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Synthesis and Structure of a New Layered Pnictide Oxide Containing Close Mn–Mn Interactions: $Ba_2Mn_2As_2O$

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The discovery of the copper-containing high-T_c superconductors has generated renewed interest in layered metal oxide compounds. However, there has been little investigation of systems containing metals other than copper, although these compounds are of interest because they frequently demonstrate low-dimensional, magnetic and electronic properties.[1] Despite the fact that there are a large number of structures with Cu–O layers, there are relatively few structures with Mn–O layers. One example is the manganese pnictide oxide system in which only two phases are known: the $A_2Mn_3Pn_2O_2$ (A = Sr, Ba; Pn = P, As, Sb, Bi)[2,3] series of compounds, which crystallize in the tetragonal space group $I4/mmm$, and the compounds $Ba_2Mn_2Sb_2O$ and $Ba_2Mn_2Bi_2O$,[4] which are hexagonal ($P6_3/mmc$). While studying the syntheses and properties of the tetragonal compounds[3], we have discovered a layered compound, $Ba_2Mn_2As_2O$, which represents a new structure type.

The compound was synthesized by combining Ba, Mn, As, and As_2O_3 in a molar ratio of 2:3:2/3:2/3. The reactants were sealed under argon in an Nb container which was subsequently sealed in a quartz ampule under a partial atmosphere of argon. The mixture was heated at 1250 °C for 24 h. The products were examined under an atmosphere of nitrogen with a microscope fitted into a glovebox. The silver crystals of $Ba_2Mn_2As_2O$ were characterized by single-crystal and Guinier powder diffraction methods. Room-temperature cell parameters from Guinier powder diffraction data are a = 7.501(2) Å, b = 4.1950(8) Å, c = 10.368(2) Å, and β = 96.18(2)° (Cu Kα_1 radiation, λ = 1.5405981 Å). The yield of $Ba_2Mn_2As_2O$ in the polycrystalline sample is estimated at 75% by Guinier. $BaMn_2As_2$[5] and the tetragonal oxide $Ba_2Mn_3As_2O_2$[2] are present as impurities. $Ba_2Mn_2As_2O$ decomposes in air within hours.

When an alumina boat is used instead of a niobium tube as the reaction vessel under the same conditions, $Ba_2Mn_3As_2O_2$[2] is present, but no $Ba_2Mn_2As_2O$ is observed. It appears that the stronger reducing power of the Nb tube buffers the oxygen concentration and thus favors the formation of $Ba_2Mn_2As_2O$.

$Ba_2Mn_2As_2O$ crystallizes in the monoclinic space group $I2/m$ with a = 7.493(4) Å, b = 4.196(1) Å, c = 10.352(3) Å, and β = 96.17(3)° (T = 130 K).[6] A structural unit displaying bond lengths and angles, and a perspective view along the b axis, are illustrated in Figure 1. The structure contains zigzagging Mn chains running along the b axis which are capped on either side with bridging As atoms. The chains are then joined into planes through the bridging O atoms. These planes are staggered relative to one another so that the Ba cations, which lie between them, are in an asymmetric environment consisting of three As and two O atoms from one plane and two As atoms from the adjacent plane. The geometry around Ba is that of a distorted capped trigonal prism. The local geometry at Mn (disregarding Mn–Mn coordination) is distorted tetrahedral with one O and three As atoms. The bond distances are 2.572(2) Å (×2) and 2.592(2) Å for Mn–As and 2.050(2) Å for Mn–O, similar to those found in the related tetragonal pnictide oxide $Ba_2Mn_3As_2O_2$.[2]

The new compound has the same stoichiometry as the heavier pnictide oxides $Ba_2Mn_2Sb_2O$ and $Ba_2Mn_2Bi_2O$,[4] which crystallize in the hexagonal space group $P6_3/mmc$. The monoclinic and hexagonal phases share many similar features. Both contain distorted $MnPn_3O$ (Pn = As, Sb, Bi) tetrahedral units and linear Mn–O–Mn units. Moreover, both structures can be built up from eight-membered rings consisting of four Mn, two O, and two Pn atoms, as illustrated in Figure 2. The difference between the two structure types lies in the way the rings are linked into two-dimensional planes. For the hexagonal phase, the rings are connected through a hexagonal net of alternating Mn and Pn atoms perpendicular to the mean plane of the eight-membered rings. In the new monoclinic phase the rings are connected in a honeycomb fashion along the mean plane of the rings. This results in a close Mn–Mn distance of 3.070(2) Å, which is a feature not found in the hexagonal phase.[7] The cell volume of $Ba_2Mn_2As_2O$ (324.4 Å^3) is much smaller than that of the hexagonal compounds $Ba_2Mn_2Sb_2O$ (385.0 Å^3) and $Ba_2Mn_2Bi_2O$ (401.6 Å^3).[4] This is attributed to the addition of this short Mn–Mn distance in addition to "ionic radius" differences.

The Mn atoms form a zigzagging chain with an Mn–Mn–Mn angle close to 90° (86.21(6)°). This unit is similar to Mn 2-D networks found in related structures. In pnictide oxides, such as $Ba_2Mn_3As_2O_2$,[2] or in the Mn-containing compounds of the $ThCr_2Si_2$ structure type, such as $BaMn_2P_2$,[8] each Mn atom is coordinated to four others at 90° in a square planar arrangement. In another common structure type, $CaAl_2Si_2$ ($SrMn_2P_2$[9]), each Mn is coordinated to three others at 90°, similar to the corner of a cube, to form a corrugated net. By removing one more Mn atom, we arrive at the corrugated chain found in $Ba_2Mn_2As_2O$. Additionally, the Mn–Mn distance in $Ba_2Mn_2As_2O$ (3.070(2) Å) is within the range of distances found in these other compounds with networks of 90° Mn–Mn–Mn units. These distances range from 2.855(1) Å in $BaMn_2P_2$[8] to 3.225(3) Å in $SrMn_2Sb_2$.[10]

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(1) (a) Examples include intercalation compounds[b] and the oxides of the K_2NiF_4 structure type, such as La_2NiO_4.[c,d] (b) Gamble, F. R.; Geballe, T. H. In *Treatise on Solid State Chemistry*; Hanny, N. B., Ed.; Plenum: New York, 1976; Vol. III, pp 106–166. (c) Buttrey, D. J.; Honig, J. M.; Rao, C. N. R. *J. Solid State Chem.* **1986**, *64*, 287. (d) Bassat, J. M.; Odier, P.; Gervais, F. *Phys. Rev. B* **1987**, *35*, 7126.

(2) Brechtel, E.; Cordier, G.; Schäfer, H. *Z. Naturforsch., B* **1979**, *34*, 777.

(3) (a) Stetson, N. T.; Kauzlarich, S. M. *Inorg. Chem.* **1991**, *30*, 3969. (b) Brock, S. L.; Kauzlarich, S. M. Unpublished results.

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(5) Brechtel, E.; Cordier, G.; Schäfer, H. *Z. Naturforsch., B* **1978**, *33*, 820.

(6) (a) $Ba_2Mn_2As_2O$ crystallizes in the monoclinic space group $I2/m$ with a = 7.493(4) Å, b = 4.196(1) Å, c = 10.352(3) Å, and β = 96.17(3)° at 130 K, with Z = 2. Mo Kα radiation, λ = 0.71073 Å, was used. A full sphere of data, to 2θ = 80°, was collected (4067 reflections, 1118 unique). The structure was solved with SHELXTL PLUS[b] using direct methods. The data were merged and corrected for absorption using the semi-empirical correction program XEMP[b] on the full sphere of data, followed by the empirical correction XABS2.[c] The data were refined using SHELXL-92.[d] For 24 parameters, $R1$ = 4.49% and $wR2$[e] = 10.18% based on 974 reflections ($F > 4\sigma(F)$). (b) Sheldrick, G.M. SHELXTL PLUS, A Program for Crystal Structure Determination, Version 4.2. Siemens Analytical X-ray Instruments, Madison, WI, 1990. (c) Program XABS2 provides an empirical correction based on F_o^2 and F_c^2 differences: Parkin, S.; Hope, H.; Moezzi, B. Department of Chemistry, University of California, Davis. (d) Sheldrick, G. M. *J. Appl. Crystallogr.*, manuscript in preparation. (e) $wR2$ obtained from SHELXL-92 is based on F^2; its value is typically about twice the value obtained for R_w based on F.

(7) (a) This distance is on the order of the Mn–Mn distances observed in Mn metal (2.24–2.97 Å): Hume-Rothery, W.; Smallman, R. E.; Haworth, C. W. *The Structure of Metals and Alloys*, 5th ed.; Richard Clay (Chaucer): Bungay, U.K. 1969; p 108. (b) The closest Mn–Mn distance in $Ba_2Mn_2Sb_2O$ is 4.71(1) Å, and in $Ba_2Mn_2Bi_2O$ it is 4.803(5) Å.

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(9) Mewis, A. *Z. Naturforsch., B* **1978**, *33*, 606.

(10) Cordier, G.; Schäfer, H. *Z. Naturforsch., B* **1976**, *31*, 1459.

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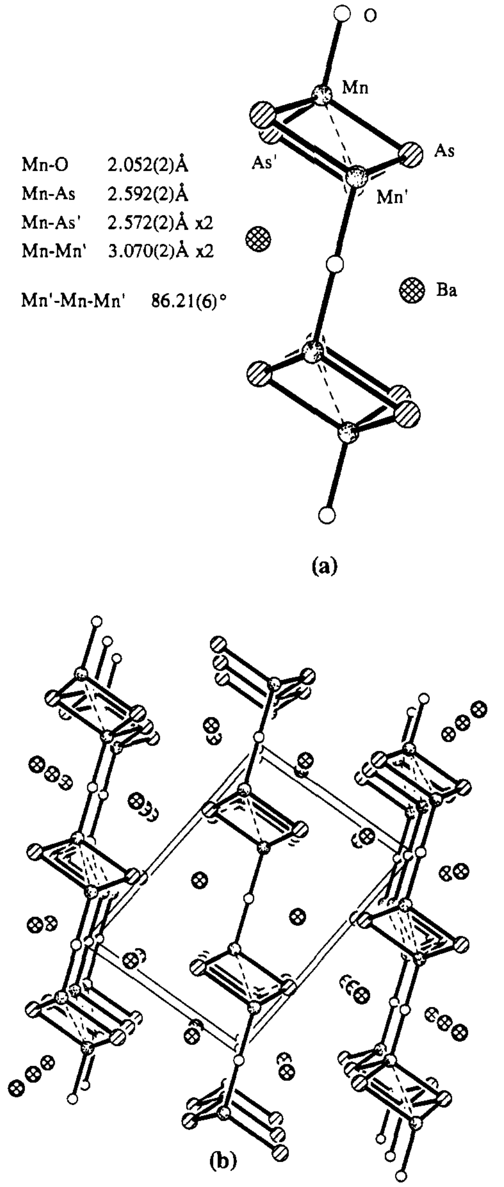

Figure 1. (a) View of the structural unit showing the local coordination around Mn. Selected bond distances and angles are included. (b) Perspective view down the *b* axis.

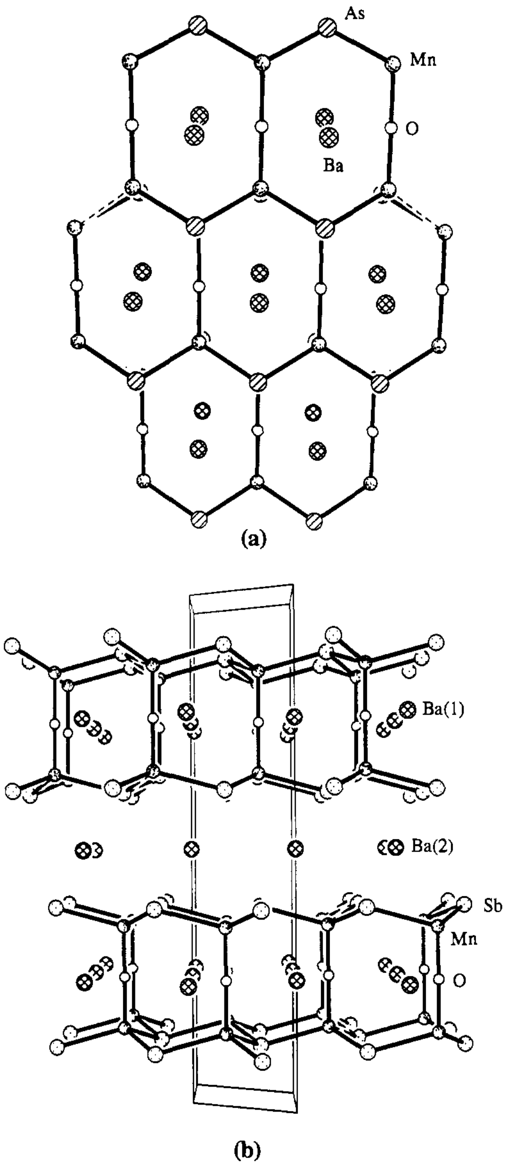

Figure 2. View down the *a* axis showing the O–Mn–Pn (Pn = As, Sb) eight-membered rings and their formation into planes in (a) $Ba_2Mn_2As_2O$ (top two rings) and (b) $Ba_2Mn_2Sb_2O$.

The compound $Ba_2Mn_2As_2O$ represents a new structure type that can be related to the hexagonal compounds, which are only observed with the heavier pnictogens. The new monoclinic structure contains the same local structure as the hexagonal phases but a different extended structure. It can also be related to the tetragonal compounds in that it can be described as built from a network of 90° Mn–Mn–Mn units. The change in structure type, as well as the short Mn–Mn distance, may be due to greater covalency in the arsenide as compared to the antimonide and bismuthide compounds. In addition, there is a change in the Ba cation coordination. In the hexagonal phase there are two different cation coordinations. Ba(2) is coordinated by six Sb or Bi atoms and lies between the planes, while Ba(1) is coordinated by six Sb or Bi atoms and three O atoms and sits in the spaces within the planes (see Figure 2b). A change to the monoclinic structure results in the loss of Ba(2). Ba(1) becomes the cation between the planes of the monoclinic compound. Because the layers are shifted with respect to one another, the Ba cation sits in an asymmetric space and is coordinated by five As and two O atoms. Despite the fact that the average coordination of Ba has been lowered, all six-coordinate Ba sites are removed in the structure change. The change may also be due to the coordination requirements of the Mn atom. In the monoclinic structure, two new close Mn–Mn interactions are observed, effectively increasing the coordination about Mn. This suggests that one O and three As atoms are not sufficient to stabilize the Mn atom (although, as illustrated by the hexagonal phases, clearly one O and three Sb or Bi atoms are).

Magnetic and transport properties of the hexagonal phases $Ba_2Mn_2Sb_2O$ and $Ba_2Mn_2Bi_2O$ have not been reported. We have been investigating the magnetic properties of the tetragonal compounds with 2-D Mn square nets.[3] They demonstrate low-dimensional magnetism. $Ba_2Mn_2As_2O$ with its Mn chains might function as a 1-D magnetic system. Magnetic and transport property measurements of this new compound, as well as of the related hexagonal phases, are in progress.

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Supplementary Material Available: Tables of crystallographic parameters, atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, and selected bond lengths and angles (2 pages). Ordering information is given on any current masthead page.