire thermoelectric data on type-I clathrate as a function of temperature and of composition throughout its homogeneity region; and finally (iv) to understand the correlation between structure and physical property in combination with density functional theory (DFT) calculations.

2. Experimental details

The samples (~1 g) for the isothermal section were prepared by arc melting mixtures of pure elements (Ba 99.9, Ag 99.9 and Ge 99.999 mass%) under an argon atmosphere. In all cases the weight loss was lower than 1 mass%. The arc-melted buttons were vacuum-sealed in quartz tubes and annealed at 800 °C for 1 week, characterized and subjected to further annealing at 600 °C for 1 month. Five samples (of about 1 cm^3 each) with nominal composition $Ba_8Ag_xGe_{46-x-y}\square_y$ ($x = 2$, 3, 4, 5, 5.3) ($\square$ denotes a vacancy) were prepared in a different manner in order to achieve a relative density (ρ/ρ_X) higher than 96% for measurements of physical properties such as thermopower, resistivity and thermal conductivity. For each sample, five alloys of 1–2 g were prepared by argon arc melting of the pure elements. After arc melting, the samples were sealed under vacuum into quartz tubes, remelted at 900 °C for ~2 h, and finally annealed for 5 days at 800 °C. Powders obtained from these alloys by a high-energy ball milling procedure in a Vario Planetenmühle (Pulverisette 4) were then compacted in a hot press (HP W 200/250-2200-200-Ks, FCT System GmbH) at 700 °C using a pressure of 56 MPa under an argon atmosphere followed by annealing in sealed quartz tubes at 800 °C for 5 days.

Details of the various sample characterization techniques, and the methods used for measurements of physical properties, have been described in our previous papers [7,8].

3. Computational details

DFT calculations were performed with the Vienna Ab initio Simulation Package (VASP) [9,10]. The pseudopotentials were constructed according to the projector augmented wave method [11,12] and the exchange–correlation functional was parametrized in terms of the local density approximation according to Ceperley and Alder [13]. The valence state configuration for the construction of the pseudopotentials included the 5*s*, 5*p* and 6*s* states for Ba, the 5*s* and 4*d* states for Ag, and the 3*d*, 4*s* and 4*p* states for Ge. For the Brillouin zone integration a $5 \times 5 \times 5$ grid of $\vec{k}$-points was chosen, which results in well-converged total energies and optimized structural parameters including fully relaxed lattice parameters and ionic positions. For the densities of states (DOS) and related quantities a dense $11 \times 11 \times 11$ $\vec{k}$-point mesh was constructed. Electronic transport calculations were carried out by solving the semi-classical Boltzmann transport equation within the relaxation time approximation as implemented in the program package BoltzTrap [14], which requires the Kohn–Sham energy eigenvalues on a very dense $25 \times 25 \times 25$ $\vec{k}$-point grid.

4. Results and discussion

4.1. The clathrate type-I solid solution $Ba_8Ag_xGe_{46-x-y}\square_y$

The solubility range of the ternary type-I clathrate was studied by X-ray powder diffraction (XRPD) and electron probe microanalysis (EPMA) on a series of samples with nominal composition $Ba_8Ag_xGe_{46-x}$ ($1 \leqslant x \leqslant 8$), which had been annealed at 800 °C. Table 1 shows a comparison of the EPMA data with the results of Rietveld refinement of the X-ray intensity data. In all cases the X-ray spectra ($x \leqslant 5.3$) were fully indexed on the basis of a cubic clathrate type-I lattice with minor amounts of Ge (< 2.2%). Starting from binary $Ba_8Ge_{43}\square_3$ the maximum solubility for Ag at 800 °C was found by EPMA to be 5.3 atoms per formula unit (= 9.8 at.%) (Fig. 1). The lattice parameters show a linear increase with increasing Ag content up to 4.8 silver atoms per unit cell ($a = 1.0840(9)$ nm). Clathrate samples with higher Ag content show only slightly different lattice parameters which are close to the reported values of Cordier and Woll for a single-crystal of stoichiometric $Ba_8Ag_6Ge_{40}$ (melted at 1300 °C and cooled at 100 K h^{-1}, $a = 1.0840(1)$ nm [3]). The decreasing content of Ba in the EPMA data (see Table 1) in combination with increasing Ag content is related to the amount of vacancies in the crystal lattice of $Ba_8Ag_xGe_{46-x-y}\square_y$. Assuming full occupancies for the Ba sites in the 2a and 6c positions of space group $Pm\bar{3}n$ (standardized setting; see also single-crystal refinements in Table 1), the vacancy concentrations calculated from EPMA correspond well to the amount of vacancies obtained from a Rietveld refinement. These findings are backed up by single-crystal data from two single-crystals of $Ba_8Ag_xGe_{46-x-y}\square_y$ ($x = 2.3$ and 4.4; see Table 2). The amount of vacancies shows only a weakly positive deviation from linear decrease with increasing Ag content whereby all vacant sites are filled to the level of 4.8 atoms of Ag per unit cell (inset Fig. 1). In addition to the experimental data, two boundary models are drawn in Fig. 1. Model A assumes substitution of Ge by Ag at a constant level of vacancies according to the compound Ba_8Ag_x-$Ge_{43-x}\square_3$. The second model eliminates all the vacancies prior to substitution. Because the experimental data are in between these two models, it seems plausible that Ag atoms ($x \leqslant 4.8$) successively fill vacancies and simultaneously replace Ge atoms. At higher Ag content, when no more vacancies are available, only Ge atoms are substituted by Ag atoms. This behaviour is well reflected in the lattice parameters and is in line with results derived for other clathrates in the systems Ba–Pd–Ge [7], Ba–Cd–Ge [8], Ba–Cu–Ge [15], Ba–Zn–Ge [16] and Ba–Pt–Ge [17].