Journal of Solid State Chemistry 184 (2011) 1875–1881

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Flux growth of a new cobalt–zinc–tin ternary phase $Co_{7+x}Zn_{3-x}Sn_8$ and its relationship to CoSn

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ARTICLE INFO

Article history:
Received 22 February 2011
Received in revised form
10 May 2011
Accepted 15 May 2011
Available online 26 May 2011

Keywords:
Metal flux growth
Tin flux
Supercell
Eutectic
Crystallography
Solder

ABSTRACT

The intermetallic compound $Co_{7+x}Zn_{3-x}Sn_8$ $(-0.2<x<0.2)$ forms from the reaction of cobalt in zinc/tin eutectic flux. This phase has a new structure type in orthorhombic space group *Cmcm*, with unit cell parameters $a=4.138(1)$ Å, $b=12.593(4)$ Å, and $c=11.639(4)$ Å ($Z=2$; $R_1=0.0301$). Varying the amount of cobalt in the synthesis leads to formation of a superstructure in space group *Pnma*, with lattice parameters $a=12.5908(2)$ Å, $b=11.6298(3)$ Å, and $c=8.2704(2)$ Å ($Z=4$; $R_1=0.0347$). A Co/Zn mixed site and a partially occupied Co site in the *Cmcm* structure order to form the *Pnma* supercell. TGA/DSC studies indicate that the binary phase CoSn initially forms in the flux at 1173 K, and then reacts with the zinc in the cooling solution to form the ternary structure at 823 K. This phase exhibits Pauli paramagnetic behavior.

1. Introduction

Metal fluxes are useful media for exploratory synthesis of intermetallics and Zintl phases and for growth of large single crystals for physical property measurements [1]. Metals commonly used as solvents in flux synthesis are inexpensive and low melting. Tin has been widely used as a flux; reactions in molten tin have led to recent discovery of new phases such as $RESn_{1+x}Ge_{1-x}$ and OsB [2,3]. Tin melts have also enabled the growth of large crystals of known phases, including the $Ba_{1-x}K_xFe_2As_2$ superconductors, which have been of particular interest recently [4,5]. We have been investigating lowering the melting point of tin by combining it with other metals to form eutectic fluxes. The Zn/Sn phase diagram is a simple eutectic system with no binary phases, featuring a eutectic at 15% Zn with a melting point of 473 K [6]. This eutectic is sold commercially for use as a lead-free solder (for example, it is marketed by Indium Corporation as Indalloy 201, recommended for soldering to high aluminum alloys). Interactions of metals with this Zn/Sn melt is therefore of interest to researchers in a number of fields, particularly given the worldwide interest in finding alternatives to lead-based solders [7,8].

In this study, cobalt was reacted in Zn/Sn eutectic to explore the growth of potentially magnetic materials. Complex peritectic behavior is seen during this reaction, similar to that observed for cobalt in pure tin flux (cobalt reacts in tin to form CoSn at high temperatures, which further reacts with the flux as the temperature is lowered, forming $CoSn_2$ and $CoSn_3$) [9]. In Zn/Sn flux, the binary CoSn forms at 1173 K, and then reacts at lower temperatures to form a new ternary phase $Co_{7+x}Zn_{3-x}Sn_8$ $(-0.2<x<0.2)$. Variation in reactant ratio leads to two different structures for the ternary phase, a subcell which crystallizes in the *Cmcm* space group and a supercell, which crystallizes in the *Pnma* space group. These two compounds are also structurally related to the CoSn binary phase.

2. Material and Methods

2.1. Synthesis

Co powder (Alfa-Aesar, 99.8%), Zn powder (Alfa-Aesar, 99.8%), and Sn granules (Alfa-Aesar, 99.9%) were combined in a 2:1.5:8.5 millimolar ratio in an alumina crucible. A second crucible containing silica wool was placed upside down above the reaction crucible to act as a filter during centrifugation. This setup was then placed in a fused silica tube, sealed under vacuum at 10^{-2} Torr, and then heated to 1173 K in 6 h, held at 1173 K for 24 h, cooled to 973 K over 36 h, held there for 24 h, and then cooled to 593 K over 36 h. At 593 K, the sample was inverted and centrifuged to remove the excess molten Zn/Sn flux. The crystals removed from the alumina crucible had a square shaped appearance and were silver colored and reflective.

In order to explore the phase width of this compound, reactions were carried out with different amounts of Co in the Zn/Sn eutectic. Co/Zn/Sn reactions were prepared with millimolar

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doi:10.1016/j.jssc.2011.05.019

ratios y:1.5:8.5, with y varying in increments of 0.5 from 1.0 up to 3.0 mmoles. These reactions were carried out in alumina crucibles as described above. Products of reactions with 1.0 or 3.0 millimoles of Co had a flatter, more plate-like appearance, noticeably different from the more blocky appearance of products of reactions with 2 millimoles of Co.

After the structure of the ternary phase was determined, stoichiometric synthesis was attempted using 3.5 millimoles of Co, 1.5 millimoles of Zn, and 4 millimoles of Sn. These reactants were loaded into an alumina crucible, which was placed in a fused silica tube and sealed under vacuum at 10^{-2} Torr. The ampoule was then heated from 298 to 1173 K in 2 h, held at 1173 K for 6 h, cooled to 300 K in 6 h and removed from the oven.

2.2. Elemental analysis

Elemental analysis was performed on all samples using a JEOL 5900 scanning electron microscope with energy-dispersive X-ray spectroscopy (EDXS) capabilities. Flux-grown crystals from each reaction were affixed to an aluminum SEM puck using carbon tape, and positioned so that flat faces were perpendicular to the electron beam. Samples were analyzed using 30 kV accelerating voltage and an accumulation time of 60 s.

Table 1
Crystallographic parameters for the $Co_{7+x}Zn_{3-x}Sn_8$ subcell and supercell structures.

	$Co_{7.2(1)}Zn_{2.9(1)}Sn_8$ (subcell)	$Co_{6.8(4)}Zn_3Sn_8$ (supercell)
Reactant ratio (Co/Zn/Sn)	2:1.5:8.5	1:1.5:8.5
Formula weight (g/mol)	1556.96	1558.04
Crystal system	orthorhombic	orthorhombic
Space group	*Cmcm*	*Pnma*
a **(Å)**	4.139(1)	12.5908(2)
b **(Å)**	12.593(4)	11.6298(3)
c **(Å)**	11.640(4)	8.2704(2)
Z	2	4
Volume	606.7(3)	1211.02(5)
Density, calc (g/cm^3)	8.585	8.485
Temperature (K)	293	
Radiation	Mo$K\alpha$	
Index ranges	$-5 \le h \le 5$ $-16 \le k \le 16$ $-15 \le l \le 15$	$-20 \le h \le 20$ $-18 \le k \le 15$ $-11 \le l \le 13$
Reflections collected	3318	12,538
Unique data/parameters	430/41	2618/99
μ (mm^{-1})	31.33	30.97
R_1/wR_2[a]	0.0301/0.0728	0.0347/0.0869
R_1/wR_2 (all data)	0.0314/0.0739	0.0580/0.0968
Residual peak/hole (e$^-$Å^{-3})	1.37/−1.72	2.70/−2.75

[a] $R_1=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$; $wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

2.3. X-ray diffraction

For each single crystal experiment, a small single crystal was selected and mounted on a glass fiber using epoxy. Single crystal X-ray diffraction data were collected at room temperature using a Bruker AXS APEX2 CCD diffractometer with a Mo radiation source. Processing of the data was accomplished using the program SAINT. An absorption correction was applied to the data using the SADABS program [10]. Refinement of the structure was performed using the SHELXTL package [11]. X-ray diffraction data were collected for representative crystals from reactions with 1 and 2 millimolar amounts of Co reactant. The crystallographic data collection parameters are summarized in Table 1; atomic positions and bond lengths are listed in Tables 2–4. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247 808 666; e-mail: crysdata@fiz-karlsruhe.dea, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the CSD numbers CSD-422703 (subcell) and CSD-422704 (supercell).

Powder X-ray diffraction was used to explore the possible phase width associated with this compound. Samples of the solid product from each flux synthesis were ground with a small amount of silicon to act as an internal standard to allow accurate determination of unit cell parameters. Powder X-ray diffraction data were collected using an original diffraction setup based on a Huber imaging plate Guinier camera 670 that uses Cu$K\alpha_1$ radiation (λ=1.54060 Å) with a Ge crystal monochromator. The accompanying JADE software was used to analyze the powder patterns. The theoretical powder pattern calculated from the crystal structure was compared to the data for products of reactions at different millimolar ratios (see Supplementary Content, Fig. S1). Refinement for each sample indicated very little change in unit cell parameters. Powder XRD data were also collected on samples of the product of attempted stoichiometric synthesis, and on flux-grown $Co_{7+x}Zn_{3-x}Sn_8$ samples after thermal analysis (to identify decomposition products); see Supplementary Content, Fig. S2.

2.4. Magnetic susceptibility

Magnetic measurements were carried out with a Quantum Design MPMS SQUID magnetometer at temperatures between 2 and 300 K. Crystals were ground into a fine powder and put into a capsule with the cap inverted to insure that the powder was tightly pressed and immobile. The capsule was placed in a plastic straw and placed into the magnetometer. Temperature dependent susceptibility data from 2 to 300 K were collected at applied fields of 500–1000 G, and field dependence data was collected at 3 K. A superconducting transition was observed at 3.7 K at low applied fields. This indicated a Sn impurity (likely from residual traces of flux) which was corrected for by increasing the applied field to 1000 G, above the critical field for Sn.

Table 2
Atom positions for the *Cmcm* subcell structure of $Co_{7.2(1)}Zn_{2.9(1)}Sn_8$.

Atom	Wyckoff site	Occupancy	*x*	*y*	*z*	U_{eq}[a]
Sn(1)	8*g*	0.505(2)	0.4373(2)	0.48324(8)	¼	0.0076(3)
Sn(2)	8*f*		0	0.34253(4)	0.02024(5)	0.0114(2)
Sn(3)	4*c*		0	0.70920(6)	0.25	0.0112(2)
Co(1)	8*f*		0	0.16053(8)	0.12905(8)	0.0110(3)
Co(2)	8*f*	0.535(4)	0	0.5204(1)	0.1357(4)	0.0059(4)
Zn(3)/Co(3)	4*c*	0.45(5)/0.55(5)	0	0.3430(1)	0.25	0.0082(5)
Zn(1)	4*a*		0	0	0	0.0092(3)

[a] U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.