

# Diagrammatic Separation of Different Crystal Structures of $A_2BX_4$ Compounds Without Energy Minimization: A Pseudopotential Orbital Radii Approach

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$A_2BX_4$  family of compounds manifest a wide range of physical properties, including transparent conductivity, ferromagnetism, and superconductivity. A 98% successful diagrammatic separation of the 44 different crystal structures of 688 oxide  $A_2BX_4$  compounds (96% for 266 oxide-only) is described by plotting the total radius of the A atom  $R_A$  versus the radius of the B atom  $R_B$  for many  $A_2BX_4$  compounds of known structure types and seeking heuristically simple, straight boundaries in the  $R_A$  versus  $R_B$  plane that best separate the domains of different structure types. The radii are sums  $R_A = R_s(A) + R_p(A)$  of the quantum-mechanically calculated "orbital radii"  $R_s(R_p)$ , rather than empirical radii or phenomenological electronegativity scales. These success rates using first-principles orbital radii uniformly exceed the success rates using classic radii. Such maps afford a quick guess of the crystal structure of a yet unmade  $A_2BX_4$  compound by placing its atomic orbital radii on such maps and reading off its structure type.

## 1. Introduction

$A_2BX_4$  compounds<sup>[1–6]</sup> constitute a centrally important group in inorganic solid state, manifesting a wide range of physical phenomena including insulation, transparent conductivity, ferromagnetism, ferroelectricity, and superconductivity. The 790 known  $A_2BX_4$  compounds<sup>[1–13]</sup> are distributed into 44 different crystal structure types as listed in Tables 1 and 2 (the Supporting Information lists the compounds belonging to each of the different structure types). This group of compounds exhibits significant chemical diversity, including chalcogen anions ( $X = O, S, Se, Te$ ) as well as halides ( $X = F, Cl, Br, I$ ), nitrides ( $X = N$ ), cyanides ( $X = CN$ ), and even nitrites ( $X = NO_2$ ). The cations manifest cases where both A and B are main-group metals ( $A$  and  $B = Al, Mg, Ge, Sn$ ) or cases where both A and B are transition elements (e.g.,  $Ni_2TiO_4, V_2MnO_4$ ) or cases where we have one of each (e.g.,  $Al_2NiO_4$ ) as well as rare-earth cationic species (e.g.,  $Yb_2FeS_4$ ). These compounds include cation-deficient structures (e.g., A-deficient  $A_3B_2X_8$  or B-deficient  $A_4BX_8$ ) as well as cases such as  $A_3B_2X_6$  with cations in excess. The structures adopted by this

group are no less fascinating than their chemical constitution. This family of compounds includes, for example, the spinel structure-type (255 members), the  $Th_3P_4$  structure-type (87 members), the  $Fe_2CaO_4$  structure-type (78 members), the  $K_2SO_4$  structure-type (69 members), the  $Cr_3S_4$  structure-type (57 members), and the Olivine ( $Al_2BeO_4$ ) structure-type (48 members).<sup>[14]</sup> The  $A_2BX_4$  structure-types differ in crystal classes (cubic, orthorhombic, rhombohedral) and local environments ("motifs"), covering tetrahedral and octahedral as well as 5- and 7-fold coordination sites.

An outstanding challenge in structural inorganic chemistry<sup>[2–4,6,15]</sup> and in solid-state physics<sup>[16,17]</sup> has been to explain the distribution of the known  $A_2BX_4$  compounds into different structure types. Two leading types of

approaches of predicting or rationalizing the crystal structure of a given  $A_2BX_4$  compound have developed. In the deductive approach, one explicitly varies the structural degrees of freedom of an  $A_2BX_4$  compound in search of a minimum of a given energy functional. In the inductive approach one offers a guess for the crystal structure of a given compound by analogy with the known structures of other compounds.

Most previous deductive approaches have focused on comparing a piece of the total (electronic + ionic) energy of different structures. The classical approach of crystal field stabilization energy (CFSE)<sup>[17]</sup> attempts to correlate the type of the observed local atomic structural motif (octahedral vs. tetrahedral) with the excess orbital energy resulting from the splitting of the  $d$ -like atomic orbital energies by the nonspherical crystal field. This approach is applicable only to the cases where A or B is open shell transition metal. Even for this restriction the method was typically applied only to a subset of the known cases that do contain open shell A or B atoms, for example, the 44 cases in Reference [17]. The predictive power of the method is rather low: 46% success. Similarly, the approach of comparing point-ion Madelung energies of different structures was tested only for a small (18 compounds)<sup>The A</sup>

Table 1. Crystal structure types of  $A_2BX_4$  compounds. The labels b1–b38 and d1, d3, and d9 of structures in the first column are taken from Wyckoff,<sup>[5]</sup> whereas labels S1–S3 indicate  $Y_2CrS_4$ -type,  $Yb_3S_4$ -type, and  $Sr_2PbO_4$ -type structures, respectively. The notation “none” refers to cases where no known Pearson symbol nor mineral name exists.

Label	Prototype Compd.	Space Group	Pearson's Symbol/Mineral Name	No. of Compd.
b5	$Al_2MgO_4$	$Fd\bar{3}m (O_h^7)$	cF56;Spinel	255
d9	$Th_3P_4$	$I\bar{4}3d (T_h^6)$	none	87
b9	$Fe_2CaO_4$	$Pnma (D_{2h}^{16})$	none	78
b11	$K_2SO_4$	$Pnma (D_{2h}^{16})$	none	69
d3	$Cr_3S_4$	$C2/m (C_{2h}^3)$	mC14	57
b10	$Al_2BeO_4$	$Pnma (D_{2h}^{16})$	Olivine	48
b1	$K_2MgF_4$	$I4/mmm (D_{4h}^{17})$	none	41
b6	$Mn_3O_4$	$I4_1/amd (D_{4h}^{19})$	tl28;Hausmanite; distorted Spinel	27
b4	$Ag_2HgI_4$	$P\bar{4}2m (D_{2d}^1)$	tl14;Thiogallate	24
b33	$Li_2WO_4$	$R\bar{3} (C_{3i}^2)$	Phenakite	14
S1	$Y_2CrS_4$	$Pca2_1 (C_{2v}^5)$	none	14
S2	$Yb_3S_4$	$Pnma (D_{2h}^{16})$	none	13
d1	$Pb_3O_4$	$P4_2/mbc (D_{4h}^{13})$	none	9
b21	$Al_3BaO_4$	$P6_322 (D_6^6)$	none	7
S3	$Sr_2PbO_4$	$Pbam (D_{2h}^9)$	none	6
b18	$Na_2SO_4$	$Fddd (D_{2h}^{24})$	Thenardite	4
b2	$K_2PtCl_4$	$P4/mmm (D_{4h}^1)$	none	3
b3	$K_2Pd(NO_2)_4$	$P2_1/c (C_{2h}^5)$	none	2
b7	$Cr_2CuO_4$	$I\bar{4}2d (D_{2d}^{12})$	distorted Spinel	2
b13	$KHSO_4$	$Pbca (D_{2h}^{15})$	none	2
b20	$LiKSO_4$	$P6_3 (C_6^6)$	none	2
b22	$KNaSO_4$	$P\bar{3}m1 (D_{3d}^3)$	Aphthitalite	2

Table 2. Crystal structure types of A

Label	Prototype Compd.	Space Group	Pearson's Symbol/Mineral Name	No. of Compd.
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competing structures from empirically parametrized interatomic potential functions. This approach too, relies on selecting certain pieces of the full ion + electron total energy and on specific, approximate analytic forms of the potential terms. This approach has been applied<sup>[20]</sup> to a very restricted number of cases (54 compounds), predicting correctly 45 compounds (or 83% success).

Instead of minimizing pre-selected pieces of the full total-energy, one might of course attempt to minimize an all-inclusive total energy expression, such as the density-functional and Hartree–Fock expressions. The density-functional calculations of the total energy were done by Marinelli et al. for  $\text{In}_2\text{MgS}_4$ ,<sup>[16]</sup> Warren et al. and Thibaudeau et al. for  $\text{Al}_2\text{MgO}_4$ ,<sup>[21]</sup> and Wei et al. for 18 spinel compounds.<sup>[22]</sup> The Hartree–Fock calculations of the total energy were done by Catti et al. for  $\text{M}_2\text{CrO}_4$  ( $M = \text{Mg}, \text{Mn}, \text{Zn}$ ) and Mitchell et al. for  $\text{M}_2\text{ZnO}_4$  ( $M = \text{Al}, \text{Fe}$ ).<sup>[23]</sup> Seko et al. used the cluster expansion method combined with density-functional calculations to investigate the ground state structures of 6 spinel compounds.<sup>[24]</sup> This successful deductive approach, however, is not easily applicable to large databases, works on a case by case basis, and requires optimization of the total energy with respect to



the conflict with the orbital radii approach is also not necessarily a contradiction. Third, ten cases are true errors.  $\text{Cd}_2\text{PbO}_4$ ,  $\text{Cd}_2\text{PtO}_4$ ,  $\text{Cd}_2\text{SnO}_4$ ,  $\text{Ga}_2\text{PbO}_4$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{Tl}_2\text{CrO}_4$ ,  $\text{Sc}_2\text{MgO}_4$ , and  $\text{Ti}_2\text{NaO}_4$  were determined experimentally to exist in S3,<sup>[6]</sup> S3,<sup>[6]</sup> S3,<sup>[13]</sup> b21,<sup>[5]</sup> d1,<sup>[5]</sup> b11,<sup>[5]</sup> b9,<sup>[12]</sup> and b9<sup>[12]</sup> structures (see Supporting Information), respectively, but appear in the map in the spinel (b5) region.  $\text{As}_2\text{NiO}_4$  has the d1 structure,<sup>[5]</sup> but is placed in the map in the region of b33.  $\text{Ni}_2\text{RhS}_4$  is reported to exist in the spinel structure,<sup>[6]</sup> while its orbital radii place it inside the d3 region. The spinel and d3 structures (see Figs. S1 and S5 in the Supporting Information) are closely related: both have their 2/3 cations octahedrally coordinated; their anion sub-lattices (fcc in61b-308.2(and)-308.9hcapinboth

The compound is that in the orbital radii structure-  
 mans above F316.7(igs.)3902.9d1 and myd bve  
 cture)66.8.9(ypegs.)616453(F320.9o)0(r.)6174.8(eamplre.)]TJ0-1.2266TD-0.2101TcCas

1.1

A and B ions,<sup>[37]</sup> including every compound that can be included. There are 40 compounds that are included in orbital radii maps but cannot be included in Shannon's radii maps (see Supporting Information). The 5 compounds containing U (not included in orbital radii maps) are included in Shannon's radii maps. The success rates of the structure-field maps and cation-distribution map using Shannon's crystal radii<sup>[37]</sup> (see Figs. S10 and S11 in the Supporting Information) are 92% and 74% compared to the success rates of the orbital radii maps at 98% and 96%, respectively. Shannon's radii<sup>[37]</sup> were revised slightly from Shannon–Prewitt crystal radii<sup>[34]</sup> in 1976. Before that, Muller and Roy<sup>[6]</sup> had







