Journal of Alloys and Compounds, 206 (1994) L15–L17
JALCOM 1099

Letter

Compounds of alkaline-earth and divalent rare-earth metals stabilized by hydrogen impurities. The Yb_5Sb_3 and Mn_5Si_3 structure types for pnictides

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(Received December 15, 1993)

Abstract

All eight reported examples of the orthorhombic (β–)Yb_5Sb_3-type structure are ternary hydrides, namely, $A_5(Sb,Bi)_3H$ for A≡Ca, Sr, Eu, Yb. One additional example is Sm_5Bi_3H. These may be obtained in quantitative yields through the inclusion of AH_2 in the syntheses. On the contrary, heating these products or the elementary reactants at 900–1100 °C in high vacuum while sealed in Ta regularly affords only hexagonal Mn_5Si_3-type products, *i.e.*, A_5Pn_3 for A≡Ca, Sr, Ba, Sm, Eu or Yb, Pn≡As, Sb or Bi, except for As with Ba or Sm. The examples with Ca_5Bi_3, $Eu_5(Sb,Bi)_3$ and Yb_5Bi_3 are new. Several problems with supposedly dimorphic phases are thus clarified. The hydrogen content of the typical sublimed or distilled alkaline-earth metals is often particularly serious (~6–20 at.% H). The A_5Pn_3 phases with either structure type take up variable amounts of hydrogen and thereby exhibit significant variations in their individual lattice constants.

1. Introduction

Problems with phases assigned to the Yb_5Sb_3 structure type [1] began with our inability to find a sensible temperature or composition variable that controlled the phase distribution of either Ca_5Sb_3 or Sr_5Bi_3 between the hexagonal Mn_5Si_3-type (M) and orthorhombic (β–)Yb_5Sb_3-type (Y) structures and to reproduce the reported lattice parameters [2]. The same problems occurred for Yb_5Sb_3, but with uncertainties about the correct composition of Y-type phase as well [1–3]. However, synthesis of single phase, stuffed alkaline-earth metal pnictide examples in one or the other of these structure types has been proven possible through either (a) utilization of the ease with which M-type phases bind certain interstitial atoms [4, 5], chloride or bromide in these cases in, *e.g.* Ca_5Sb_3Cl, or (b) the synthesis of ternary derivatives of the Y-type such as Ca_5Sb_3F and Ca_3Bi_3F (but not for Ba_5Sb_3 or with oxide instead) in which the fluoride is tetrahedrally bound in a supposed interstitial site [2]. Both Ba_5Sb_3Cl and Ca_5Bi_3F were later found to be semiconductors, as expected valence-wise, but the apparent M-type Ba_5Sb_3 binary also turned out to be a semiconductor ($E_g \sim 0.3$ eV) even though a metallic behavior was expected in the simplest analysis because of the presence of one extra valence electron [6]. No superstructure could be found that might be responsible for this irregularity.

We then realized that gross interference by impurity hydrogen might be responsible because of two considerations: first, that even sublimed (or distilled) alkaline-earth metals retain significant amounts of hydrogen, typically from 6–10 at.% in Ca up to 12–20 at.% or more in Ba [7], and second, that H^- and F^- exhibit very similar effective sizes in many solid compounds [8, 9] so that hydride might also be bound in a stuffed Yb_5Sb_3-type (Ca_5Sb_3F) structure instead. These suppositions have been confirmed directly through conscious and purposeful control of the hydrogen contents.

2. Methods

The syntheses started with sublimed alkaline-earth metals available from either the Ames Laboratory or APEI Engineered Materials (Urbana, IL), which were handled only in a high quality glovebox. Tantalum, the obvious container, becomes permeable to H_2 above about 600 °C [10]. Following consideration of the H_2 pressures above α-alkaline-earth metal solutions [11], treatment of either the metals or their A_5Pn_3 compounds at 900–1100 °C in high vacuum for about 2 h was found to be sufficient to remove nearly all of this impurity from ~200 mg samples sealed in 0.38 mm thick Ta tubing. Guinier powder patterns have been utilized for all estimates of phase distributions.

For the well-known and supposedly dimorphic Ca_5Sb_3, for instance, a single phase M-type product is always obtained after the above treatment of (a) Ca first, followed by its reaction with Sb near 1000 °C and slow cooling, (b) the appropriate mixture of Ca and Sb as received, or (c) previously synthesized Y–Ca_5Sb_3. In contrast, an M–Y mixture was always obtained after reaction, typically near 1000 °C, of visibly clean, sublimed calcium as received with antimony under the customary procedures, that is, within a welded Ta container in turn sealed within a fused silica jacket that had first

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0925-8388/94/$07.00
SSDI 0925-8388(93)01099-4

been flammed well under high vacuum. A larger proportion of, even only, a Y-type $Sr_5(Sb,Bi)_3H$ is obtained with the more contaminated Sr source. On the contrary, a larger proportion of the M-type is obtained for the same compositions on quenching, probably because some hydrogen from dissociation at temperature remains in the jacket. Annealing M-type Ca_5Sb_5 or Yb_5Sb_3 in the same sealed Ta/SiO_2 arrangement for only 2 h at 900–1100 °C produces a few percent Y, while ~2 weeks or more at temperature affords nearly only the corresponding Y phase. These differences clearly arise from continued dehydration (or atmospheric permeation) of the silica at temperature.

Starting from the other direction, introduction of hydrogen as CaH_2, etc. to furnish about one hydrogen atom per Ca_5Sb_3, etc., always gives a substantially quantitative yield of the Y-type compound. This structure type appears to have a stoichiometry limit close to A_5Pn_3H since the lattice constants cease to change when still more hydrogen is added, while some hydrogen substoichiometries are indicated by cell constant variations (below). Extension to the analogous systems of divalent Sm, Eu, Yb systems gives similar results, although the metals now available appear to have significantly lower hydrogen contents.

3. Results

Experiments of the above character have now established that all eight reported examples of a binary orthorhombic (β–)Yb_5Sb_3 structure pertain to ternary hydrides, *i.e.*, for $Ca_5(Sb,Bi)_3$ [2, 12, 13], $Sr_5(Sb,Bi)_3$ [2, 14, 15], $Eu_5(Sb,Bi)_3$ [16] and $Yb_5(Sb,Bi)_3$ [1, 17]. One new example was also found, Sm_5Bi_3H. All of the previously reported quasibinary members presumably originated with hydrogen impurities either in the starting metals or from contamination by H_2O, etc. before or during reaction (hydrogen is usually retained on reaction of these metals with water except at high temperatures under vacuum). Troubles with the true compositions of particularly Y-type Yb_5Sb_3 and Yb_5Bi_3 phases, which once were thought to be more metal-rich, can now be understood as reactions in a quasibinary intermetallic system in which hydrogen was limiting, such that greater yields of the Y-type were obtained with excess Yb. (As with Wang *et al.* [18], we distinguish the above Y-type structure from that of Y_5Bi_3; the latter occurs for binary pnictides of the smaller trivalent metals and has the distinctive *c* and *a* directions interchanged from those in Ca_5Bi_3F when compared in the same *Pnma* space group. We note that two Ca1 neighbors of the interstitial tetrahedral F in Ca_5Sb_3F or, presumably, of H are the atoms that move most relative to those in Y_5Bi_3 and thereby give the characteristically different buckling of certain layers [2, 18, 19].)

Our conclusions regarding the distribution of M and Y type lattices for the divalent metal pnictides are summarized in Table 1. The Mn_5Si_3-type phases (M) exist for Ca, Sr, Ba, Sm, Eu or Yb with As, Sb, or Bi except for the combinations of As with Ba or Sm. The last two only form $Th_3P_4^-$ or NaCl-type products, respectively, near this stoichiometry with or without hydrogen (the second example was already known [20]). The M examples of Ca_5Bi_3, $Eu_5(Sb,Bi)_3$ and Yb_5Bi_3 are new. (There is some evidence for a deformation of the basic structure type for Eu_5As_3 and Yb_5Sb_3.) The orthorhombic Ca_5Bi_3H is such an excellent hydrogen getter, better than Y metal, that quenching of an M-type sample from 1100 °C in high vacuum is necessary to retain a majority of the latter type. The Yb_5Bi_3 version is the next most difficult to get free of hydrogen

Some hydrogen is also bound in the Mn_5Si_3 structure so that biphasic systems contain $Mn_5Si_3(H_x)$ analogues in equilibrium with $Yb_5Sb_3H_{1-y}$ types. Hydrogen has a constricting effect on both lattices, and the widths of the monophasic regions for each can be qualitatively compared according to the range of lattice constants (or volumes) achieved in each structure type. (These also make evident the hydrogen contamination that was present with most literature reports of M-phases.) Hydrogen variation affects the cell volumes of Y-types from 0.18% (Sr_5Bi_3H, Eu_5Sb_3H) to ~0.46% ($Yb_5(Sb,Bi)_3H$, Ca_5Sb_3H). The exception is $Ca_5Bi_3H_{1-y}$ where the dominant stability of this phase relative to the hexagonal form corresponds to a 1.0% cell volume range, largely from variation of the *a* dimension, as noted before with fluoride [2]. M-structure volume reductions because of interstitial hydrogen range from 0.3% (Sr_5Sb_3) in equilibrium with the Y-phase to 0.6–0.7% for Eu_5As_3 and Sr_5As_3 and 2.1–2.7% for Ca_5As_3 and $Ba_5(Sb,Bi)_3$ where there are no Y-phases in competition. The hydrogen content of the usual Ba is sufficient to give a nearly saturated M phase, ~$Ba_5Sb_3H_{0.5}$, when ordinary conditions are employed.

TABLE 1. A_5Pn_3 and A_5Pn_3H pnictide phases for divalent metals A[a]

A/Pn	As	Sb	Bi
Ca	M	M, Y	***M***, Y
Sr	M	M, Y	M, Y
Ba	[b]	M	M
Sm	[c]	M	M, ***Y***
Eu	M	***M***, Y	***M***, Y
Yb	M	M, Y	***M***, Y

[a] New phases are italics bold face.

[b] Inverse Th_3P_4-type phase only.

[c] NaCl-type phase only [20].

M: Mn_5Si_3-type binary phase; small to moderate hydrogen solution.

Y: $Yb_5Sb_3(H)$-type, substoichiometry possible.

The particularly pervasive hydrogen impurities in these divalent metals certainly merit extra thought and precautions regarding possible effects of hydrogen on compound stability. We have, for example, been unsuccessful in duplicating the synthesis of the novel Ba_5Ga_6 [21] without the inclusion of hydrogen. The yield of a particular phase from a supposedly stoichiometric reaction is an especially important criterion for its correct formulation. Purity problems with the divalent (and other) rare-earth element examples have been noted before [22, 23], but hydrogen–alkaline-earth-metal hazards seem to be known to a much lesser extent [24]. Further results on the foregoing systems will be reported in detail later.

Acknowledgments

We are indebted to David T. Peterson for guidance regarding hydrogen impurities in the alkaline-earth metals. This work was supported by the Office of the Basic Energy Sciences, Materials Sciences Division, DOE. The Ames Laboratory is operated for the US Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

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