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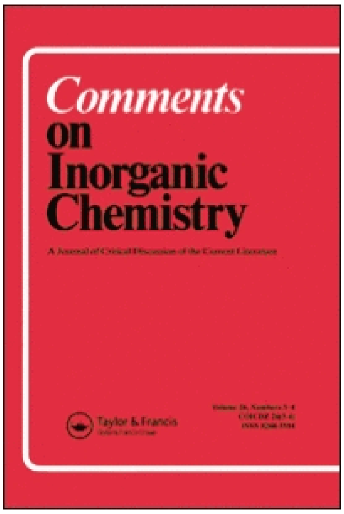

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Pnictide Oxides: A Unique Class of Compounds

Stephanie L. Brock[a]; Susan M. Kauzlarich[a]
[a] Department of Chemistry, University of California, Davis, California

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Pnictide Oxides: A Unique Class of Compounds

STEPHANIE L. BROCK and SUSAN M. KAUZLARICH
Department of Chemistry,
University of California,
Davis, California 95616

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Layered pnictide oxides are an unusual class of compounds which have received little attention. The characteristic feature of these materials is the presence of pnictogen and oxygen atoms which are not bonded to each other and are considered to be anions. This class of compounds is made up of ternary pnictide oxides of alkaline or rare earth metals, and quaternary pnictide oxides of alkali or alkaline earth metal along with transition metals. This Comment discusses structure and bonding in this small group of compounds. Additionally, magnetic and electronic properties of many of the transition metal pnictide oxide compounds are presented.

INTRODUCTION

This Comment is concerned with the small number of layered compounds that are designated as pnictide oxides. 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 simplest pnictide oxides were initially assumed to be binaries consisting of alkaline earth or rare earth cations and pnictogen anions. Subsequent

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investigation showed that most, if not all, of these compounds contain oxygen. In addition to these ternary materials, it is also possible to make quarternary pnictide oxides through inclusion of transition metals. There are four known transition metal pnictide oxide structures. The $Sr_2Mn_3As_2O_2$ tetragonal structure,[1] which is composed of alternating metal–pnictide and metal–oxide layers with intervening cations, forms for a variety of alkaline earth metals and pnictogens, and will also form with zinc.[2] In contrast, the $Ba_2Mn_2Sb_2O$ hexagonal structure,[3] the $Ba_2Mn_2As_2O$ monoclinic structure,[4] and the $Na_2Ti_2Sb_2O$ tetragonal structure[5] are layered structures with a single repeating layer interspersed with cations; each of these structure types is limited to a few representative compounds.

Low dimensional compounds are of interest because of the properties that they exhibit. There are a very large number of layered oxide compounds which have been extensively studied and show interesting properties such as charge density waves, ionic conduction, and superconductivity.[6] In sharp contrast, until 1990, transition metal pnictide oxides were limited to two structure types, the $Sr_2Mn_3As_2O_2$ tetragonal structure and the $Ba_2Mn_2Sb_2O$ hexagonal structure. In addition, although the crystal structures were reported, high yield syntheses had not been developed, and property measurements had not been performed. Since the novelty of the structures warrant further investigation of these unusual compounds, this group set out to explore the synthesis of transition metal pnictide oxide compounds and structure–property relationships among these materials. In this paper we will present the synthesis and structure of the known ternary pnictide oxides, the known quaternary pnictide oxides and magnetic properties of the transition metal pnictide oxide compounds reported to date.

I. TERNARY PNICTIDE OXIDE COMPOUNDS

Many of the ternary pnictide oxides were initially thought to be binaries. Since their structures could not be rationalized based on simple valence electron counting rules, most were considered to be intermetallics. Table I gives the compositions, structure types, and lattice parameters of recognized pnictide oxide compounds. Actinide pnictide oxides[7,8] are not included in Table I and make up a small subset of this type of compound. In contrast to the alkaline earth or

TABLE I

Recognized ternary pnictide oxides

Compound	Structure Type	a (Å)	b (Å)	c (Å)	Ref.
Eu_4As_2O	anti-K_2NiF_4 or filled La_2Sb	4.7924 (4)		16.1933 (9)	9
Ca_4P_2O	anti-K_2NiF_4 or filled La_2Sb	4.492 (1)		15.087 (4)	13
Ca_4As_2O	anti-K_2NiF_4 or filled La_2Sb	4.537 (1)		15.449 (4)	13
Ca_4Sb_2O	anti-K_2NiF_4 or filled La_2Sb	4.677 (2)		16.342 (7)	12
Ca_4Bi_2O	anti-K_2NiF_4 or filled La_2Sb	4.72 (2)		16.54 (3)	11
Sr_4P_2O	anti-K_2NiF_4 or filled La_2Sb	4.794 (1)		15.985 (4)	10
Sr_4As_2O	anti-K_2NiF_4 or filled La_2Sb	4.831 (1)		16.364 (4)	10
Ba_4P_2O	La_2CuO_4	7.335 (1)	7.164 (1)	16.732 (3)	10
Ba_4As_2O	anti-K_2NiF_4 or filled La_2Sb	5.1246 (4)		17.336 (1)	10
Ce_2O_2Sb	anti-$ThCr_2Si_2$	4.012 (1)		13.697 (8)	19
Ce_2O_2Bi	anti-$ThCr_2Si_2$	4.034 (1)		13.736 (2)	19

lanthanide compounds, these were purposefully made as products of the oxidation of actinide pnictides and published as oxide compounds. Since our interests lie with the alkaline earth pnictide oxides, the actinide pnictide oxides will not be discussed further.

Eu_4As_2O,[9] shown in Fig. 1, is the first discovered pnictide oxide. It can be described either as a filled $LaSb_2$ or anti-K_2NiF_4 structure type. With the exception of Ba_4P_2O,[10] all the alkaline earth pnictide oxides crystallize in this structure type. If one omits the bonds to the pnictogens the relationship to the K_2NiF_4 structure is obvious. The oxygen coordination is a distorted octahedron of cations, O–A_6, whereas the pnictogen coordination is a tri-capped trigonal prism of cations, Pn–A_9. Figure 1 shows two views of this structure type, one emphasizing the local coordination about the pnictogen and oxygen atoms and the other emphasizing the relationship to the K_2NiF_4 structure. The other alkaline earth pnictide oxide structure type has been found for only one compound to date, Ba_4P_2O.[10] It crystallizes in the anti-La_2CuO_4 structure type and is shown in Fig. 2. This structure is simply an orthorhombic variant of the anti-K_2NiF_4 structure type. The coordinations of the various ions are similar to that described above except that in the anti-La_2CuO_4 structure type, the oxygen octahedra are tilted whereas in the anti-K_2NiF_4 structure type

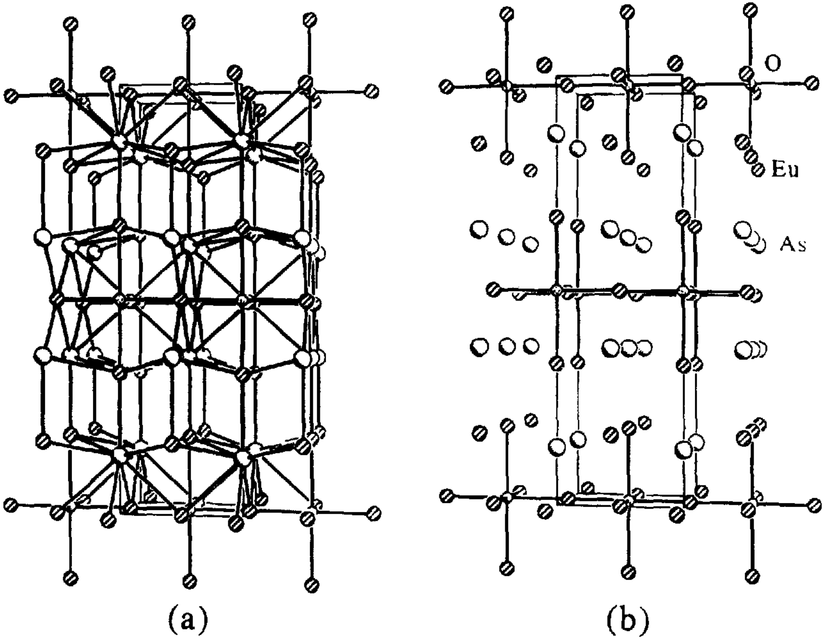
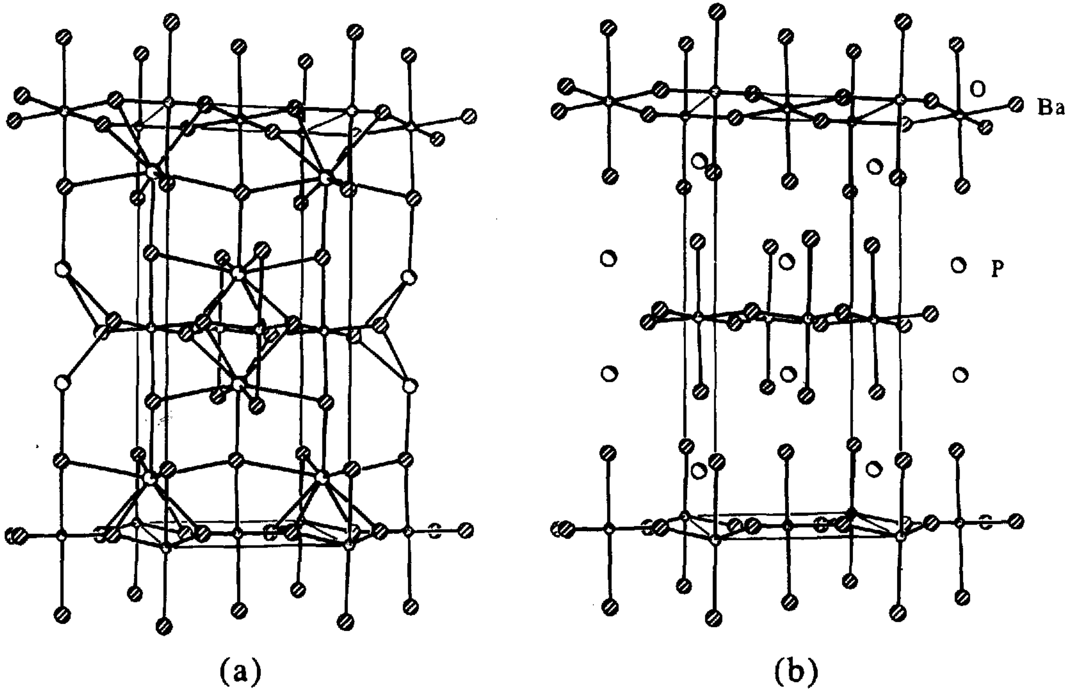


FIGURE 1 The structure of Eu_4As_2O (a) with all bonds shown, and (b) with only the O–Eu_6 octahedra shown in order to reflect the relationship to the K_2NiF_4 structure type.



(a)

(b)

FIGURE 2 The structure of Ba_4P_2O (a) with all bonds shown, and (b) with only the O–Ba_6 octahedra shown. Notice this anti-La_2CuO_4 structure type is an orthorhombic variant of the anti-K_2NiF_4 structure type pictured in Fig. 1.

they are not. In addition, in the anti-K_2NiF_4 structure type there is a close pnictogen–pnictogen distance which is not present in the anti-La_2CuO_4 structure type. The Ca analogs of the compounds A_2Pn (Pn = P, As, Sb, Bi)[11-13] and the Sr and Ba compounds of A_2Pn (Pn = P, As)[10] have all been corrected in the literature. One may assume that all remaining compounds of the composition A_2Pn (A = Sr, Ba; Pn = Sb, Bi) are oxygen stabilized compounds.[14-17] The presence of oxygen in these compounds provides the formula A_4Pn_2O and all atoms have a filled valence shell. These compounds are therefore expected to be insulators or semiconductors and the crystals of Ca_4Sb_2O are red,[12] suggesting that this is the case. Since the A_4Pn_2O compounds can also be described as adopting a filled La_2Sb structure type, one might suspect that La_2Sb is also a pnictide oxide, but evidence to date suggests that it is not.[18] In the case of the alkaline earth compounds, the presence of oxygen provides filled valence shells for all the atoms and the bonding can be interpreted as ionic in nature. In contrast, the presence of oxygen in La_2Sb does not provide enough electrons to fill the valence shell of Sb and would not simplify the interpretation of bonding in this compound.

Figure 3 shows the structure for Ce_2O_2Pn (Pn = Sb, Bi)[19] which adopts an anti-$ThCr_2Si_2$ structure type. The pnictogen is in a cubic environment, Pn–Ce_8, and the oxygen coordination is tetrahedral, O–Ce_4. Figure 3 shows a view which illustrates the coordination around the pnictogen and oxygen atoms and a view which emphasizes the relationship to the $ThCr_2Si_2$ structure. The electronic structure of this compound is not easily rationalized unless the Ce is mixed valent, +3/+4, and thus one might expect unusual properties. It is probable that pnictide oxides can be prepared with other lanthanides, but it appears that this is a relatively unexplored area.

II. TRANSITION METAL PNICTIDE OXIDE COMPOUNDS

$A_2M_3Pn_2O_2$: We have been studying a series of quaternary layered compounds, $A_2Mn_3Pn_2O_2$ (A = Sr, Ba; Pn = P, As, Sb, Bi)[1,20,21] which can be described as an intergrowth of $ThCr_2Si_2$-type slabs interfaced by a layer of alkaline earth cations to CuO_2-type planes. These compounds crystallize in the tetragonal $Sr_2Mn_3As_2O_2$ structure type (*I4/mmm*) shown in Fig. 4. Until recently, the $Sr_2Mn_3As_2O_2$

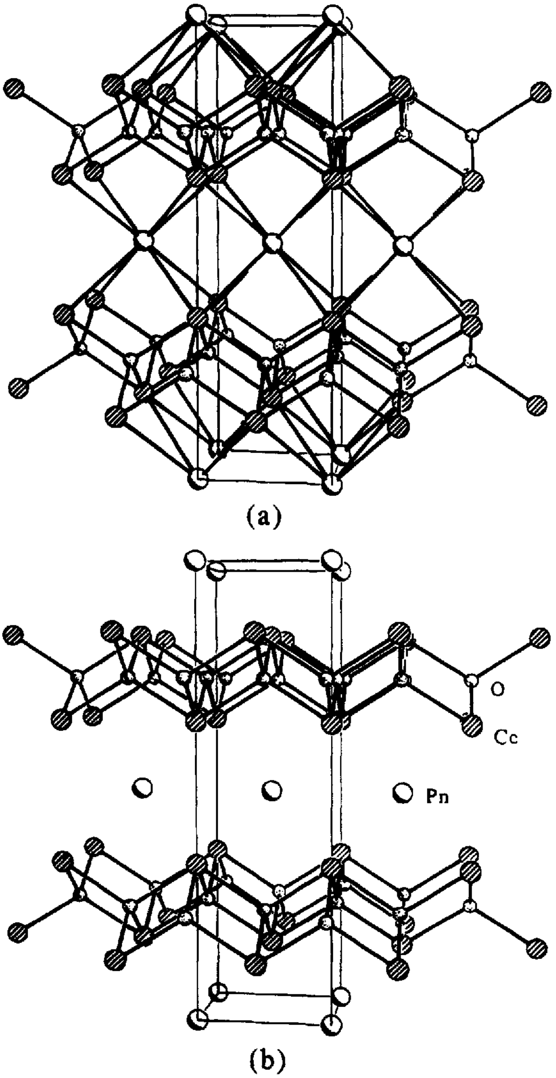


FIGURE 3 The structure of Ce_2O_2Pn(Pn = Sb, Bi) (a) with all bonds shown, and (b) with the bonds to the pnictogens pruned in order to reflect the relationship to the $ThCr_2Si_2$ structure type.

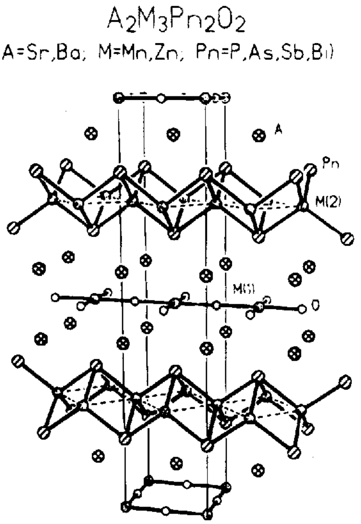


FIGURE 4 A view of the unit cell of the mixed layer transition metal pnictide oxides of the $Sr_2Mn_3As_2O_2$ structure type.

structure type has been observed only for Mn. This is surprising considering the metal pnictide planes are isostructural to those in compounds of the $ThCr_2Si_2$ structure type, of which over 400 compounds are known.[22] 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. To date the only other compounds reported with this structure type are $A_2Zn_3As_2O_2$ (A = Sr, Ba). These new compounds, $Ba_2Zn_3As_2O_2$ and $Sr_2Zn_3As_2O_2$, provide evidence for some versatility in this structure type and have further significance in that they contain zinc in a square planar arrangement of oxygen, a rare geometry for zinc. This section describes the synthesis, structure and properties of the quaternary transition metal pnictide oxides of the $Sr_2Mn_3As_2O_2$ structure type.

Synthesis. The first reported synthetic method to prepare $A_2Mn_3Pn_2O_2$ is to react a stoichiometric mixture of A, Mn, Pn, and Pn_2O_3

in a corundum crucible, sealed in a quartz ampoule, under argon, at 1250–1400°C. The reaction was cooled at a rate of 100°C per hour. Although crystals were obtained using this method, it has proved to be unsuccessful in producing single phase material. An improved method of synthesis involves reacting stoichiometric amounts of AO, Mn, and Pn.[20,21] The mixture is pressed into a pellet, placed in a dried alumina crucible and sealed in a quartz ampoule under a half atmosphere of purified argon. The reaction is heated at 30°C per hour to 1000°C and held at that temperature for one week. All of the products are air stable, except $Ba_2Mn_3P_2O_2$ which is moisture sensitive and slowly decomposes over extended periods of exposure to air. To date, this method has not been successful in producing either $Sr_2Mn_3P_2O_2$ or $Ba_2Mn_3Bi_2O_2$. Table II gives lattice parameters of the Mn compounds reported to date.

Both the $Ba_2Zn_3As_2O_2$ and $Sr_2Zn_3As_2O_2$ compounds have been synthesized under a variety of different conditions.[2,23] Single crystals of $Ba_2Zn_3As_2O_2$ are obtained from heating stoichiometric quantities of either BaO, Zn, and As, or Ba, Zn, As_2O_3, and As to 1100°C for one week. Below this temperature, only microcrystalline powders are obtained. X-ray quality single crystals of $Sr_2Zn_3As_2O_2$ have remained elusive. Very small crystals were obtained at 1000°C in a Ta tube from stoichiometric amounts of SrO, Zn, and As,[23] and optimization of conditions may lead to the growth of larger crystals. To date, it

TABLE II

Lattice parameters for the tetragonal transition metal pnictide oxides $A_2M_3Pn_2O_2$ (A = Sr, Ba; M = Mn, Zn; Pn = P, As, Sb, Bi)

Compound	*a* (Å)	*c* (Å)	Reference
$Sr_2Mn_3As_2O_2$[a]	4.1459(6)	18.856(2)	1
$Ba_2Mn_3P_2O_2$	4.2029(7)	19.406(5)	20
$Ba_2Mn_3As_2O_2$[a]	4.2539(5)	19.755(4)	1
$Sr_2Mn_3Sb_2O_2$[a]	4.2599(4)	20.093(3)	1
$Sr_2Mn_3Bi_2O_2$[a]	4.2816(6)	20.554(3)	1
$Ba_2Mn_3Sb_2O_2$[a]	4.3650(2)	20.789(2)	1
$Sr_2Zn_3As_2O_2$	4.0954(7)	18.918(4)	2
$Ba_2Zn_3As_2O_2$	4.2202(3)	19.713(4)	2

[a] Reference given provides the single crystal structure. Lattice parameters were obtained from Ref. 20.

has not been possible to prepare either compound in quantitative yield. The highest yields are 70% for $Ba_2Zn_3As_2O_2$ and 90% for $Sr_2Zn_3As_2O_2$, and the major impurity phase in each case is AZn_2As_2 (A = Sr, Ba).[24,25] Both compounds have been characterized by Guinier X-ray powder diffraction techniques, and room temperature lattice parameters are given in Table II. Additionally, an X-ray structure determination has been performed on single crystals of $Ba_2Zn_3As_2O_2$.

Structure. Table III provides important bond lengths for compounds crystallizing in the $Sr_2Mn_3As_2O_2$ structure type. The structure is composed of alternating layers of $M_2Pn_2^{2-}$ and MO_2^{2-} anionic nets separated by the alkaline earth cations. The alkaline earth cation sits in a square antiprism composed of four Pn from the $M_2Pn_2^{2-}$ layer and four O from the MO_2^{2-} layer. The $M_2Pn_2^{2-}$ nets are of the $ThCr_2Si_2$ ($BaAl_4$) structure type. They are built up of a square net of M atoms which are capped alternatively above and below the plane by Pn atoms to form edge sharing $MPn_{4/4}^{1-}$ tetrahedrons. There are two $M_2Pn_2^{2-}$ planes in the unit cell related by a mirror plane so that one of the capping Pn atoms from each layer is pointing towards the M atom of the interpenetrating MO_2^{2-} layer. The long distances of 3.2–3.5 Å preclude any M–Pn bonding between the two different layers. Therefore, in the MO_2^{2-} layer, M is in a square planar geometry of four O atoms, not a distorted octahedral geometry. The M–Pn

TABLE III

Bond distances in compounds of the $Sr_2Mn_3As_2O_2$ structure type

Compound	M(1)–O (Å)	M(1)–Pn (Å)	M(2)–M(2) (Å)	M(2)–Pn (Å)	A–O (Å)	A–Pn (Å)
$Sr_2Mn_3As_2O_2$	2.078	3.191	2.939	2.574 (1)	2.625 (2)	3.340 (3)
$Ba_2Mn_3P_2O_2$[a]	2.1015 (4)		2.9719 (5)			
$Ba_2Mn_3As_2O_2$	2.124	3.458	3.004	2.593 (1)	2.748 (2)	3.457 (3)
$Sr_2Mn_3Sb_2O_2$	2.131	3.304	3.014	2.741 (1)	2.654 (2)	3.471 (4)
$Sr_2Mn_3Bi_2O_2$	2.140	3.321	3.026	2.806 (1)	2.661 (2)	3.491 (5)
$Ba_2Mn_3Sb_2O_2$	2.183	3.516	3.088	2.755 (2)	2.772 (3)	3.578 (3)
$Sr_2Zn_3As_2O_2$[a]	2.0477 (4)		2.8959 (5)			
$Ba_2Zn_3As_2O_2$	2.1030 (5)	3.4342 (6)	2.9737 (7)	2.5785 (6)	2.7339 (5)	3.4142 (7)

[a] A single crystal structure determination was not performed. Bond distances which are a function of only the lattice parameter *a* are included in the table.

interlayer distance is affected by the identity of both the pnictide and the alkaline earth cation.

The intralayer Zn–As bond distance in $Ba_2Zn_3As_2O_2$ of 2.5785 (6) Å is in the range expected for tetrahedral $ZnAs_4$ units.[24,26] The Zn–As interplaner distance of 3.4342 (6) Å is considerably longer and is outside the range expected for a van der Waals interaction.[27] The Zn–O distance in the ZnO_2^{2-} layer is 2.1030 (5) Å, an intermediate bond distance compared to zinc oxide distances in tetrahedral and octahedral coordination[28,29] which is what one would expect for square planar. This is a rare example of zinc in a square planar geometry, and the first example of square planar zinc in an extended structure.

The bond lengths found within the $A_2Mn_3Pn_2O_2$ series of compounds are typical for both Mn–Pn and Mn–O.[30–36] Mn–O square planar coordination is not common but, as mentioned above, the long interplanar Mn–Pn distance precludes the presence of a covalent bond leading to octahedral coordination. However, these distances are on the order of a van der Waals interaction. The strength of this interaction may influence the mechanism which couples the two different layers ($Mn_2Pn_2^{2-}$ and MnO_2^{2-}). This effect is expected to be the greatest for $Sr_2Mn_3As_2O_2$ which has the shortest M–Pn interlayer distance (3.191 Å) in this series.

Properties. Temperature dependent magnetic susceptibility measurements on members of the series $A_2Mn_3Pn_2O_2$ (A = Sr, Ba; Pn = P, As, Sb) are shown in Figs. 5 and 6.[20,37] The data suggests that the majority of the compounds have low-dimensional antiferromagnetic coupling and the intraplaner coupling constants have been determined assuming a 2-D Heisenberg antiferromagnetic model.[38] Table IV summarizes the magnetic susceptibility data and intraplanar exchange parameter J/k_B. $Sr_2Mn_3As_2O_2$ is the exception to the rule and has an overall susceptibility approximately five times larger than the other members of the series. Additionally, there is a pronounced rounding on the high temperature end of the maxima in the susceptibility suggestive of a second magnetic transition. The sharpness of the maxima is indicative of three-dimensional coupling in this compound which might arise from the shorter interlayer Mn–As distance of 3.191 Å, as mentioned above. In order to probe the contribution to the magnetism from the two unique manganese environments in

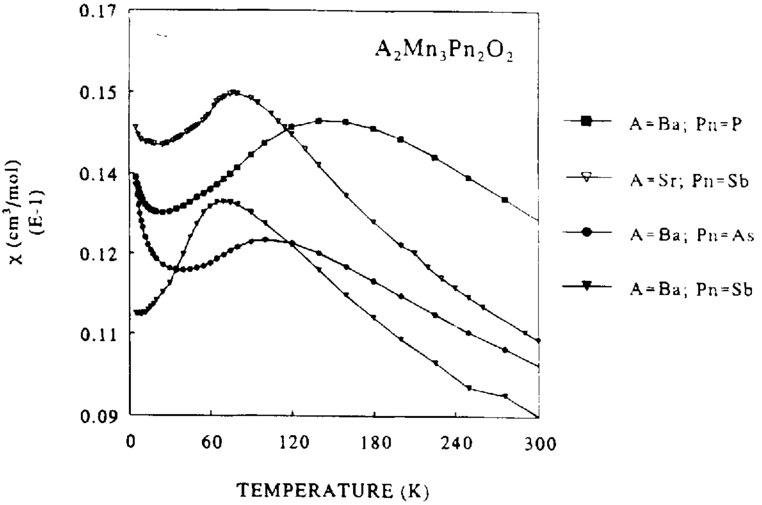


FIGURE 5 Magnetic susceptibility as a function of temperature for the compounds $Ba_2Mn_3Pn_2O_2$ (Pn = P, As, Sb) and $Sr_2Mn_3Sb_2O_2$.

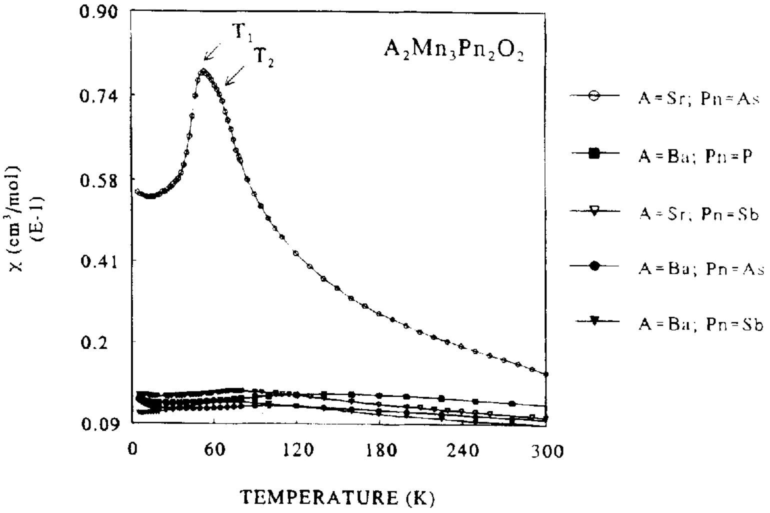


FIGURE 6 Magnetic susceptibility as a function of temperature for $Sr_2Mn_3As_2O_2$ presented along with the data from Fig. 5. The two presumed magnetic transitions for $Sr_2Mn_3As_2O_2$ are indicated.

TABLE IV

Summary of magnetic and crystallographic data for the compounds $A_2Mn_2Pn_2O_2$ (A = Sr, Ba; Pn = P, As, Sb)

Compound	$T_{\chi max}$(K)	T_N(K)[a]	J/k_B(K)[b]	a (Å)	c (Å)	d (MnO_2^{2-}) Å
$Sr_2Mn_3As_2O_2$[c]	51(2), 65(2)	46(2)[d]		4.1459(6)	18.856(2)	9.428(2)
$Ba_2Mn_3P_2O_2$	125(5)	98(7)	12.6(5)	4.2029(7)	19.406(5)	9.703(5)
$Ba_2Mn_3As_2O_2$	100(7)	74(5)	10.1(7)	4.2539(5)	19.755(4)	9.878(4)
$Sr_2Mn_3Sb_2O_2$	79(2)	62(2)	8.0(2)	4.2599(4)	20.093(3)	10.097(3)
$Ba_2Mn_3Sb_2O_2$	69(2)	44(2)	7.0(2)	4.3650(2)	20.789(2)	10.395(2)

[a] T_N was obtained from finding the maxima in the derivative plot $d_\chi T/dT$.

[b] $J/k_B = T_{\chi max}/1.12S(S + 1) + 0.10$

[c] The 2-D Heisenberg model has not been applied in this case.

[d] T_N is ascribed to the magnetic transition at $T_{\chi max}$ = 51(2) K.

these compounds, neutron powder diffraction data were obtained on $Sr_2Mn_3As_2O_2$, which shows unique magnetic behavior, and $Sr_2Mn_3Sb_2O_2$, which appears to be representative of the series.[39] The neutron data indicate the presence of two different magnetic lattices in these materials: one lattice which forms near room temperature (lattice I) and one which forms at much lower temperature (lattice II). Lattice I can be modeled as antiferromagnetic G-type coupling of the $Mn_2Pn_2^{2-}$ layers and is the same in both compounds. Lattice II is more complex and has not been solved; however, it is attributed to coupling of the MnO_2^{2-} layers. The transition temperature for lattice II of $Sr_2Mn_3Sb_2O_2$ is 65 K, which correlates well with the transition temperature of 63 K obtained from magnetic susceptibility measurements. Since the $Mn_2Pn_2^{2-}$ layers (lattice I) are already coupled at room temperature, the transition observed in the magnetic susceptibility for the $A_2Mn_3Pn_2O_2$ series of compounds must be attributed to the coupling of the MnO_2^{2-} layers (lattice II). Thus the exchange parameter, J/k_B, given in Table IV is for the MnO_2^{2-} intraplanar coupling. Neutron diffraction data indicate that lattice II is not the same for $Sr_2Mn_3As_2O_2$ and $Sr_2Mn_3Sb_2O_2$. $Sr_2Mn_3As_2O_2$ is more complex and appears to have at least two different sets of magnetic peaks with different reflection conditions and transition temperatures. This is consistent with the double maxima observed in the magnetic susceptibility and discussed above.

Temperature dependent resistivity measurements have been obtained on two members of the Mn series, $Ba_2Mn_3As_2O_2$ and

$Ba_2Mn_3Sb_2O_2$,[37] as well as $Ba_2Zn_3As_2O_2$.[2] All compounds exhibit semiconducting behavior indicated by an exponential increase in resistivity as the temperature is lowered.[37] Although the other compounds in this series have not been measured, one would predict that all the compounds should be semiconductors.

$Na_2Ti_2Pn_2O$: The $Na_2Ti_2Pn_2O$ (Pn = As, Sb) compounds are the only transition metal pnictide oxide structures which can be directly related to the non-metallated pnictide oxides. They crystallize in the Eu_4As_2O structure type (anti-K_2NiF_4) as shown in Fig. 7 where Na and Ti are found on the Eu(1) (4e), and Eu(2) (4c) sites, respectively. The synthesis, structure, and magnetic properties of these two compounds are described below.

Synthesis. While investigating the Na–Ti–Sb phase diagram, Adam and Schuster were able to obtain crystals of $Na_2Ti_2Sb_2O$.[5] Adventitious oxygen apparently came from an oxide coating on the titanium

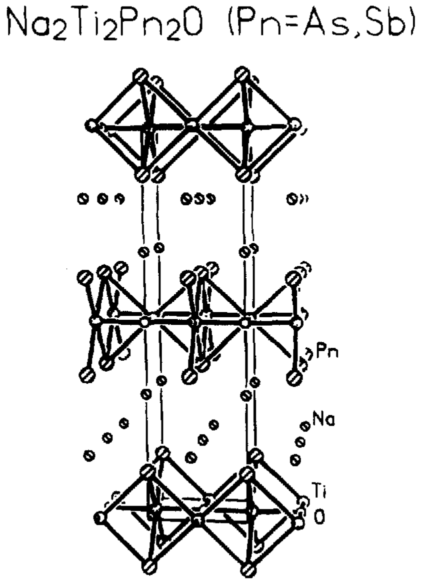


FIGURE 7 A view of the structure of $Na_2Ti_2Pn_2O$ (Pn = As, Sb).

metal surface. Attempts to prepare the compound with TiO_2 or Sb_2O_3 as the source of oxygen were unsuccessful; however, they were able to prepare homogeneous powders of $Na_2Ti_2Sb_2O$ by reacting Na_2O and "TiSb" in stoichiometric amounts. The reagents were placed in an alumina crucible sealed in quartz under argon and heated from 800 to 900°C. Homogeneous powder of $Na_2Ti_2As_2O$ is prepared in the same manner.

Structure. Figure 7 shows a view of the $Na_2Ti_2Sb_2O_2$ structure[5] and Table V provides the lattice parameters and bond distances. The structure is composed of $Ti_2Sb_2O^{2-}$ layers separated by a double layer of sodium cations. The Ti is coordinated by two oxygen atoms in a linear fashion and by four pnictogens in an approximately square planar fashion to produce distorted TiO_2Pn_4 octahedra. The octahedra are corner-shared at oxygen and edge-shared by Pn to form the layers. The oxygen is coordinated to four Ti atoms in a square plane and to two Na^+ cations to provide an overall octahedral coordination. The pnictogen is 10 coordinated in a bi-capped square antiprism so

TABLE V

Cell parameters and bond distances for $Na_2Ti_2As_2O$ and $Na_2Ti_2Sb_2O$

	$Na_2Ti_2As_2O^a$	$Na_2Ti_2Sb_2O$
Cell Parameters		
a (Å)	4.070 (2)	4.140 (0)
c (Å)	15.288 (4)	16.56 (1)
Bond Distances (Å)		
Ti–O	2.035(1)	2.072 (0)
Ti–Ti	2.878 (1)	2.930 (2)
Ti–Sb		2.885 (2)
Ti–Na		3.659 (3)
Na–O		3.016 (3)
Na–Na		3.694 (4)
Sb–O		3.552 (2)
Sb–Na		3.099 (2) × 4
		3.257 (3) × 1
Sb–Sb		4.015 (5)

[a] A single crystal structure determination was not performed. Bond distances which are a function only of the *a* lattice parameter are included in the table.

that four Na^+ cations make up one plane and one caps the square, and four Ti atoms make up the other plane with one pnictogen capping the square. The Na cation is coordinated by 5 pnictogens and one oxygen to provide a distorted octahedral environment.

Properties. Magnetic susceptibility has been reported for the $Na_2Ti_2Sb_2O$ compound.[5] The data has been interpreted as indicating antiferromagnetic coupling within the Ti–O planes and no superconductivity was observed by the ac-shielding method down to 4 K.

$Ba_2Mn_2Pn_2O$: While studying the syntheses and properties of the tetragonal compounds[1,20] we have discovered a layered compound, $Ba_2Mn_2As_2O$, which represents a new structure type.[4] This section will describe the synthesis and structure of $Ba_2Mn_2As_2O$ and the structurally related hexagonal compounds $Ba_2Mn_2Sb_2O$ and $Ba_2Mn_2Bi_2O$ (*$P6_3/mmc$*). Figs. 8 and 9 show the structures and Table VI provides the lattice parameters and bond distances.

Synthesis. The synthesis described in the literature for the tetragonal compound $Ba_2Mn_3As_2O_2$ involves reaction of Ba, Mn, As, and As_2O_3 in an alumina boat sealed in a fused silica tube and heating to 1250°C for an unspecified time.[1] Under these conditions, $Ba_2Mn_3As_2O_2$ is obtained, but significant amounts of $BaMn_2As_2$ are also present and the material is coated with transported silica. In an attempt to improve upon this synthesis and protect the reaction from silica, the reaction was repeated using a sealed Nb tube as the reaction vessel. The products from this reaction appeared homogeneous, consisting of silver gray irregularly shaped crystals and polycrystalline material. From an X-ray powder analysis, the majority of the Bragg peaks could be attributed neither to the tetragonal oxide $Ba_2Mn_3As_2O_2$, nor to any other known phase. An X-ray single crystal structure study was undertaken and the material was identified as a new monoclinic phase, $Ba_2Mn_2As_2O$, the structure of which is described below. The fact that this material is obtained only when the reaction is performed in a Nb or Ta tube suggests that the tube is in some way participating in the reaction. Consistent with this analysis is the fact that the tube frequently is observed to change from metallic gray to blue or yellow, indicative of oxidation, and in fact the highest yields of $Ba_2Mn_2As_2O$ are obtained when excess

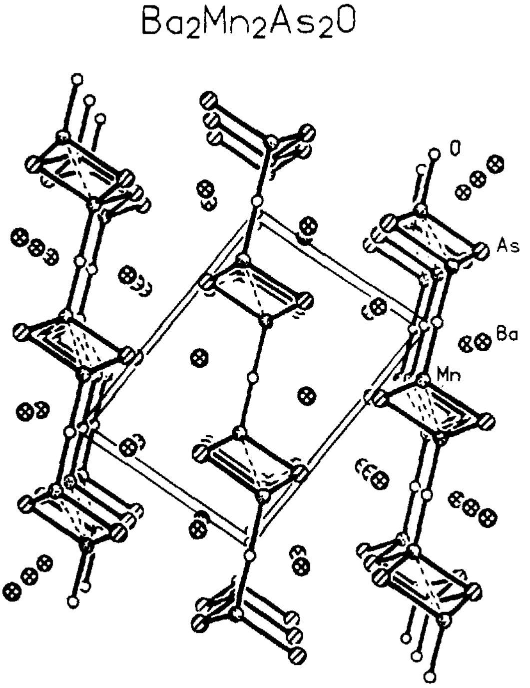


FIGURE 8 A perspective view down the *b* axis of $Ba_2Mn_2As_2O$.

oxygen is employed in the reaction. It appears that the stronger reducing power of the Nb tube, relative to an alumina boat, buffers the oxygen concentration and thus favors the formation of $Ba_2Mn_2As_2O$. To date, it has not been possible to prepare $Ba_2Mn_2As_2O$ completely free of $Ba_2Mn_3As_2O_2$ and $BaMn_2As_2$, the most common impurities. The highest yield of $Ba_2Mn_2As_2O$ is estimated at 75%. The presence of adventitious oxygen, or the activity of the individual Nb or Ta tube (related to the freshness of the metal surface), may have a profound effect on the products observed. Indeed, the relative amounts of the different phases are observed to change significantly from reaction to reaction.

The synthesis of single crystals of the heavier pnictide oxides $Ba_2Mn_2Sb_2O$ and $Ba_2Mn_2Bi_2O$ has been reported in the literature.[3] Ba, Mn, Pn, and Pn_2O_3 are reacted in a corundum boat under argon at 1350°C. Initial attempts in our lab to make these compounds in high yield

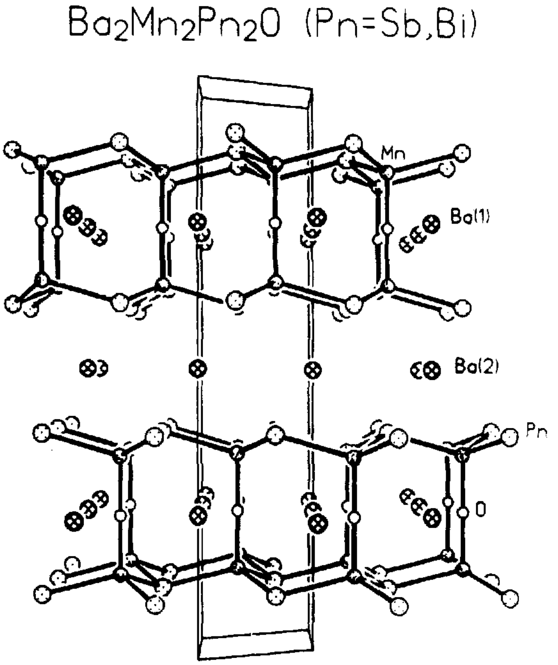


FIGURE 9 A perspective view down the *a* axis of $Ba_2Mn_2Pn_2O$ (Pn = Sb, Bi).

employed alumina boats and relatively low reaction temperatures (700–800°C).[40] The preparation of $Ba_2Mn_2Sb_2O$ was found to include significant amounts of $Ba_2Mn_3Sb_2O_2$ and $BaMn_2Sb_2$, whereas $Ba_2Mn_2Bi_2O$ was contaminated with unreacted Bi, $BaBi_3$, and MnO (the phase $Ba_2Mn_3Bi_2O_2$ is unknown in this system). The success of Nb reaction vessels in the synthesis of $Ba_2Mn_2As_2O$ suggested that perhaps high yields of $Ba_2Mn_2Pn_2O$ (Pn = Sb, Bi) might be prepared in the same way. Indeed, this has been successful for $Ba_2Mn_2Sb_2O$, which can be prepared in > 90% yield when Ba, Mn, Sb, and Sb_2O_3 are reacted in a Nb tube at 1100°C. However, the yield of $Ba_2Mn_2Bi_2O$ is not improved by the use of Nb tubes.

Structure. $Ba_2Mn_2As_2O$ crystallizes in the monoclinic space group *I2/m* with $a = 7.493$ (4), $b = 4.196$ (1), $c = 10.352$ (3) Å and

TABLE VI

Cell parameters and bond distances for $Ba_2Mn_2Pn_2O$ (Pn = As, Sb, Bi)

	$Ba_2Mn_2As_2O$	$Ba_2Mn_2Sb_2O$	$Ba_2Mn_2Bi_2O$
Crystal System and Space Group	Monoclinic *I2/m*	Hexagonal $P6_3/mmc$	Hexagonal $P6_3/mmc$
Cell Parameters			
a (Å)	7.493 (4)	4.71 (1)	4.803 (5)
b (Å)	4.196 (1)		
c (Å)	10.352 (3)	20.04 (2)	20.097 (10)
β (°)	96.17 (3)		
Bond Distances (Å)			
Mn–Pn	2.572 (2) × 2 2.592 (2) × 1	2.818 (1)	2.881 (3)
Mn–O	2.050 (2)	2.014 (5)	2.000 (11)
Mn–Mn	3.070 (2)	4.71 (1)	4.803 (5)
Ba–Pn	3.275 (2) × 1 3.433 (2) × 2 3.487 (2) × 2	3.868 (2) Ba(1) 3.535 (3) Ba(2)	3.928 (2) Ba(1) 3.567 (3) Ba(2)
Ba–O	2.881 (2)	2.719	2.773

β = 96.17 (3)° (T = 130 K). A perspective view along the *b* axis illustrating how the layers are stacked is illustrated in Fig. 8 and the repeating structural unit is presented in Fig. 10. Lattice parameters and bond distances are given in Table VI. The local geometry at Mn (disregarding Mn–Mn coordination) is distorted tetrahedral with one O and three As atoms. These tetrahedral units are joined into planes through corner-sharing of O along one direction and edge-sharing of As along both directions. 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. An alternate way to view the structure is to shift the perspective to be along the *a* axis and build up one planar unit. This is illustrated in Figs. 11 and 12. The structure contains zigzagging Mn chains running along the *b* axis which are joined into planes through the bridging O atoms. The Mn atoms are then capped on either side of the plane with bridging As atoms and the Ba cations sit above and below the

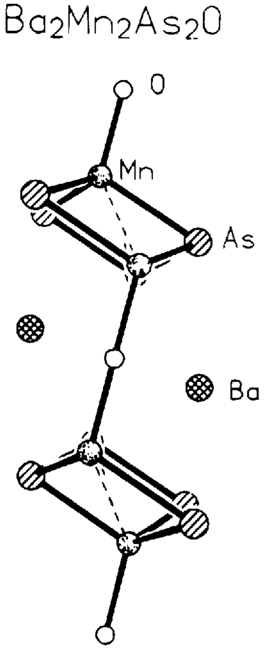


FIGURE 10 View of a structural unit of $Ba_2Mn_2As_2O$.

rings created by the O–Mn–As framework. 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 $Ba_2Mn_3As_2O_2$.[1]

The new compound has the same stoichiometry as the heavier pnictide oxides $Ba_2Mn_2Sb_2O$ and $Ba_2Mn_2Bi_2O$,[3] which crystallize in the hexagonal space group $P6_3/mmc$. Their lattice parameters and bond distances are provided in Table VI. 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 Fig. 13. The difference between the two structure types lies in the way the rings are linked into 2-dimensional planes. For the hexagonal phase, the rings are connected through a hexagonal net

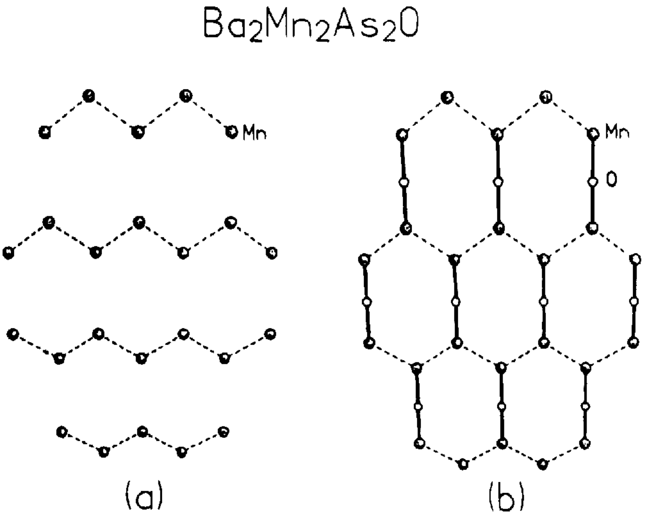


FIGURE 11 A view down the *a* axis illustrating how the elemental components are assembled into a layer: (a) Mn–Mn 1-D chains, (b) Mn–Mn 1-D chains and oxygen atoms which connect the chains into planes.

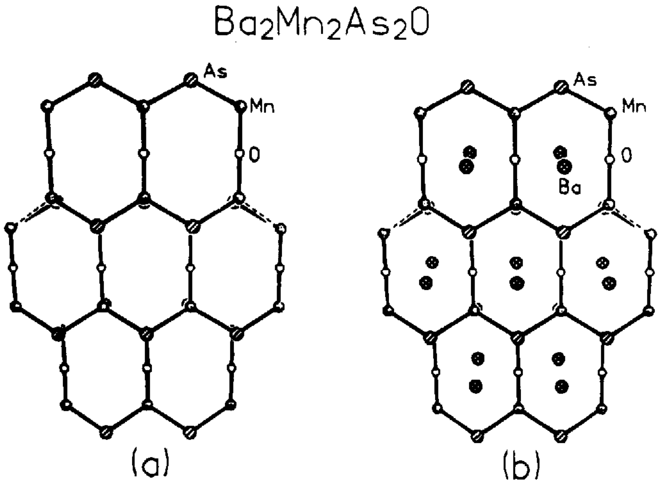


FIGURE 12 A view down the *a* axis illustrating how the elemental components are assembled into a layer: (a) Mn–O planes capped above and below the plane by bridging As atoms, (b) O–Mn–As framework and the interpenetrating Ba cations.

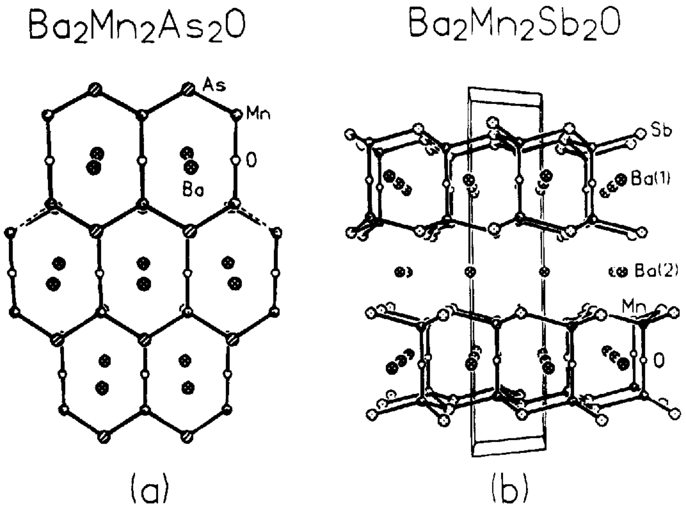


FIGURE 13 A view down the *a* axis showing the O–Mn–Pn (Pn = As, Sb) eight membered rings and their formation into planes in (a) $Ba_2Mn_2As_2O$ (top two rings), and (b) $Ba_2Mn_2Sb_2O$.

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 where the nearest Mn–Mn interaction is greater than 4.7 Å.[41] 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 $Å^3$).[3] This is attributed to the addition of this short Mn–Mn distance in addition to "ionic radius" differences.

In $Ba_2Mn_2As_2O$, 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, as is illustrated in Fig. 14. In pnictide oxides such as $Ba_2Mn_3As_2O_2$,[1] or in the Mn containing compounds of the $ThCr_2Si_2$ structure type, such as $BaMn_2P_2$,[34] each Mn atom is coordinated to four others at 90° in a square planar arrangement. In another common structure type, $CaAl_2Si_2$ ($SrMn_2P_2$[33]), each Mn is coordinated to three others at 90°, similar

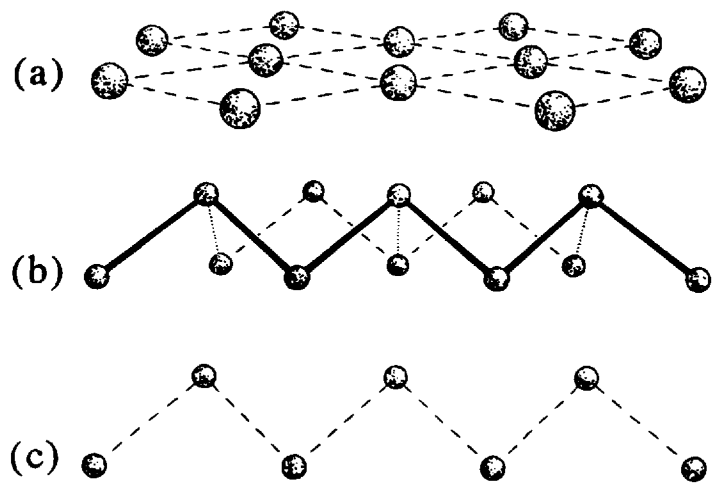


FIGURE 14 Illustration of Mn–Mn 2-D and 1-D frameworks and representative compounds: (a) 2-D square planar framework ($BaMn_2P_2$, $Ba_2Mn_3As_2O_2$), (b) 2-D corrugated net ($SrMn_2P_2$), (c) 1-D zigzagging chain ($Ba_2Mn_2As_2O$).

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 $BaMn_2P_2$[34] to 3.225 (3) Å in $SrMn_2Sb_2$.[32]

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, as indicated in Fig. 15. 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

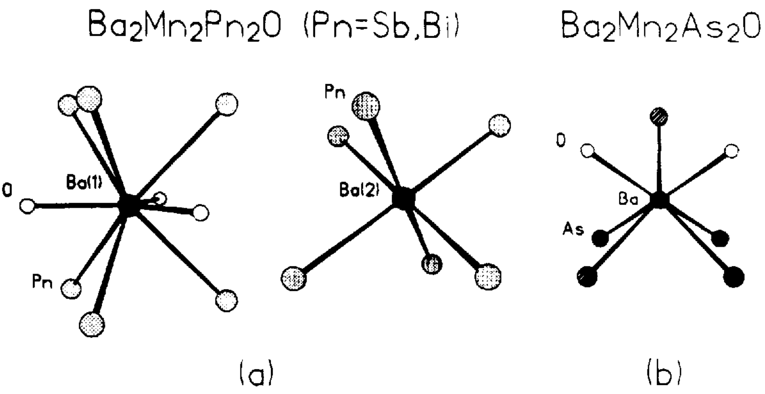


FIGURE 15 The coordination geometry of the Ba cations in (a) $Ba_2Mn_2Sb_2O$ (6 and 9 coordinate Ba sites), and (b) $Ba_2Mn_2As_2O$ (7 coordinate Ba site).

O atoms and sits in the spaces within the planes (see Fig. 14). A change to the monoclinic structure results in the loss 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 sufficient).

SUMMARY

The pnictide oxides are a unique class of compounds encompassing both ternary pnictide oxides of alkaline or rare earths and the quaternary pnictide oxides of alkali and alkaline earth metals and transition metals. Investigation of the synthesis of pnictide oxides in the past few years has resulted in six new compounds and two new structure types. In addition to the new phosphide oxide $Ba_2Mn_3P_2O_2$, two other new compounds, $A_2Zn_3As_2O_2$ (A = Sr, Ba), have been prepared in the $Sr_2Mn_3As_2O_2$ tetragonal structure type, providing the first evidence for electronic versatility in this structure type. The recent report of the two compounds $Na_2Ti_2Pn_2O$ (Pn = As, Sb) indicates that pnictide oxides can be prepared with early transition metals as well as the middle (Mn) and late (Zn) metals. The new monoclinic compound $Ba_2Mn_2As_2O$ represents a new structure type and provides further evidence that synthetic efforts in this area will be profitable. Whereas all the other compounds discussed above exhibited two-dimensional properties, one might expect this compound to exhibit one-dimensional properties due to the chains of Mn atoms running through the structure. The novel structures of the reported compounds warrant more detailed investigations of the magnetic and electronic properties. In conclusion, the synthesis and characterization of pnictide oxides is a relatively new area of research and preliminary evidence indicates that synthetic efforts will provide new compounds with unique structures whose properties are well worth investigating.

Acknowledgments

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