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

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$_2BX_4$ 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 $\boldsymbol{R}_A$ versus the radius of the B atom $\boldsymbol{R}_B$ for many A_2BX_4 compounds of known structure types and seeking heuristically simple, straight boundaries in the $\boldsymbol{R}_A$ versus $\boldsymbol{R}_B$ plane that best separate the domains of different structure types. The radii are sums $\boldsymbol{R}_A = \boldsymbol{R}_s(A) + \boldsymbol{R}_p(A)$ of the quantum-mechanically calculated ''orbital radii'' $\boldsymbol{R}_s(\boldsymbol{R}_p)$, 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[1–6] 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[1–13] 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-dificient 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).[14] 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[2–4,6,15] and in solid-state physics[16,17] 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)[17] 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$^{\text{The A}}$

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,[5] 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	$I\bar{4}3d(T_d^6)$	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	$I4_1/amd(D_{4h}^{19})$	tI28;Hausmanite; distorted Spinel	27
b4	Ag_2HgI_4	$P\bar{4}2m(D_{2d}^1)$	tI14;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_2BaO_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

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[20] 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 In_2MgS_4,[16] Warren et al. and Thibaudeau et al. for Al_2MgO_4,[21] and Wei et al. for 18 spinel compounds.[22] The Hartree–Fock calculations of the total energy were done by Catti et al. for M_2CrO_4 ($M = Mg, Mn, Zn$) and Mitchell et al. for M_2ZnO_4 ($M = Al, Fe$).[23] Seko et al. used the cluster expansion method combined with density-functional calculations to investigate the ground state structures of 6 spinel compounds.[24] 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

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the conflict with the orbital radii approach is also not necessarily a contradiction. Third, ten cases are true errors. Cd_2PbO_4, Cd_2PtO_4, Cd_2SnO_4, Ga_2PbO_4, Pb_3O_4, Tl_2CrO_4, Sc_2MgO_4, and Ti_2NaO_4 were determined experimentally to exist in S3,[6] S3,[6] S3,[13] b21,[5] d1,[5] b11,[5] b9,[12] and b9[12] structures (see Supporting Information), respectively, but appear in the map in the spinel (b5) region. As_2NiO_4 has the d1 structure,[5] but is placed in the map in the region of b33. Ni_2RhS_4 is reported to exist in the spinel structure,[6] 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 in6lb-308.2(and)-308.9hcapin both

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cture)66.8.9(ypegs.)616453(F320.9o)0(r.)6174.8(eamplre,)]TJ0-1.2266TD-0.2101TcCas

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A and B ions,[37] 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[37] (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