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Synthesis, crystal structure, phase relations and chemical bonding analysis of the new Nowotny chimney-ladder compound $ZrBi_{1.62}$

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Abstract

$ZrBi_{1.62}$ is a new compound crystallising with an incommensurate Nowotny chimney-ladder structure, which was refined from single crystal X-ray diffraction data using a four-dimensional formalism. The tetragonal unit cell has the lattice parameters $a = 6.958(7)$ Å, $c = 3.460(3)$ Å and $q = (0\ 0\ 0.382)$. The symmetry is described by the superspace group pair $W{:}P4/nnc{:}q\text{-}1q1\text{–}P{:}I4_1/amd{:}1\text{-}1ss$. The full phase relations of $ZrBi_{1.62}$ were established with DTA and phase analysis by X-ray powder diffraction, showing that the compound is thermodynamically stable only in the limited temperature range of 740–820 °C. The chemical bonding in $ZrBi_{1.62}$ was analyzed using the electron localization function (ELF) for the 5-fold and the 13-fold approximants of the incommensurate structure. The attractors of the ELF are located near the shortest Zr–Bi contacts, showing a covalent interaction between the zirconium and the bismuth atoms. No indication was found for direct bonding within the Zr and Bi networks, which usually is assumed in the crystal structure description of chimney-ladder phases. The calculated electron density of states (DOS) indicates metallic behavior.

Keywords: Chimney-ladder phase; Incommensurately modulated structure; Binary Zr–Bi system; Single-crystal X-ray diffraction; Phase relationship; Electron localization function

1. Introduction

The Zr–Bi system was investigated by Hamilton and Wilhelm [1] and was found to contain five intermetallic compounds; $ZrBi_2$ (Pearson symbol $oP24$, $TiAs_2$ type) [2–5], ZrBi ($oC24$, ZrSb type) [5–7], Zr_3Bi_2 [1] and Zr_3Bi ($tI32$, Ni_3P type) [5,8]. Recently, the possibly impurity-stabilised compound Zr_5Bi_3 ($hP16$, Mo_5Si_3 type) was reported and was suggested to be identical to the previously mentioned Zr_3Bi_2 [6]. Possibly, also a compound with the composition Zr_2Bi exists [1].

We here report on the crystal structure, phase relations and analysis of the chemical bonding in the new intermetallic phase $ZrBi_{1.62}$, which has a Nowotny chimney-ladder (NCL) structure. The NCLs belong to the class of composite structures (or intergrowth structures). Composites are a special class of crystal structures, as their total structure can be divided into two (or more) individuals. Because these individuals commonly are incommensurate in one or several directions, or commensurate with very long periods, it is convenient to divide the structure into the subunits. This means that each substructure (individual) will have its own unit cell dimensions, modulation vector, space group and set of reflections in the diffraction pattern. The total reflection material can be indexed and integrated with either of the subcells, but as all reflections have contributions from both individuals, both of them need to be taken into account to get the intensity distribution right and solve the crystal structure correctly. The chimney-ladder structures were recently reviewed and some of them rerefined with the composite-structure approach from single crystal X-ray data by Rohrer et al. [9]. This structure model works equally well for commensurate and incommensurate cases. For further reading on composite structures, confer [10].

NCL phases are formed by transition metals (T, groups 4–9) together with main group elements (E, groups 13–15). Only re-

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cently, NCL phases were found containing a transition metal from the fourth group and an element from the fifteenth group [11]. Their structures are usually described as built up from two parts; the first part being a diamond-type network formed by the transition metal, and the second part formed by the main group element, which build up unidirectional helices interpenetrating the diamond-type network [12].

The chimney-ladder phases have since their discovery in the 1960s been labelled as electron compounds [13], i.e., the stability of the intergrowth structure has been believed to be governed by a specific concentration of the total number of valence electrons ($s + d$ electrons for transition metals and $s + p$ electrons for main group elements) divided by the number of transition metal atoms. Investigations have resulted in the empirical valence electron concentration (VEC) of about 14 e^-/T atom for transition metals of groups 7–9, around 13 e^-/T for transition metals of group 6 and 12.0–12.3 e^-/T for transition metals from groups 4–5 [13,14]. Moreover, an "intergrowth" model has been proposed for the topological description of the chimney-ladder structures [15]. According to this model, all known commensurate chimney-ladder structures (unit cell, composition and symmetry) can be understood by stacking structural segments of the $TiSi_2$ archetype structure (TE_2) and its derivatives with the compositions T_2E_2 and T_3E_4. The chemical bonding reasons for this behaviour was found by Fredrickson et al. [16,17] who showed with the examples $RuGa_2$ and Ir_3Ga_5 that the filling up of the orbital system explains both the stacking and the 14 e^--rule for compounds of late transition metals.

For NCL phases with early transition metals and VECs around 12 e^-/T atom a different bonding mechanism may be expected. Examples of such compounds are $V_{17}Ge_{31}$ [18], $Zr_{11}Sb_{18}$ [11], the (M, Ti)$_5$Sb$_8$ series ($M =$ Zr, Hf, Nb, Mo) [19] and $TiSi_2$, which structure is the basic motif for chimney-ladder structures. The discovery of $ZrBi_{1.62}$ adds a new representative to this low-VEC group.

2. Experimental

2.1. Synthesis

Bismuth (99.999%, needles, ABCR) was purified from oxides by melting the metal in a quartz tube under dynamic vacuum. Gas bubbles evolved when oxygen left the system. The heating was stopped when no more bubbles were formed and the resulting solid bismuth body was crushed into suitable pieces in an agate mortar under liquid nitrogen.

1.70 g of the purified bismuth and 0.31 g zirconium (99.8%, 0.25 mm foil, Alfa Aeser) were put in a quartz tube prepared with a quartz wool filter according to the high temperature centrifugation aided filtration technique (HTCAF) [20]. The quartz tube was sealed under vacuum and heat treated at 780 °C for 48 h. The centrifugation-aided removal of the melt was performed during 3 minutes at 2000 G, whereafter the sample was quenched in water.

In order to verify the phase relations of the title compound, a part of the synthesized sample was annealed at 700 °C for 66 h in an evacuated quartz ampoule. An additional sample with the nominal composition $Zr_{43.5}Bi_{56.5}$ was prepared from 1.00 g Zr and 2.96 g Bi and heat treated at 850 °C for 26 h in an evacuated quartz ampoule.

2.2. SEM

Elemental analysis and morphology studies on single crystals were carried out with a Jeol 820 Scanning Electron Microscope (SEM) equipped with an EDXS system.

2.3. DTA

Difference thermal analysis (DTA) was carried out (Netzsch, STA 404, thermocouple type S, heating/cooling rate 10 K/min) in argon atmosphere (Messer–Griesheim, 99.999%, additionally purified by passing over BTS catalyst, Merck) using Al_2O_3 pans. The melting points of five pure metals were employed for temperature calibration.

2.4. X-ray diffraction

X-ray powder diffraction patterns of the powdered bulk samples mounted between air-tight Vaseline treated Kapton® polyimide films were collected with a Huber Imaging Plate Guinier Camera 670 using Cu K_{α_1} radiation ($\lambda = 1.54056$ Å).

A single-crystal with well-developed faces was chosen for the X-ray diffraction experiment. The data set was recorded on a STOE IPDS diffractometer equipped with a rotating anode X-ray source (Mo K_α radiation, $\lambda = 0.71073$ Å). Details of the measurement are given in Table 1. The crystal structure was refined using the Jana2000 program [21].

2.5. Approximants

Analysis of the chemical bonding was performed on two hypothetical commensurate approximants of the $ZrBi_{1.62}$ structure with the compositions Zr_3Bi_5 and Zr_8Bi_{13}.

As pointed out by Yamamoto [10], the subperiodic groups of the superspace group of the Nowotny chimney-ladder structures are determined by the multiplicity of the two sublattices. A super-cell description must always belong to one of three possible cases, cf. also [15]. These are:

- Diamond network repeat odd, helix repeat odd, space group $P\bar{4}n2$.
- Diamond network repeat even, helix repeat odd, space group $P\bar{4}c2$.
- Diamond network repeat odd, helix repeat even, space groups $I4_122$, $I4_1/a$.

Once this information is generated, it is straight-forward to generate the appropriate approximants for any chosen q-vector by simply applying the shifts from the ideal positions given by the modulation functions for the two atoms. This procedure is fully automated in the program package Jana2000. The crystallographic information for these two models is listed in Table 2.