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

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Condensation and commentary by

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Research by :

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Condensation of the Research

Purpose of the Study

To explore the synthesis of novel solid-state compounds that could potentially exhibit interesting or useful physical properties. The authors' goal was to extend the class of compounds $A_2Mn_3Pn_2O_2$ (A = Sr, Ba; Pn = P, As, Sb, Bi) to include a transition metal other than Mn. High-temperature fluxes were used to produce these new compounds.

Background

The $ThCr_2Si_2$ structure type is incredibly versatile with hundreds of compounds known to crystallize with this atomic arrangement. The $ThCr_2Si_2$ structure accommodates rare earth elements, main group elements and several transition metals with varying oxidation states and d electron counts. The structure consists of PbO-type $Cr_2Si_2^{2-}$ layers that are separated by Th^{2+} cations (Figure 1a). These layers can be described as square nets of Cr atoms capped alternatively above and below by Si atoms to form edge-sharing $CrSi_4$ tetrahedra. Within the $Cr_2Si_2^{2-}$ layers, there is not only significant covalent Cr—Si bonding, but Cr—Cr metal - metal bonding present as well. As one might anticipate from the degree of bonding in this region, this $Cr_2Si_2^{2-}$ layer is quite rigid. The bonding between the Th^{2+} and the $Cr_2Si_2^{2-}$ layers is largely ionic.

The new compounds $Ba_2Zn_3As_2O_2$ and $Sr_2Zn_3As_2O_2$ are closely related to this classic $ThCr_2Si_2$ structure and provide a rare example of square planar coordination of zinc with unusually long Zn—O distances. Interestingly, the recently reported solid-state compound $Na_{1.9}Cu_2Se_2{\bullet}Cu_2O$ and the new superconductor $LuNi_2B_2C$ (Figure 1b), are also variants of the $ThCr_2Si_2$ structure. These new compounds have structures that, although are remarkably similar to $ThCr_2Si_2$, exhibit unusual coordination environments and bond lengths in the layer that separates the PbO-type layers.

What Researchers Accomplished

$Ba_2Zn_3As_2O_2$ can be considered as an intergrowth of the $ThCr_2Si_2$ and the "infinite layer" high temperature cuprate superconductor, (Sr, La)CuO_2, that contains

vertex-sharing square planes (Figure 2a). Hence, the formula could be written as $BaZn_2As_2 \cdot BaZnO_2$ to emphasize this framework. $Ba_2Zn_3As_2O_2$ exhibits semiconducting behavior.

The compound $Ba_2Zn_3As_2O_2$ provides a rare example of Zn in a square planar coordination and perhaps the only such example found in extended structures. In addition to this unusual coordination environment around Zn, the Zn(1)—O distances are quite long. When comparing the Zn(1)—O distance in $Ba_2Zn_3As_2O_2$ (2.1010(5) Å) to that in zincite[1] (1.953 Å), a compound that also contains Zn in a four-fold coordination with O, the Zn(1)—O distance in $Ba_2Zn_3As_2O_2$ is considerably longer.

Researchers' Approach

$Ba_2Zn_3As_2O_2$ was synthesized by heating a pressed pellet of BaO, Zn, and As in a 2:3:2 ratio in an alumina boat sealed in a quartz tube sealed in argon at 1100°C for one week. A slow cooling rate of 5°C/h was used to produce silver crystals of $Ba_2Zn_3As_2O_2$. These crystals formed within a melt and were manually extracted. $Sr_2Zn_3As_2O_2$ was prepared in a similar manner using SrO, Zn, and As and heating at 900°C.

Four probe temperature dependent resistivity measurements were performed at temperatures from 15 to 300 K. The resistivity behavior indicates that both compounds are semiconductors.

Commentary on the Research

It is intriguing that the structures of $LuNi_2B_2C$ and $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ are so remarkably similar to $A_2Zn_3As_2O_2$ (A = Ba, Sr.) These three compounds are of significant importance because of their physical properties (superconductivity!), and their unusual structural features that include uncommon coordination environments, and unusual bond lengths. Common to all three of these new compounds is their close structural relationship to the versatile $ThCr_2Si_2$ structure-type.

$LuNi_2B_2C$ represents the first example of superconductivity observed in the rare earth - transition metal - borocarbides and will certainly lead to an entirely new class of superconductors[2]. It is is nearly isostructural with $ThCr_2Si_2$, differing only in the layer that separates the PbO-type layer. In $ThCr_2Si_2$, this layer consists of elemental Th, whereas in the $LuNi_2B_2C$ structure this layer also contains C. This LuC layer adopts the rock-salt arrangement (Figure 1b). Within this LuC layer the Lu—C bond lengths are

markedly longer (2.449(1) Å) than commonly found in the binary rare earth compounds (2.343 Å in LuC_2[3]).

The recently reported compound $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ is isostructural with $Ba_2Zn_3As_2O_2$.[4] However, $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ contains some very unusual structural features and uncommon bonding modes. In the "infinite layer" portion of the structure, the stoichiometry is now Cu_2O *not* CuO_2 (Figure 2b). These Cu_2O sheets can be considered the anti-type of the CuO_2 sheets that are found in all the high temperature cuprate superconductors.

The coordination geometry about oxygen in these Cu_2O layers is most unusual. The O atoms are coordinated by 4 Cu atoms resulting in a square planar oxygen environment. NbO and its more complex relatives provide most of the known examples of this oxygen coordination environment. In addition to the unusual oxygen coordination, the Cu(2)—O distance associated with this layer (1.957 Å) is longer than those typically found in the cuprate superconductors (1.89 -1.93 Å). This sufficiently longer Cu(2)—O distance in $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ suggests that these bonds are in considerable tension compared to those in the high T_c copper oxides. As determined by resistivity and Seebeck measurements, $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ is a p-type metal.

Conclusions

In all three compounds, the unusual structural features occur in the layers that separate these $Cr_2Si_2^{2-}$ -type layers; in $LuNi_2B_2C$ the long Lu-C distance is found in the rock salt-type layer that separates the Ni_2B_2 layers; in $Ba_2Zn_3As_2O_2$, the rare example of square planar coordinated Zn atoms that are also associated with unusually long Zn(1)—O distances are found in the "CuO_2"-type sheets; and in $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ the highly unusual square planar coordinated oxygen atoms are found in the "CuO_2 anti-type" sheets.

That all these uncommon features occur in the same layer of these closely related structures suggests that the PbO-type layer is incredibly rigid and unyielding to accommodate competing bonding requirements of other atoms. The bonding in this PbO-type layer is highly covalent by virtue of the strong bonding between unlike atoms and the metal - metal bonding between the atoms on the Cr site. This layer is apparently bonded so strongly that it stabilizes the long/short bond distances and uncommon coordination environments of atoms residing in the separating layer.

The structures of the $Ba_2Zn_3As_2O_2$ and $Na_{1.9}Cu_2Se_2{\bullet}Cu_2O$ compounds are particularly interesting in light of the high temperature cuprate superconductors and the recently discovered rare earth-transition metal-borocarbide superconductors. $Ba_2Zn_3As_2O_2$ and $Na_{1.9}Cu_2Se_2{\bullet}Cu_2O$ contain structural features found in both these classes of superconductors yet, themselves do not exhibit superconductivity. The distorted metal-oxygen distances found in the "CuO_2-type" layers as compared to known cuprate superconductors may provide a clue for this behavior.

The $ThCr_2Si_2$ structure-type provides the synthetic solid-state chemist with a framework to stabilize new compounds with uncommon features. These three new compounds illustrate the versatility and stability of the $ThCr_2Si_2$ structure and the related structures of $LuNi_2B_2C$, $Ba_2Zn_3As_2O_2$ and $Na_{1.9}Cu_2Se_2{\bullet}Cu_2O$.

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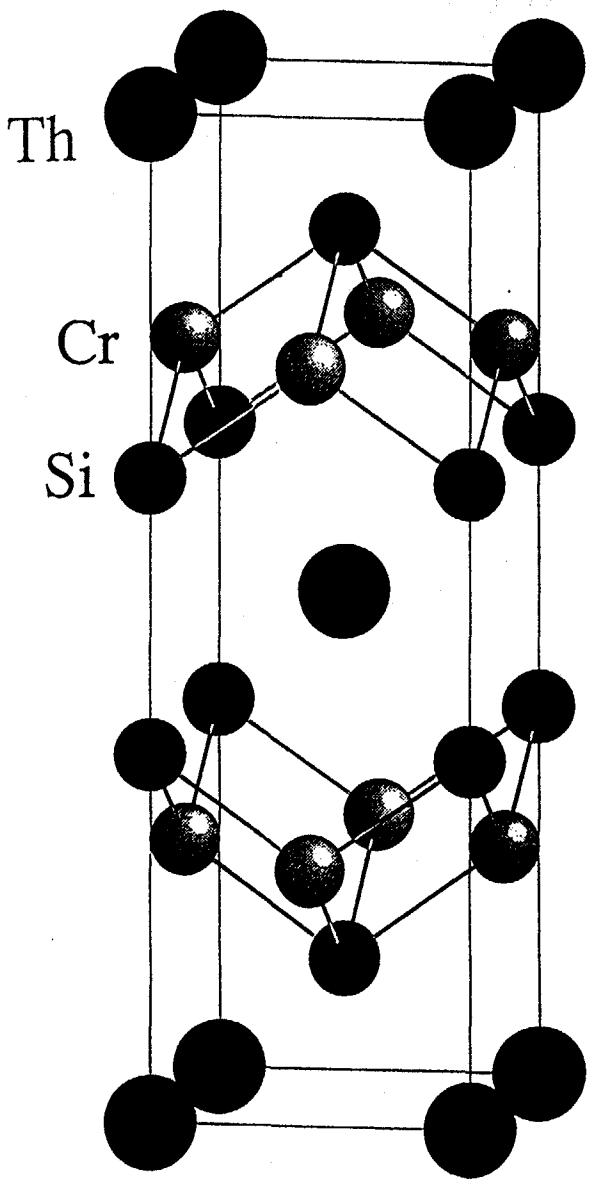
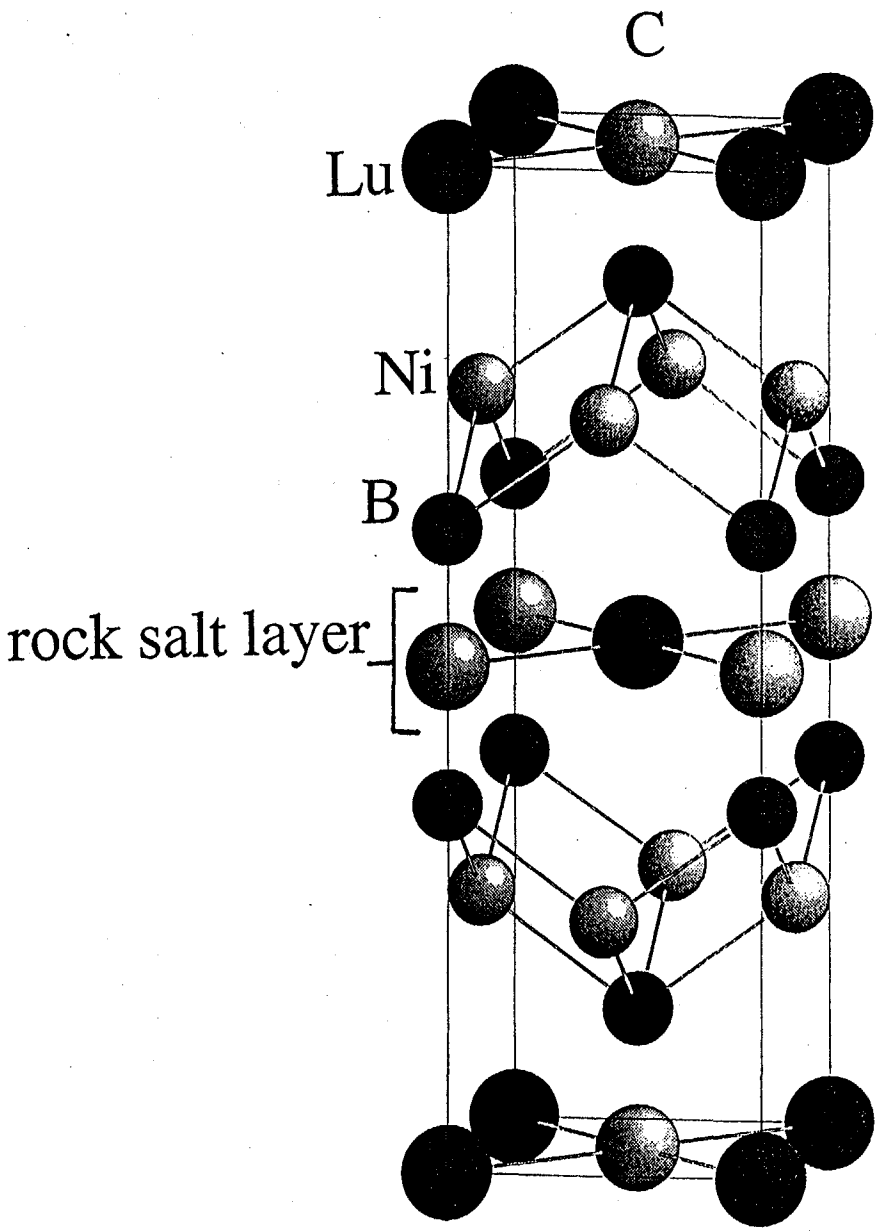


1a



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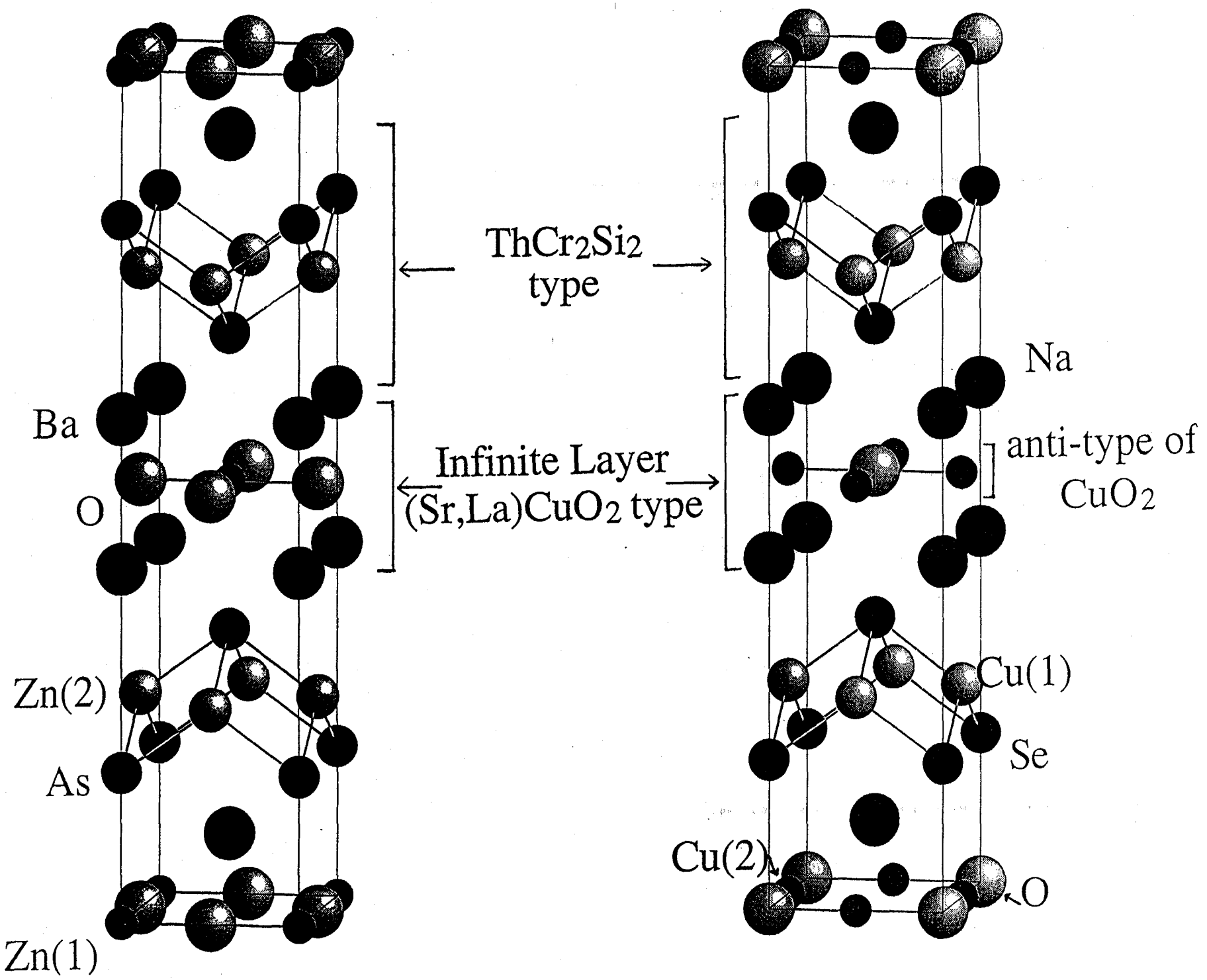
ThCr2Si2
type
Infinite Layer
(Sr,La)CuO2 type
Ba
O
Zn(2)
As
Zn(1)
Na
anti-type of
CuO2
Cu(1)
Se
Cu(2)
O

2a

2b