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# Isothermal section of the Ho–Co–Bi system at 800 °C and new ternary $Mo_5B_2Si$-type bismuthides $R_5Co_2Bi$ (R = Gd, Ho, Dy)

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The isothermal section of the ternary Ho–Co–Bi phase diagram has been investigated at 800 °C. The existence of three previously known compounds was confirmed: $Ho_{12}Co_5Bi$ (own type, *Immm*, $a = 9.3730(5)$ Å, $b = 9.3873(5)$ Å, $c = 9.8544(5)$ Å), $Ho_6CoBi_2$ ($Zr_6CoAl_2$-type, $P\bar{6}2m$, $a = 8.2520(3)$ Å, $c = 4.0974(2)$ Å), and $Ho_5CoBi_2$ (β-$Yb_5Sb_3$-type, *Pnma*, $a = 12.1526(9)$ Å, $b = 8.9270(7)$ Å, $c = 7.9247(6)$ Å). $Ho_5CoBi_2$ was demonstrated to be the end-member of a solid solution, $Ho_5Co_xBi_{3-x}$, with a homogeneity range of $0.65 < x < 1.0$. A new ternary compound, $Ho_5Co_2Bi$, has been discovered, adopting the $Mo_5B_2Si$-type structure ($I4/mcm$, $a = 7.4816(4)$ Å, $c = 13.8838(9)$ Å). Rare-earth substitution can be extended to yield $R_5Co_2Bi$ (R = Gd, Dy).

## 1. Introduction

Ternary rare-earth transition-metal antimonides have now been extensively examined because of their diverse structures and properties [1], but the corresponding bismuthides have not been studied systematically [2]. Phase diagrams for ternary R–M–Bi systems have barely been investigated; isothermal sections in the whole concentration range have been determined so far for only R–Ni–Bi (R = Y, Ho) [3] and R–Fe–Bi (R = Pr, Sm) [4]. On the other hand, increasing numbers of compounds have now been identified among the R–M–Bi systems, with M being limited largely to the first-row or later transition metals. In particular, several R–Co–Bi phases are now known, which display interesting electrical and magnetic properties: $R_{12}Co_5Bi$ (R = Y, Gd–Tm) [5], $R_6CoBi_2$ (R = Y, Ho, Er, Tm) [6–8], $R_5CoBi_2$ (R = Gd–Er) [9], and $La_6Co_{13}Bi$ [10]. We present here the isothermal section of the ternary Ho–Co–Bi phase diagram at 800 °C. In addition to clarifying the nature of the previously known phases in this system, we report the structure of a new bismuthide, $Ho_5Co_2Bi$. The rare-earth analogues $Gd_5Co_2Bi$ and $Dy_5Co_2Bi$ were also prepared.

## 2. Experimental

Starting materials were powders of holmium (99.9%, Alfa-Aesar), cobalt (99.8%, Cerac), and bismuth (99.999%, Alfa-Aesar). Samples were prepared by arc-melting of cold-pressed pellets (0.25 g) of the elemental components in an Edmund Bühler MAM-1 compact arc melter under high-purity argon gettered with Ti. A 5 wt.% excess of Bi was required to compensate for evaporative losses during arc-melting. The ingots were then sealed in evacuated fused-silica tubes and annealed at 800 °C for 360 h. After the heat treatment, the ingots were quenched in cold water. Phase analyses were carried out through examination of powder X-ray diffraction patterns (Cu K$\alpha_1$ radiation; Si external standard) collected on an Enraf–Nonius FR552 Guinier camera or on an Inel powder diffractometer equipped with a CPS 120 detector. Polished samples embedded in resin were examined through metallographic analyses. Approximate elemental compositions of phases were determined by energy-dispersive X-ray (EDX) analysis on a Hitachi S-2700 scanning electron microscope.

Crystal structures of ternary Ho–Co–Bi phases were refined from powder X-ray diffraction data collected at room temperature on an Inel powder diffractometer. Full-profile Rietveld refinements were carried out with use of the program LHPM-Rietica [11]. Initial atomic positions for $Ho_5Co_2Bi$ were taken from literature values for related compounds [12,13], and the fit of the Rietveld refinement results to the powder pattern is shown in Fig. 1. Although refinement of occupancy factors from powder data is not as reliable as from single-crystal data, all sites appear to be fully occupied in $Ho_5Co_2Bi$.

Attempts to prepare other rare-earth members in $R_5Co_2Bi$, through arc-melting reactions followed by annealing at 800 °C, were only successful for R = Gd and Dy. The tetragonal cell parameters for $Dy_5Co_2Bi$, determined from powder X-ray

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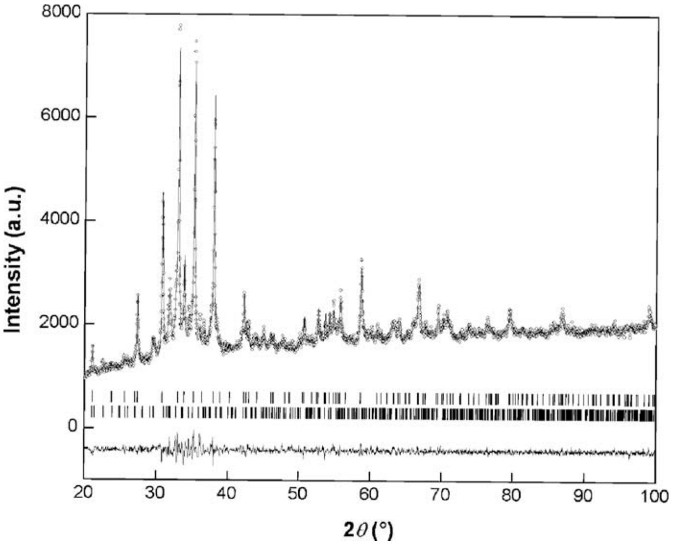

**Fig. 1.** Rietveld refinement results for $Ho_5Co_2Bi$. The observed profile is indicated by circles and the calculated profile by the solid line. The upper set of vertical tick marks corresponds to the Bragg peak positions of $Ho_5Co_2Bi$, and the lower set to those of small amounts of $Ho_5CoBi_2$. The difference plot is shown at the bottom.

diffraction data, are $a = 7.5748(8)$ Å, $c = 13.846(2)$ Å, and $V = 794.4(2)$ Å$^3$. Single crystals of $Gd_5Co_2Bi$ could be isolated from the crushed sample after the 800 °C annealing treatment. Intensity data for $Gd_5Co_2Bi$ were collected on a Bruker Platform/SMART 1000 CCD diffractometer at 22 °C using ω scans. Calculations were carried out with use of the SHELXTL (version 6.12) package [14]. Face-indexed numerical absorption corrections were applied. The centrosymmetric space group *I*4/*mcm* was chosen and initial atomic positions were located by direct methods. The structure was refined by full-matrix least-squares methods on $F^2$ with anisotropic displacement parameters. Refinements on the occupancy factors confirmed that all the sites are fully occupied except for Co, which has an occupancy of 86(1)%, corresponding to the formula $Gd_5Co_{1.73(2)}Bi$.

**Table 2**
Positional and equivalent isotropic displacement parameters for $R_5Co_2Bi$ (R = Gd, Ho)

| Atom | Wyckoff position | *x* | *y* | *z* | $U_{eq}$ or $U_{iso}$ (Å$^2$)[a] |
|---|---|---|---|---|---|
| $Gd_5Co_{1.73(2)}Bi$ | | | | | |
| Gd1 | 16l | 0.16012(5) | $x + 1/2$ | 0.13591(4) | 0.0168(2) |
| Gd2 | 4c | 0 | 0 | 0 | 0.0181(3) |
| Co[b] | 8h | 0.3741(3) | $x + 1/2$ | 0 | 0.0187(8) |
| Bi | 4a | 0 | 0 | 1/4 | 0.0151(2) |
| | | | | | |
| $Ho_5Co_2Bi$ | | | | | |
| Ho1 | 16l | 0.1658(4) | $x + 1/2$ | 0.1389(3) | 0.015(2) |
| Ho2 | 4c | 0 | 0 | 0 | 0.005(2) |
| Co | 8h | 0.3881(11) | $x + 1/2$ | 0 | 0.014(4) |
| Bi | 4a | 0 | 0 | 1/4 | 0.007(2) |

[a] $U_{eq}$ applies to $Gd_5Co_{1.73(2)}Bi$ and $U_{iso}$ to $Ho_5Co_2Bi$. $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.
[b] Occupancy of 0.86(1).

Full details for refinement results from powder X-ray diffraction data on all Ho–Co–Bi phases identified are provided as Supplementary data. Atomic positions were standardized with the program STRUCTURE TIDY [15]. For $R_5Co_2Bi$ (R = Gd, Ho), Table 1 summarizes crystallographic data, Table 2 lists the final values of the atomic positions and displacement parameters, and Table 3 lists selected interatomic distances. Further data for $Gd_5Co_{1.73(2)}Bi$, in CIF format, have been sent to Fachinformationszentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany, as supplementary material No. CSD-419762 and can be obtained by contacting FIZ (quoting the article details and the corresponding CSD numbers).

Tight-binding extended Hückel band structure calculations were performed with use of the EHMACC suite of programs [16,17] on the hypothetical compound "$Y_5Co_2Bi$", to model $Ho_5Co_2Bi$ ($Mo_5B_2Si$-type) but without the complications associated with the presence of f electrons. Atomic parameters (valence shell ionization potentials $H_{ii}$ (eV) and orbital exponents $\zeta_i$) were taken from literature values for related compounds [5,12] and are as follows: for Y 5s, $H_{ii} = -6.82$, $\zeta_i = 1.39$; for Y 5p, $H_{ii} = -4.30$, $\zeta_i = 1.39$; for Y 4d, $H_{ii} = -6.56$, $\zeta_{i1} = 4.33$, $c_1 = 0.5657$, $\zeta_{i2} = 1.06$, $c_2 = 0.6575$; for Co 4s, $H_{ii} = -7.80$, $\zeta_i = 2.00$; for Co 4p, $H_{ii} = -3.80$, $\zeta_i = 2.00$; for Co 3d, $H_{ii} = -9.70$, $\zeta_{i1} = 5.55$, $c_1 = 0.5550$, $\zeta_{i2} = 1.90$, $c_2 = 0.6678$; for Bi 6s, $H_{ii} = -15.19$, $\zeta_i = 2.56$; for Bi 6p, $H_{ii} = -7.79$, $\zeta_i = 2.07$. Properties were extracted from the band structure using 108 *k* points in the irreducible portion of the Brillouin zone.

## 3. Results and discussion

The isothermal section at 800 °C of the Ho–Co–Bi system has been determined by means of X-ray diffraction analysis of 39 samples (Fig. 2). Annealing of Bi-rich samples at 800 °C generally led to formation of elemental bismuth, so compositions with >70 at.% Bi were not examined further. Bounding the phase diagram at this temperature, the Co–Bi system forms no

**Table 1**
Crystallographic data for $R_5Co_2Bi$ (R = Gd, Ho)

| | | |
|---|---|---|
| Formula | $Gd_5Co_{1.73(2)}Bi$ | $Ho_5Co_2Bi$ |
| Formula mass (amu) | 1096.59 | 1151.49 |
| Space group | *I*4/*mcm* (No. 140) | *I*4/*mcm* (No. 140) |
| *a* (Å) | 7.7435(9) | 7.4816(4) |
| *c* (Å) | 13.734(2) | 13.8838(9) |
| *V* (Å$^3$) | 823.5(2) | 777.14(8) |
| *Z* | 4 | 4 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 8.845 | 9.837 |
| Radiation | Mo Kα, $\lambda = 0.71073$ Å | Cu K$\alpha_1$, $\lambda = 1.54056$ Å |
| $\mu$ (mm$^{-1}$) | 64.21 | 165.02 |
| 2θ range | $5.94° \le 2\theta(\text{Mo K}\alpha) \le 60.92°$ | $20° \le 2\theta(\text{Cu K}\alpha_1) \le 110°$ |
| Refinement method | SHELXTL | Rietveld |
| No. of data collected | 4549 ($R_{int} = 0.055$) | 3104 Data points |
| No. of unique data | 363 (347 with $F^2 > 2\sigma(F^2)$) | 147 Bragg reflections |
| No. of variables | 17 | 23 |
| Residuals[a] | $R(F)$ $(F^2 > 2\sigma(F^2)) = 0.027$, $R_w(F^2) = 0.074$ | $R_B = 0.024$, $R_p = 0.027$, $R_{wp} = 0.038$ |

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$ where $p = [\max(F_o^2, 0) + 2F_c^2]/3$; $R_B = \sum|I_o - I_c|/\sum I_o$; $R_p = \sum|y_o - y_c|/\sum y_o$; $R_{wp} = [\sum[w(y_o - y_c)]/\sum wy_o^2]^{1/2}$.