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$A_2Zn_3As_2O_2$ (A = Ba, Sr): A Rare Example of Square Planar Zinc

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Layered transition metal oxides are of interest because of the variety of properties which they exhibit. These include low-dimensional magnetic and electronic properties[1] and superconductivity.[2] Compared to the huge number of layered copper oxide compounds, there are relatively few layered oxides containing other first-row transition metals. We have been investigating a series of compounds, $A_2Mn_3Pn_2O_2$ (A = Sr, Ba; Pn = P, As, Sb, Bi),[3,4] containing Mn–O planes. These compounds crystallize in the $Sr_2Mn_3As_2O_2$ structure type ($I4/mmm$) and are members of a small class of compounds designated as pnictide oxides.[3-5] In the majority of pnictogen oxygen compounds, the pnictogen is in the +3 or +5 oxidation state and there is Pn–O bonding. However, in these compounds both pnictogen and oxygen are anions. This unusual class of compounds has received very little attention.

To date, the $Sr_2Mn_3As_2O_2$ structure type, which consists of alternating metal pnictide and metal oxide planes, has been observed only for Mn. This is suprising considering the metal pnictide planes are isostructural with those in compounds of the $ThCr_2Si_2$ structure type, of which over 400 compounds are known.[6] The $ThCr_2Si_2$ structure type is observed for a variety of transition metals with different d electron counts and oxidation states. One might expect the $Sr_2Mn_3As_2O_2$ structure type to show a versatility similar to that observed in the $ThCr_2Si_2$ structure type. There are a number of examples of similar or identical solid-state structures for Mn^{2+} and Zn^{2+} compounds.[7] Thus, a logical starting place for the investigation of the electronic requirements of this structure type is Zn. This paper describes the synthesis and structure of the first new compounds which crystallize in this structure type with a transition metal other than manganese. These new compounds, $Ba_2Zn_3As_2O_2$ and $Sr_2Zn_3As_2O_2$, have further significance in that they contain zinc in a square planar arrangement of oxygen, a rare geometry for zinc.

Experimental Section

Synthesis. The compound $Ba_2Zn_3As_2O_2$ was synthesized by heating a pressed pellet of BaO, Zn, and As (2:3:2) in an alumina boat sealed in quartz under argon at 1100 °C for 1 week. A cooling rate of 5 °C/h yielded highly reflective silver crystals of $Ba_2Zn_3As_2O_2$ which could be broken from the melt. Grinding of the melt resulted in a black powder. The yield of $Ba_2Zn_3As_2O_2$, estimated from X-ray powder diffraction data, was 70%. The only other crystalline product was $BaZn_2As_2$.[8] X-ray fluorescence on crystals of $Ba_2Zn_3As_2O_2$ confirmed the presence of Ba, Zn, and As. No other elements were detected.

$Sr_2Zn_3As_2O_2$ was made in a similar manner using SrO, Zn, and As and heating to 1000 °C. At these temperatures, silver crystals of Zn_3As_2 transport to the cool end of the tube. Polycrystalline chunks and a black powder remain in the boat. The material in the boat consists of $Sr_2Zn_3As_2O_2$ (90%) and $SrZn_2As_2$[9] (10%) (yields estimated from X-ray powder diffraction data).

X-ray Guinier Powder Diffraction. The materials were ground and placed on a piece of cellophane tape with NBS silicon as a standard. X-ray data were obtained using a focusing Enraf-Nonius Guinier camera equipped with a silica monochromator to give Cu $K\alpha_1$ radiation (λ = 1.540 562 Å). The powder patterns were indexed using single-crystal information from $Ba_2Zn_3As_2O_2$ and $Sr_2Mn_3As_2O_2$.[3] The lattice constants a = 4.2202(3), c = 19.713(4) Å (Ba) and a = 4.0954(7), c = 18.918(4) Å (Sr) were determined from a standard least-squares refinement.

Resitivity Measurements. Temperature-dependent four-probe resistivity measurements were performed on irregularly shaped pieces obtained from the reaction melt. The sample was placed on a small piece of alumina, and four 0.002 in. diameter platinum leads were attached by means of silver epoxy. Temperature-dependent dc resistivity was measured from 15 to 300 K in 5 K increments. The resistivity apparatus has been described in detail previously.[10] Minimization of thermal voltages was achieved by reversal of current bias. All samples exhibited ohmic behavior.

Single-Crystal X-ray Structure Determination. A silver platelet crystal of $Ba_2Zn_3As_2O_2$ (0.24 × 0.10 × 0.02 mm) was mounted on a glass fiber, and X-ray data were obtained on a Siemens R3m/v diffractometer equipped with a graphite monochromator and a modified LT-1 low-temperature apparatus. $Ba_2Zn_3As_2O_2$ crystallizes in the tetragonal space group $I4/mmm$ with a = 4.206(1) Å, c = 19.665(6) Å, and Z = 2. The symmetry and I centering were verified by axial photographs and systematic extinctions, respectively. Half of a sphere of data, to $2\theta_{max} = 60°$, was collected (ω scans, 2°/min, 1025 reflections, 193 unique). The structure was solved using atom positions from $Ba_2Mn_3As_2O_2$.[3] The data were corrected for absorption using the semiempirical correction XEMP[11] and the empirical correction XABS2,[12] and the data were refined using SHELXL-93.[13] Neutral-atom scattering factors were those of Cromer and Waber.[14] For 14 parameters, R1 = 2.54% and wR2[13] = 4.77% based on all reflections. The structure was also refined in the tetragonal space groups $I\bar{4}m2$, $I\bar{4}2m$, $I4mm$, and $I422$. In all cases, similar results were obtained, and therefore the structure is reported in the highest symmetry space group $I4/mmm$. Table 1 lists crystallographic parameters, and Table 2 lists atomic coordinates and isotropic thermal parameters. Interatomic distances are included in the caption to Figure 1. The rest of the crystallographic data are available as supplementary material.

Results and Discussion

Both $Ba_2Zn_3As_2O_2$ and $Sr_2Zn_3As_2O_2$ have been synthesized and characterized by Guinier X-ray powder diffraction techniques. Room-temperature lattice parameters are a = 4.2202(3), c = 19.713(4) Å for $Ba_2Zn_3As_2O_2$ and a = 4.0954(7), c = 18.918(4) Å for $Sr_2Zn_3As_2O_2$. An X-ray structure determination has been done on crystals of $Ba_2Zn_3As_2O_2$. However, to date, attempts to obtain single crystals of $Sr_2Zn_3As_2O_2$ have been unsuccessful. In addition, attempts to synthesize $A_2Zn_3Sb_2O_2$ (A = Sr, Ba) or the Cd analogues $A_2Cd_3Pn_2O_2$ (A = Sr, Ba; Pn = As, Sb) have also failed. The primary products in these reactions are the ternary

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(1) (a) Examples include intercalation compounds[1b] and the oxides of the K_2NiF_4 structure type, such as La_2NiO_4.[1c] (b) Gamble, F. R.; Geballe, T. H. In *Treatise on Solid State Chemistry*; Hanny, N. B., Ed.; Plenum: New York, 1976; Vol. 3, pp 106–166. (c) Buttrey, D. J.; Honig, J. M.; Rao, C. N. R. *J. Solid State Chem.* **1986**, *64*, 287.

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(7) (a) Examples of solid-state systems in which Mn^{2+} and Zn^{2+} form similar or identical structures include AM_2P_2 (A = Ca, Sr, Ba; M = Mn, Zn)[7b] and $AMPn_2$ (A = Ca, Sr, Ba; M = Mn, Zn; Pn = Sb, Bi).[7c] (b) Mewis, A. *Z. Naturforsch., B* **1978**, *33*, 606. (c) Brechtel, E.; Cordier, G.; Schäfer, H. *J. Less-Common Met.* **1981**, *79*, 131.

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(13) Sheldrick, G. M. *J. Appl. Crystallogr.*, in preparation. wR2 obtained from SHELXL-93 is based on F^2; its value is typically about twice the value obtained for R_w based on F.

(14) Neutral-atom scattering factors and corrections for anomalous dispersion were from: *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

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Table 1. Crystallographic Parameters for $Ba_2Zn_3As_2O_2$

fw = 652.63
space group = $I4/mmm$ (No. 139)
$a = 4.206(1)$ Å
$c = 19.665(6)$ Å
$V = 347.8(2)$ Å^3
$Z = 2$
$\rho_{calcd} = 6.232$ g cm^{-3}
$T = -143$ °C
radiation = Mo Kα ($\lambda = 0.710\,73$ Å)
$\mu = 306.99$ cm^{-1}
rel range of transm factors = 0.3–1.0
R1[a] = 0.025
wR2[b] [$w = 1/\sigma^2(F_o^2)$] = 0.048

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ based on all unique reflections. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ based on all unique reflections.

Table 2. Atomic Coordinates and Isotropic Equivalent Thermal Parameters (Å^2 × 10^4) for $Ba_2Zn_3As_2O_2$

atom	x	y	z	U[a]
Ba	0	0	0.41117(2)	146(2)
Zn(1)	0	0	0	190(3)
Zn(2)	0	0.5	0.25	155(2)
As	0	0	0.17413(3)	145(2)
O	0	0.5	0	322(14)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

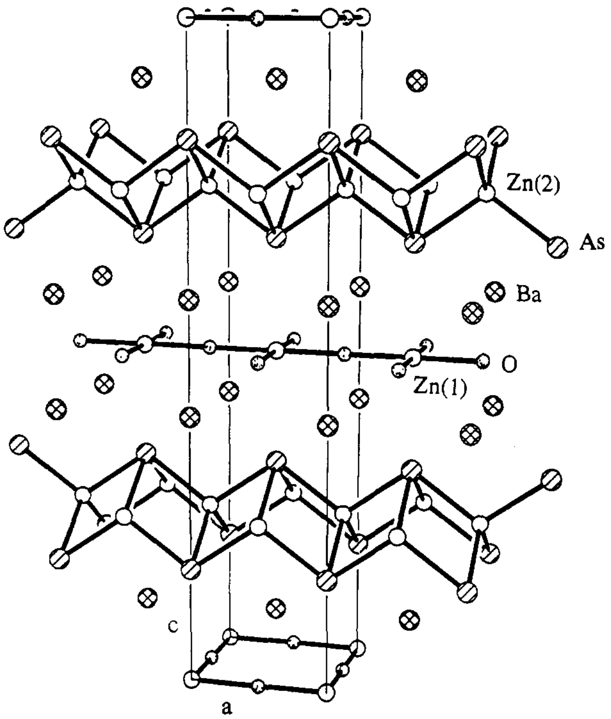

Figure 1. View showing the unit cell of $Ba_2Zn_3As_2O_2$. Selected distances (Å): Zn(1)–O = 2.1030(5), Zn(1)–As = 3.4342(6), Zn(2)–As = 2.5785(6), Zn(2)–Zn(2) = 2.9737(7), Ba–O = 2.7339(5), Ba–As = 3.4142(7).

compounds AM_2Pn_2 (A = Sr, Ba; M = Zn, Cd; Pn = As, Sb).[9,15] We are currently exploring a number of different synthetic conditions for these analogues as well as other transition metal compounds in order to prepare new compounds of this structure type.

A view of the unit cell of $Ba_2Zn_3As_2O_2$ is presented in Figure 1. Important interatomic distances are provided in the figure caption. The structure is composed of alternating layers of $Zn_2As_2^{2-}$ and ZnO_2^{2-} anionic nets separated by the Ba cations. The Ba cation sits in a square antiprism composed of four As atoms from the $Zn_2As_2^{2-}$ layer and four O atoms from the ZnO_2^{2-} layer. The $Zn_2As_2^{2-}$ nets are of the $ThCr_2Si_2$ structure type. They are built up of a square net of Zn atoms which are capped alternatively above and below the plane by As atoms to form edge-sharing $ZnAs_{4/4}^-$ tetrahedrons. The Zn–As bond distance in this compound is 2.5785(6) Å, which is in the range expected for tetrahedral $ZnAs_4$ units (2.501–2.624 Å for $BaZn_2As_2$[8] and 2.390–2.880 Å for α-Zn_3As_2[16]). It is interesting to note that neither of the AZn_2As_2 (A = Ba, Sr) compounds crystallizes in the $ThCr_2Si_2$ structure type.[8,9] The Zn–O distance in the ZnO_2^{2-} layer is 2.1030(5) Å, which is an intermediate bond distance compared to zinc oxide distances in tetrahedral and octahedral coordinations. These distances range from 1.92 Å in $BaZnO_2$[17] (tetrahedral) to 2.123 Å in $Zn_2Mo_3O_8$[18] (octahedral). There are two $Zn_2As_2^{2-}$ planes in the unit cell related by a mirror plane so that one of the capping As atoms from each layer is pointing toward the Zn atom of the interpenetrating ZnO_2^{2-} layer. The long distance of 3.4342(6) Å precludes any Zn–As bonding between the two different layers. Therefore, in the ZnO_2^{2-} layer, Zn is in a square planar geometry of four O atoms, not a distorted octahedral geometry. This is a rare example of zinc in a square planar geometry and the first example, to our knowledge, of square planar zinc in an extended structure. Temperature-dependent resistivities of irregularly shaped pieces of $A_2Zn_3As_2O_2$ obtained from the melt indicate that both compounds are semiconductors.

X-ray crystal structures of complexes of square planar zinc are few. The zinc coordination in porphyrins and phthalocyanines is restricted by the ligand. However, because of the tendencies of zinc porphyrins and phthalocyanines to take on a fifth ligand, there are only a handful of crystal structures of four-coordinate zinc complexes with these ligands.[19] The compound bis(glycinyl)zinc is also reported to be square planar;[20] however, the structure has never been completely solved.[21] It is surprising that it is possible to make zinc in the sterically unfavorable square planar geometry at the temperature (1100 °C) at which $Ba_2Zn_3As_2O_2$ is formed. Clearly, the energy afforded by the lattice is sufficient to overcome any destabilizing influence the square planar zinc may have.

In conclusion, these compounds provide the first evidence for electronic versatility in the $Sr_2Mn_3As_2O_2$ structure type. In addition, this structure type accommodates Zn in an unusual geometry as well as in unusual layered nets. Aside from the novelty of square planar zinc, the $Zn_2As_2^{2-}$ layers are unique in their own right because the corresponding ternary compounds AZn_2As_2 (A = Sr, Ba) do not crystallize in the $ThCr_2Si_2$ structure type.

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Supplementary Material Available: Tables of crystallographic parameters and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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