Inorg. Chem. **2003**, *42*, 3183–3186

Inorganic Chemistry
Article

NaCl/KCl Flux Single Crystal Growth and Crystal Structure of the New Quaternary Mixed-Metal Pnictide: $BaCuZn_3As_3$

Tadashi C. Ozawa and Susan M. Kauzlarich*

Department of Chemistry, One Shields Avenue, University of California, Davis, California 95616

Received January 20, 2003

Synthesis and crystal structure of a new compound, $BaCuZn_3As_3$, are reported. Single crystals of $BaCuZn_3As_3$ are synthesized via NaCl/KCl flux reaction in a sealed fused silica ampule. Its elemental composition has been determined to be Ba/Cu/Zn/As = 1.03(4):1(0):2.91(6):2.98(3), suggesting $BaCuZn_3As_3$ as the chemical formula. The structure of $BaCuZn_3As_3$ has been determined by X-ray diffraction. It crystallizes in the orthorhombic *Cmcm* space group with $a = 4.2277(3)$ Å, $b = 12.970(1)$ Å, and $c = 12.011(1)$ Å at $T = 90.7$ K, and it exhibits a columnar structure along the *a*-axis. This structure is isotypic to β-$BaCu_4S_3$ but highly distorted. β-$BaCu_4S_3$ is considered to be a layered structure whereas $BaCuZn_3As_3$ is a three-dimensional network.

Introduction

Recently, several 3d-metal pnictides have been discovered to exhibit practical physical properties such as magnetoresistance[1,2] and thermoelectricity, [3−6] thus, attracting growing interests. Among pnictides, mixed-metal compounds are of particular interest because their physical properties such as magnetic properties can be controlled by the selection of metal combinations.[7] In the course of our exploration of a Cu analogue of a layered mixed-metal pnictide oxide compound, $Ba_2(MnO_2)(Zn_2As_2)$,[8] as a new possible candidate for a new high-T_c superconductor,[9] we have discovered a new quaternary mixed-metal pnictide, $BaCuZn_3As_3$. This paper reports synthesis, elemental composition analysis, and structure characterization of the new compound, $BaCuZn_3As_3$, as well as its comparison with other Cu containing pnictides and an isotypic compound, $BaCu_4S_3$.[10]

Experimental Procedures

Synthesis. Single crystals of $BaCuZn_3As_3$ were grown by NaCl/KCl flux reaction.[11−14] Charge was prepared by heating 2:1:2:2 mol ratio of BaO (prepared by the thermal decomposition of $BaCO_3$ (J. Matthey, 99.999%)), Cu (Cerac, 99.999%), Zn (Fisher Scientific, 99.4%), and As (J. Matthey, 99.999%) at 1000 °C under $^1/_5$ atm of Ar.[15] This ratio of starting material was used because the reaction was originally intended to synthesize a hypothetical compound, $Ba_2(CuO_2)(Zn_2As_2)$.[8] The charge and flux (1:1 mol ratio of NaCl and KCl) were mixed at the 1 (charge):4 (flux) mass ratio, placed in an alumina boat, sealed in a fused silica ampule under $^1/_5$ atm of Ar, heated to 860 °C, and cooled to room temperature at 15 °C/h.

Electron Microprobe Analysis. The elemental composition of the sample was determined by electron microprobe analysis. Secondary electron map and the X-ray fluorescence map were obtained on a Cameca SX electron microprobe using the acceleration voltage of 15.0 kV and beam current of 0.0363 mA. $Na[AlSi_3O_8]$ (albite, 8.5 wt % Na), $CuFeS_2$ (chalcopyrite, 34.62 wt % Cu), Zn metal, InAs (39.49 wt % As), biotite (1.11 wt %

---

* To whom correspondence should be addressed. E-mail address: smkauzlarich@ucdavis.edu.

(1) Chan, J. Y.; Kauzlarich, S. M.; Klavins, P.; Shelton, R. N.; Webb, D. J. *Phys. Rev. B* **1998**, *57*, R8103.
(2) Webb, D. J.; Cohen, R.; Klavins, P.; Shelton, R. N.; Chan, J. Y.; Kauzlarich, S. M. *J. Appl. Phys.* **1998**, *83*, 7192.
(3) Tang, X. F.; Chen, L. D.; Goto, T.; Hirai, T.; Yua, R. Z. *Wuli Xuebao* **2000**, *49*, 1123.
(4) Chen, L. D.; Kawahara, T.; Tang, X. F.; Goto, T.; Hirai, T.; Dyck, J. S.; Chen, W.; Uher, C. *J. Appl. Phys.* **2001**, *90*, 1864.
(5) Tang, X.; Chen, L.; Goto, T.; Hirai, T. *J. Mater. Res.* **2001**, *16*, 837.
(6) Kawaharada, Y.; Kurosaki, K.; Uno, M.; Yamanaka, S. *J. Alloys Compd.* **2001**, *315*, 193.
(7) Ozawa, T. C.; Kauzlarich, S. M.; Bieringer, M.; Wiebe, C. R.; Greedan, J. E.; Gardner, J. S. *Chem. Mater.* **2001**, *13*, 973.
(8) Ozawa, T. C. Synthesis and Physical Property Characterization of Layered Transition Metal Pnictide-Oxide Compounds. Ph.D. Dissertation, University of California at Davis, 2001.
(9) Cava, R. J.; Zanbergen, H. W.; Krajewski, J. J.; Siegrist, T.; Hwang, H. Y.; Batlogg, B. *J. Solid State Chem.* **1997**, *129*, 250.
(10) Iglesias, J. E.; Pachali, K. E.; Steinfink, H. *Mater. Res. Bull.* **1972,** *7*, 1247.
(11) Düenner, J.; Mewis, A.; Roepke, M.; Michels, G. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1523.
(12) Brylak, M.; Möller, M. H.; Jeitschko, W. *J. Solid State Chem.* **1995**, *115*, 305.
(13) Nientiedt, A. T.; Jeitschko, W.; Pollmeier, P. G.; Brylak, M. *Z. Naturforsch.* **1997**, *52b*, 560.
(14) Nientiedt, A. T.; Jeitschko, W. *Inorg. Chem.* **1998**, *37*, 386.
(15) Ozawa, T.; Olmstead, M. M.; Brock, S. L.; Kauzlarich, S. M.; Young, D. M. *Chem. Mater.* **1998**, *10*, 392.

10.1021/ic034061k CCC: $25.00

Cl), $BaSO_4$ (Barite, 58.84 wt % Ba), and (K, Na)[$AlSi_3O_8$] (orthoclase, 12.5 wt % K) were used as the standards for Na, Cu, Zn, As, Cl, Ba, and K, respectively.

Single Crystal X-ray Diffraction. X-ray diffraction data were acquired using a SMART 1000 Bruker AXS CCD diffractometer equipped with a CRYO COOLER low temperature apparatus (CRYO INDUSTRIES of America, Inc.). A dark silver thin rectangular plate shaped crystal (0.219 mm × 0.028 mm × 0.006 mm) was mounted in the cold nitrogen gas stream (91(2) K) of the diffractometer. X-rays were generated at 50 kV and 40 mA using a Mo target and graphite monochromator. A total of 9266 reflections were collected for the full sphere using a 0.3° ω-scan with a 20 s exposure. The crystal structure was solved by direct methods using SHELXS-97[16] and refined utilizing the SHELXL-97 software package[16] using 616 unique reflections and 30 parameters.

Results and Discussions

Single crystal products from the flux reaction were washed with deionized water and ethanol in order to remove the flux from their surface. The crystals have a lustrous dark silver color and thin rectangular plate shape. Most crystals have an approximate length of ~0.2−0.3 mm. Decomposition of the sample in air was not observed over the period of a few months.

The result of electron microprobe analysis indicates that the molar elemental ratio (normalized to Cu content) of the product is Ba/Cu/Zn/As = 1.03(4):1(0):2.91(6):2.98(3), suggesting $BaCuZn_3As_3$ as the chemical formula, and no inclusion of Na, K, and Cl was observed. This elemental ratio agrees with a simplistic charge balancing of the compound with expected oxidation states of Ba, Cu, Zn, and As being 2+, 1+, 2+, and 3−, respectively, yielding the neutral total charge of the compound.

The crystal structure of the product was determined by single crystal X-ray diffraction. $BaCuZn_3As_3$ crystallizes in the orthorhombic space group *Cmcm* ($Z = 4$). Refinement of the single crystal X-ray diffraction data was performed using three models:

model I	(0.50000	0.03710	0.35994)	site occupied only by Zn
	(0.0000	0.16823	0.44349)	site shared between Cu and Zn
model II	(0.50000	0.03710	0.35994)	site shared between Cu and Zn
	(0.0000	0.16823	0.44349)	site shared between Cu and Zn
model III	(0.50000	0.03710	0.35994)	site shared between Cu and Zn
	(0.0000	0.16823	0.44349)	site occupied only by Zn

For the site occupancy of all these models, the linear restraint, % Cu occupancy + % Zn occupancy = 100% occupancy, was employed. The models I and II converged with the 100% of Zn occupancy of (0.0000 0.16823 0.44349) site within less than three times their estimated standard deviations. However, model II converged with smaller *R*-factor than that of model II suggesting that (0.50000 0.03710 0.35994) site is shared between Cu and Zn. Thus, the final refinement was performed using model III. This model provided the *R*-factor smaller than that from model I by about 3% suggesting that it is the best model. The refinement of the site occupancy factors indicates that the (0.50000 0.03710 0.35994) site is occupied by both Cu (47.4(8)%) and Zn (52.6(8)%). Crystallographic parameters and atomic coordinates along with equivalent isotropic displacement parameters from the refinement of model III are summarized in Tables 1 and 2, respectively.

Table 1. Crystal Data and Structure Refinement Data for $BaCuZn_3As_3$

fw	621.82
temp	91(2) K
space group	*Cmcm* (No. 63)
unit cell dimensions	$a = 4.2277(3)$ Å $b = 12.9700(11)$ Å $c = 12.0118(10)$ Å
V	658.65(9) Å^3
Z	4
d (calcd)	6.271 g/cm^3
abs coeff	34.674 mm^{-1}
F(000)	1096
cryst size	0.22 × 0.03 × 0.01 mm^3
final R indices [$I > 2\sigma(I)$]	R1 = 0.0221, wR2 = 0.0477
R^a indices (all data)	R1 = 0.0284, wR2 = 0.0504

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (0.0305P)^2 + 28.39P]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)^a for $BaCuZn_3As_3$

	x	y	z	U(eq)
Ba(1)	0.00000	0.18418(4)	0.75000	8.06(13)
As(1)	0.00000	0.09032(6)	0.25000	7.26(17)
As(2)	0.50000	0.13221(4)	0.54890(1)	7.64(14)
Cu(1)/Zn(1)	0.50000	0.03710(5)	0.35994(6)	9.89(16)
Zn(2)	0.00000	0.16823(6)	0.44349(6)	10.22(16)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The oxidation state of Cu is expected to be 1+ for two reasons. First, the pnictide anionic environment is not electronegative enough to induce 2+ or higher state of Cu, and to our best knowledge, such a compound has never been discovered.[11,12,17−21] Second, charge balancing of the chemical formula suggested by elemental ratio from electron microprobe experiment requires Cu to be in the 1+ state as $Ba^{2+}Cu^{1+}(Zn^{2+})_3(As^{3-})_3$. Similar charge balancing was also found in other mixed-metal pnictides such as $YbZnCuP_2$[22] and $YbMnCuP_2$[23] where the oxidation state of Cu is also 1+ and those of the other 3d-metals, Zn and Mn, are 2+. In order to distinguish these two d-metal sites, (0.50000 0.03710 0.35994) and (0.0000 0.16823 0.44349), are designated as Cu(1)/Zn(1) and Zn(2) sites, respectively, in this paper.

The [100] projection of the structure is shown in Figure 1. This structure is isotypic to β-$BaCu_4S_3$;[10] however, structures of $BaCuZn_3As_3$ and β-$BaCu_4S_3$ appear significantly different at first glance. The former has a three-dimensional network structure, and the latter has a layered structure. The

---

(16) Sheldrick, G. M., *SHELXTL*, version 5.10; Bruker AXS Inc.: Madison, WI, 1997.

(17) Mewis, A. *Z. Naturforsch.* **1980**, *35b*, 141.

(18) Cava, R. J.; Siegrist, T.; Carter, S. A.; Krajewski, J. J.; Peck, W. F. J.; Zandbergen, H. W. *J. Solid State Chem.* **1996**, *121*, 51.

(19) Chykhrij, S. I.; Loukashouk, G. V.; Oryshchyn, S. V.; Kuz'ma, Y. B. *J. Alloys Compd.* **1997**, *248*, 224.

(20) Wang, M.; McDonald, R.; Mar, A. *J. Solid State Chem.* **1999**, *147*, 140.

(21) Jemetio, J.-P.; Doert, T.; Rademacher, O.; Böttcher, P. *J. Alloys Compd.* **2002**, *338*, 93.

(22) Klüfers, P.; Mewis, A. *Z. Kristallogr.* **1979**, *149*, 211.

(23) Mewis, A. *Z. Naturforsch.* **1980**, *35b*, 939.

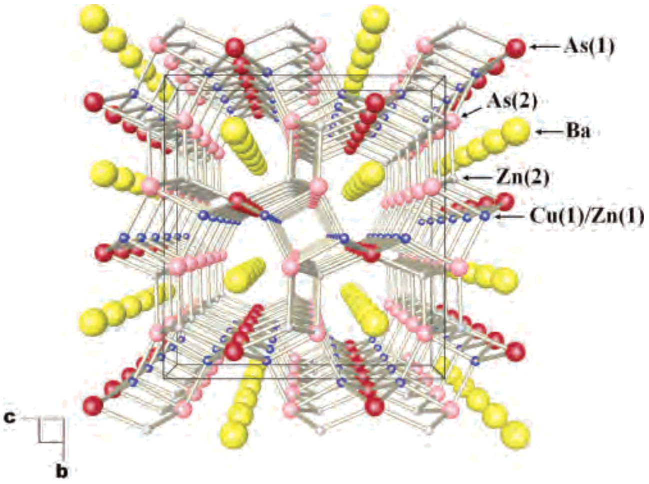

Figure 1. Perspective view of the $BaCuZn_3As_3$ structure.

main factor for this difference is the atomic position of Zn(2) along the *b*-axis. The fractional *y*-coordinate of this site is 0.16823(6) whereas that of the equivalent position of Cu in β-$BaCu_4S_3$ is 0.1076(2).[10] With this Zn(2) position, Zn(2) forms Zn(2)−As(2) bonds (2.5900(9) Å) in the case of $BaCuZn_3As_3$. On the other hand, the equivalent Cu−S distance in the β-$BaCu_4S_3$ structure would be greater than 3.3 Å, breaking the three-dimensional network structure into a layered one. As a consequence, the coordination environment is quite different between these two structures. Thus, the structure of $BaCuZn_3As_3$ can be classified as a highly distorted β-$BaCu_4S_3$ type. The GIF-animation depicting these structural differences between $BaCuZn_3As_3$ and β-$BaCu_4S_3$ is shown at our website.[24]

The view in Figure 1 depicts the infinite columns through which Ba^{2+} aligns linearly along the *a*-axis reminiscent of $BaZn_2As_2$[25] and $Eu_4Ga_8Ge_{16}$ structures.[26] These columns consist of a series of horseshoe shaped linkages, Cu(1)/Zn(1)−As(2)−Zn(2)−As(1)−Zn(2)−As(2)−Cu(1)/Zn(1), each linked by a backbone chain of As(1) along the *a*-axis (Figure 2). This column structure including Cu is a quite peculiar feature of this compound because in a majority of pnictide compounds Cu usually forms Cu_2Pn_2 (Pn = pnicogen) two-dimensional layers.[11,12,17,19−21] In this column structure, the short Cu(1)/Zn(1)−Cu(1)/Zn(1) distance of 2.6412(14) Å suggests the existence of significant metal−metal interaction.[27]

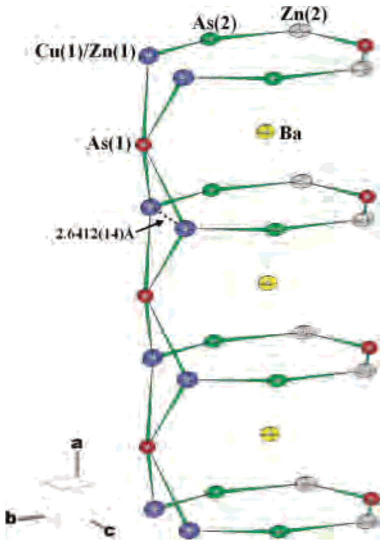

Figure 2. Column substructure of $BaCuZn_3As_3$ depicting the coordination of Ba depicting 90% thermal vibrational ellipsoids.

Table 3. Selected Interatomic Distances (Å) for $BaCuZn_3As_3$

Ba(1)⋯Cu(1)/Zn(1)	3.8013(7)
Ba(1)⋯Cu(1)/Zn(1)	3.8486(9)
Ba(1)⋯Zn(2)	3.6790(6)
Ba(1)⋯Zn(2)	3.6875(8)
Ba(1)⋯As(1)	3.5603(10)
Ba(1)⋯As(1)	3.6086(8)
Ba(1)⋯As(2)	3.2799(5)
Cu(1)/Zn(1)⋯Cu(1)/Zn(1)	2.6412(14)
Cu(1)/Zn(1)⋯Zn(2)	2.8927(7)
Cu(1)/Zn(1)−As(1)	2.5863(5)
Cu(1)/Zn(1)−As(2)	2.4538(9)
Cu(1)/Zn(1)−As(2)	2.5833(9)
Zn(2)−As(1)	2.5343(8)
Zn(2)−As(2)	2.5079(5)
Zn(2)−As(2)	2.5900(9)

Important distances in the structure are given in Table 3, and the polyhedra about Cu(1)/Zn(1), Zn(2), As(1), and As(2) are illustrated in Figure 3. Cu(1)/Zn(1) is four coordinated with two As(1) and two As(2) (Figure 3a). This coordination of a 3d-metal with four anions is common in pnictide compounds.[7] In this environment, three of Cu(1)/Zn(1)−As(1) distances are almost the same whereas the other distance is about 0.13 Å shorter. On the other hand, Zn(2) is one coordinated with As(1) and three coordinated with As(2) (Figure 3b). Among three Zn(2)−As(2) distances, two are 2.5079(5) Å and the other is 2.5900(9) Å, and the Zn(2)−As(1) distance is 2.5343(8) Å. The average Zn(2)−As distance is 0.25350 Å which is slightly smaller than that of Cu(1)/Zn(1)−As (0.2552 Å). This difference is a probable indication that (0.50000 0.03710 0.35994) site is more likely to host Cu^{1+} than (0.0000 0.16823 0.44349) site because the ionic radius of Cu^{1+} is slightly larger than that of Zn^{2+}.[28] Consequently, two of the As sites also have quite different coordination environments. As(1) is four coordinated with Cu(1)/Zn(1) and two coordinated with Zn(2) (Figure 3c). As(1) and Cu(1)/Zn(1) form a distorted square pyramidal configuration with As(1) as the apical atom. Here, two of the Cu(1)/Zn(1)−As(1)−Cu(1)/Zn(1) angles are 109.64(3)°, and the other two are 61.41(3)° even though all As(1)−Cu(1)/Zn(1) distances are 2.5863(5) Å. Also, two of the As(1)−Zn(2) distances are equal (2.5343(8) Å). On the other hand, As(2) is two coordinated with Cu(1)/Zn(1) and three coordinated with Zn(2) (Figure 3d). Two of the As(2)−Cu(1)/Zn(1) distances are 2.4538(9) and 2.5833(9) Å, and two of the As(2)−Zn(2) distances are both 2.5079(5) Å. Finally, the other As(2)−Zn(2) distance is 2.5900(9) Å. It is this linkage which is missing in the β-$BaCu_4S_3$ structure.[10]

---

(24) Ozawa, T. C.; Kauzlarich, S. M. http://www-chem.ucdavis.edu/groups/kauzlarich/si/bacuznas/.
(25) Klüfers, P.; Mewis, A. *Z. Naturforsch.* **1978**, *33b*, 151.
(26) Bryan, J. D.; Stucky, G. D. *Chem. Mater.* **2001**, *13*, 253.
(27) Ouammou, A.; Mouallem-Bahout, M.; Peña, O.; Halet, J.-F.; Saillard, J.-Y.; Carel, C. *J. Solid State Chem.* **1995**, *117*, 73.
(28) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

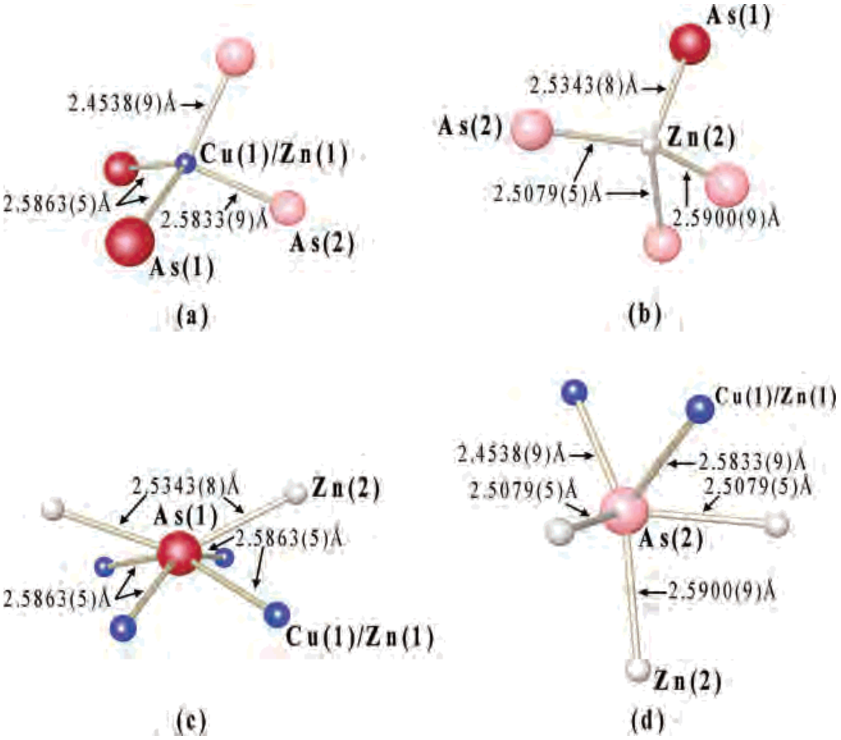

Figure 3. Polyhedra about (a) Cu(1)/Zn(1), (b) Zn(2), (c) As(1), and (d) As(2) in the $BaCuZn_3As_3$ structure.

Except the tetrahedral coordination of Cu(1)/Zn(1), atomic coordination in this structure is distinct compared with that of other pnictide families.[11,12,17,19−21] In this respect, we expect this compound to exhibit quite different physical properties from other 3d-metal pnictides.

Conclusions

We have synthesized a new quaternary pnictide, $BaCuZn_3As_3$, via a NaCl/KCl flux route, and its crystal structure was determined. Pnictide compounds tend to exist in various combinations of 3d-metals for a given structure type. Thus, it will be worthwhile to explore the synthesis and characterization of other 3d-metal analogues of this structure type in order to search for new compounds. Furthermore, investigation of the physical property of this new compound as well as other possible 3d-metal analogues would be a cardinal approach to discover a material with interesting and useful properties as well as to further the understanding of chemistry and physics of intermetallic compounds.

Acknowledgment. We thank M. M. Olmstead for assistance in single crystal X-ray diffraction work, and the X-ray analytical lab housed in the Geology Department, UC Davis, for microprobe analysis. In addition, we acknowledge one of the reviewers for pointing out the isotypic structural relation between $BaCuZn_3As_3$ and $BaCu_4S_3$. This research was supported by NSF Grant DMR-9803074, and the Bruker SMART 1000 diffractometer was funded in part by NSF Instrumentation Grant CHE-9808259.

Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034061K