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# Crystal Chemistry of $AB_2X_4$ (X = S, Se, Te) Compounds*

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An attempt is made to correlate the crystal structures of ternary chalcogenides of composition $AB_2X_4$ with the cationic radius ratio and a pseudo force-constant involving their electronegativities. The resultant diagram adequately resolves structures based on the types $K_2SO_4$, monoclinic, olivine, $MnY_2S_4$, $Th_3P_4$, and $CaFe_2O_4$ but structure types based on spinel, $Cr_3Se_4$, and $Ag_2HgI_4$ are not resolved. Crystal chemical arguments are used to explain these observations and to advance reasons for the successes and failures of this method for predicting structure types.

## Introduction

A voluminous literature is extant dealing with the crystal chemistry and physical properties of compounds $AB_2X_4$ where A and B are metal cations and X is S, Se, or Te. The phases in which either A or B, or both, are rare earth elements have been reviewed by Flahaut and Laruelle (*1*) and, indeed, they have been responsible for a considerable amount of the reported data. Hahn and coworkers (*2–4*) studied the phases which result when A = Zn, Cd, Mg, Be, Ca, Sr, Ga, Sn, Ge, Pb, Hg, Ti, V, Cr, Mn, Fe, Co, Ni, and B = Al, Ga, In. The ternary chalcogenides $AB_2X_4$, where A, B = Ti, V, Cr, Mn, Fe, Co, Ni, X = S, Se, Te have been extensively studied by Chevreton, Sapet, and Berodias (*5–8*). The cadmium chromium spinels, which are of great interest because of their physical properties, were prepared by Passerini and Baccaredda (*9*). Compounds in which A = Si, Ge, Sn and B = Mg, Ca, Sr, Ba, Cd, Hg, Mn have been reported by Röckstachel et al. (*10*), Susa and Steinfink (*11*), and Hagenmuller et al. (*12, 13*). Gattow and Franke (*14*) investigated a series of compounds of the type $MoB_2S_4$ and $WB_2S_4$, where B = $NH_4^+$, $K^+$, $Rb^+$, and $Cs^+$. Compounds of the type $ARh_2X_4$, A = Ni, Cr, Co, X = Se, Te have been reported by Plovnik and Wold (*15*). Bok and de Wit (*16*) have studied $AB_2S_4$ systems with A = Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, and B = Sb, Bi, Ti, Fe, Co, Ni, Mo, V, Sn, and Pb.

Recently an attempt was made by Kugimiya and Steinfink (*17*) to predict the crystal structures of compounds with stoichiometry $AB_2X_4$, X = O, S, Se, Te. It was found that a plot of the radius ratio $r_A/r_B$ versus a bond stretching force constant $K_{AB} = \chi_A\chi_B/r_e^2$, where $\chi_A$ and $\chi_B$ are the cation electronegativities and $r_e$ is an equilibrium distance defined in Ref. (*17*), produced domains in which the crystal structure is constant. Although this approach was quite successful for the oxides, $AB_2O_4$, a major feature of the corresponding map for sulfides and selenides was the random distribution of the spinel and $Ag_2HgI_4$ structures over the same region of the map. Otherwise the map distinguishes successfully among all other important structures, namely, $Th_3P_4$, $CaFe_2O_4$, and olivine. No sulfides have been reported with the $K_2MgF_4$ structure, which, however, is well represented in the oxide system. The $K_2SO_4$ structure type was also quite rare. More recently, studies (*11*) have been carried out on the crystal chemistry of sulfides $AB_2S_4$ whose predicted structures were the $K_2SO_4$, $K_2MgF_4$, and olivine structures. Several representatives of the $K_2SO_4$ structure were synthesized, but no compound with the $K_2MgF_4$ structure could be prepared. In general, agreement was found between the observed and predicted structures, although it was apparent

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that some of the boundaries between the different phases had to be redrawn.

In order to explore further the validity of the structure predictions in the sulfide and selenide systems, we attempted syntheses of compounds whose values of $r_A/r_B$ and $K_{AB}$ place them in the domains of the spinel, $K_2SO_4$, and olivine structure-types, as well as in a region characterized by monoclinic structures.

## Sample Preparation

Stoichiometric quantities of the elements A, B, and X (X = S, Se), or of the corresponding binary compounds were mixed and placed in vycor tubes 9 mm in diameter and 1 mm wall thickness. The starting materials were obtained from commercial sources and they had a stated purity of 99.9% or better. The vycor tubes were evacuated to a nominal pressure of $10^{-3}$ mm of Hg and sealed off. The vials containing S were first heated at 400°C for 4 hr and those containing Se were heated at 600°C for the same length of time. The samples were then raised to temperatures in the range 600–1100°C and maintained at the elevated temperatures for 1 or 2 days. In several cases the temperature was raised to 1350°C using an induction furnace. The reacted materials were examined under the optical microscope for homogeneity and crystallinity, and X-ray powder diffractometer traces were obtained for identification of the products. Single crystals were selected, whenever possible, for further X-ray identification or complete crystal structure investigation. In some cases a qualitative chemical analysis of single crystals was carried out using an electron-beam microprobe.

## Results

The spinel structure was predicted for the compounds $CdFe_2S_4$, $CdCo_2S_4$, $SnEr_2S_4$, $SnCr_2S_4$, $SnCo_2S_4$, $SnMg_2S_4$, $SnIn_2S_4$, $CuIn_2S_4$, $CaSb_2S_4$, $CaBi_2S_4$, $CaCr_2S_4$, $MoNi_2S_4$, $MgCr_2S_4$, $PbV_2S_4$, $PbSb_2S_4$, $PbIn_2S_4$, $GeIn_2S_4$, $GeSb_2S_4$, $ZnV_2S_4$, and $YbIn_2S_4$, and syntheses at several different temperatures were attempted. In many of the products only the initial reactants were found or else one or more of the well known binary sulfides were observed. In samples where reaction took place and ternary phases formed the following were identified:

(1) $CuInS_2$, a chalcopyrite-type compound, which is found in nature as the mineral roquesite.

(2) The reaction mixture PbS + 2V + 3S always contained excess sulfur but the X-ray powder pattern did not show PbS lines. Most of the peaks could be indexed in terms of a tetragonal unit cell with dimensions $a = 4.16$ Å and $c = 11.78$ Å, which are very similar to those reported for $PbTiS_3$ (*18*). It is very likely that the composition of the phase is $PbVS_3$.

(3) The product obtained by reacting PbS + 2Sb + 3S gave a diffraction pattern corresponding to that of zinckenite which has the composition $PbSb_2S_4$. Single crystals in the form of extremely small needles were isolated and oscillation pictures around the needle axis gave a lattice parameter of 8.50 Å, in good agreement with the *c* value reported for zinckenite. The odd order layer lines were extremely weak and diffuse, so that a superstructure must exist along *c*. The space group and the other lattice parameter as reported by Nuffield (*19*) could not be verified completely because of the small crystal size. A zero-level Weissenberg showed sixfold symmetry and a possible value of $a = 22.05$ Å. This is almost exactly half of the *a* axis value reported by Nuffield for zinckenite. Upper level Weissenberg pictures were never sufficiently intense to indicate whether a doubling of this axis occurred.

(4) The system Pb–2In–4S apparently produced a single-phase product. It was obvious from the powder pattern that this phase was not a spinel. Single crystals were isolated in the form of extremely narrow and long needles which were red in transmitted light and metallic black in reflected light. The needles had a tendency to cluster together and most of the time a line running along the needle axis could be seen, strongly suggesting that the crystal was a twin. Oscillation and Weissenberg photographs from such a needle showed orthorhombic symmetry with lattice parameters $a = 22.60$ Å, $b = 3.91$ Å, $c = 15.06$ Å and space group *Pba*2 or *Pbam*. Electron microprobe analysis of a single crystal showed that both In and Pb were present. No single crystals of reasonable size could be grown and therefore no structure analysis was undertaken.

(5) The product obtained from Sn + 2In + 4S was very similar to that obtained in the Pb–In–S system, and they may be isostructural.

Syntheses of compounds with the general formula $A^{IV}B^{II}X_4$, A = Si, Ge, Sn, Ti, B = Cu, Zn, Cr, Fe, Yb, Pb and X = S, Se were also tried. These compounds have predicted structures which should be related to olivine, $K_2SO_4$, and the monoclinic type. The reaction products from mixtures having A = Si, Ge, B = Cu, and X = S, Se always contained unreacted sulfur and a stoichiometry $AB_2S_3$ which always crystallizes with a tetrahedral structure (*20*, *21*). The system Si + 2Yb + 4Se yielded a product which appeared homogeneous under the optical microscope. No elemental Yb or Yb selenides could be recognized in the X-ray powder pattern but the diffraction lines could not be indexed and no single crystals could be found. The system Ti + 2Pb + 4S produced PbS and $PbTiS_3$ as reported by Sterzel (*18*).

The compounds $SiPb_2S_4$ and $SiPb_2Se_4$ were synthesized and represented new structure types. Their crystal structures are reported elsewhere (*22*).

## Crystal Chemistry of $AB_2X_4$ Compounds

A previously published map of $K_{AB}$ vs $r_A/r_B$ for chalcogenides $AB_2X_4$ was based on 180 reported structures (*17*), and in Fig. 1 a revised diagram has been constructed in which the literature has been surveyed through 1971 and about 400 compounds were included. The ionic radii of Ahrens were used, except for $Cr^{II}$, $Ti^{II}$, $Nb^{III}$, and $Ni^{III}$ whose radii were taken from Shannon and Prewitt (*23*), and for $Yb^{II}$, $Sm^{II}$, and $Eu^{II}$, whose radii were taken from Van Tien and Khodadad (*24*). The observed structures are distributed among ten major types: spinel, olivine, $K_2SO_4$, $Th_3P_4$, $Ag_2HgI_4$, $CaFe_2O_4$, $MnY_2S_4$, $Yb_3S_4$, $Yb_3Se_4$, and a monoclinic type. The compounds with the $Yb_3S_4$ and $Yb_3Se_4$ structures were omitted from the plot.

As previously reported, the plot does not resolve between the spinel and the $Ag_2HgI_4$ types, although some tendency for separation is observed because most of the reported $Ag_2HgI_4$ structures fall in the region of the map where $r_A/r_B$ is relatively high. It is found, however, that another important group of compounds with the $Cr_3Se_4$ structure also falls in the same region of the plot as that occupied by the spinel structure, and no tendency for separation is observed. The resolution is considerably better for those regions of the map in which at least one of the coordinates is small. Thus, the olivine region is well resolved from the spinel region if one does not consider the extreme case of $SnMg_2S_4$ and $SnMg_2Se_4$, whose points fall in the middle of the spinel region. This anomaly is discussed below.

The $Th_3P_4$ and $CaFe_2O_4$ regions are also fairly well resolved from each other as well as from the spinel region. The area occupied by the $K_2MgF_4$ type in the oxide map now corresponds to the $MnY_2S_4$ type (orthorhombic; $Cmc2_1$) in which the metal atoms are disordered. For low values

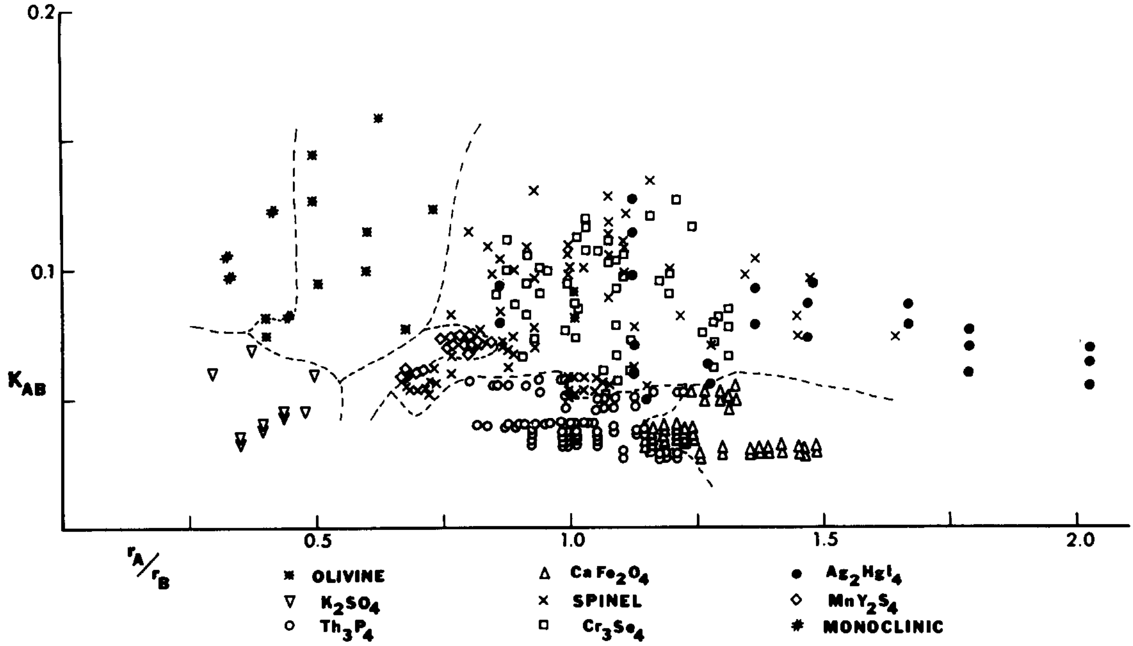

FIG. 1. Plot of $K_{AB}$ vs $r_A/r_B$ for ternary chalcogenides $AB_2X_4$.

of $K_{AB}$, the radius ratio (and of course the temperature for those compounds which are dimorphs) is the factor which determines whether or not the metal atoms are ordered. Thus for $0.03 < K_{AB} < 0.05$, one traverses the ordered $K_2SO_4$ structure ($0.20 < r_A/r_B < 0.55$) to a region in which no compounds have been reported ($0.55 < r_A/r_B < 0.80$); from there one goes to the disordered $Th_3P_4$ structure which occurs for $0.80 < r_A/r_B < 1.15$, and then to the ordered $CaFe_2O_4$ structure when $r_A/r_B > 1.2$.

Similarly, for high values of $K_{AB}$ (0.09–0.15), the transition is from an ordered monoclinic structure for low values of $r_A/r_B$ to the olivine structure for values of $r_A/r_B$ between 0.45 and 0.75, and from this to the unresolved region of the map where inverted spinels and compounds with the disordered $Cr_3Se_4$ structure coexist with normal spinels. It is to be noted, however, that the $Cr_3Se_4$ structure occurs for an interval of $r_A/r_B$ which is roughly centered about $r_A/r_B = 1$ as one would expect if the metal positions are to be interchangeable. No attempt was made in the plot to distinguish between partially disordered spinels (inverse) and normal ones, although Kugimiya and Steinfink found that they also fall relatively close to $r_A/r_B = 1$. For higher values of $r_A/r_B$ one goes without transition to the ordered $Ag_2HgI_4$ type.

For values of $K_{AB}$ between 0.05 and 0.07, the situation is complicated by the interweaving of the spinel, $MnY_2S_4$, and $Th_3P_4$ regions, but the general trend is the same. It is to be noted that some of the compounds which exhibit the $MnY_2S_4$ type also display an ordered structure of the type $Yb_3S_4$ at lower temperatures (1), consistent with the fact that for those compounds $r_A/r_B$ is far from 1, but not as much as in the compounds which only have ordered structures.

It is interesting to note that for high values of $K_{AB}$, structures involving close packing of the anions are frequent (olivine, spinel, $Ag_2HgI_4$), whereas a close-packed arrangement is not observed at low values of $K_{AB}$.

### *$Th_3P_4$ Type*

It is expected that the cationic radius ratio will be close to 1 because the structure is disordered. The coordination number around the metallic atoms is 8 and only reasonably big cations will form this structure. The position of this structure type in the map also suggests that low values of electronegativity are required. This rules out the possible configurations $A^{IV}B_2^{II}X_4$ (except as noted below) and $A^{VI}B_2^{I}X_4$, because cations of the types $A^{IV}$ and $A^{VI}$ are always small and they have high electronegativities. Consequently, only the $A^{II}B_2^{III}X_4$ configuration is possible. Among $B^{III}$ cations the largest radii and the lowest electronegativities are exhibited by the light rare earths, and for $A^{II}$ only $Ba^{II}$, $Sr^{II}$, $Ca^{II}$, $Cd^{II}$, $Pb^{II}$, $Hg^{II}$, and of course $Sm^{II}$, $Eu^{II}$, and $Yb^{II}$ seem to satisfy these criteria. Compounds involving light rare earths and one of the above-mentioned divalent cations have indeed been reported, except for the case of $Hg^{II}$ (1). Among tetravalent cations only $Th^{IV}$, $Pa^{IV}$, and $U^{IV}$ meet the specifications but none of the possible compounds between them and possible divalent cations has been reported.

### *$CaFe_2O_4$ Type*

In this structure the coordination around the A and B atoms is eight- and sixfold, respectively, and again a low value of the electronegativity product is required. Those conditions are met by the heavier of the rare earth metals and the divalent ions with a large radius like $Ba^{II}$, $Sr^{II}$, $Pb^{II}$, $Hg^{II}$, $Eu^{II}$, $Sm^{II}$, and $Yb^{II}$. As in the $Th_3P_4$ type, $Hg^{II}$ is the only ion for which no compound of this nature has been reported. $In^{III}$ also could satisfy the required conditions, provided that the divalent cation has a very low value of the electronegativity. Consequently, this structure is predicted for $SrIn_2S_4$, $BaIn_2S_4$, $SmIn_2S_4$, and $EuIn_2S_4$. However, none of these compounds appears to have been synthesized.

### *$K_2SO_4$ Type*

The crystal chemistry of the compounds $AB_2X_4$ having this structure type for $X = S$ has been reviewed by Susa and Steinfink (11).

### *Olivine Type*

The crystal chemistry of this structure type has been discussed by Susa and Steinfink (11). Several attempts were made to synthesize additional phases with this structure. The compounds $SiCu_2S_4$, $SiCu_2Se_4$, $GeCu_2S_4$, and $GeCu_2Se_4$ could not be formed and instead the phase $ACu_2X_3$ was observed in each case. In these compounds (20, 21) both cations are tetrahedrally coordinated and the structure is based on the zinc blende type. The failure of these compounds to form is due to the tendency of $Cu^{II}$ to occupy a tetrahedral site. It is to be noted that $SnCu_2S_4$ exists (25), and has the spinel structure, as predicted. However, it is known (26) that for $A^{IV}B_2^{II}X_4$ spinels the electrostatic interactions (Madelung energy) favor the inverse configuration except for the case $A^{IV} = Ge^{IV}$. Thus it is logical to expect $SnCu_2S_4$ to be an inverse spinel, and hence some of the $Cu^{II}$ ions are in tetrahedral positions.

The only structures known to occur in compounds having the $AB_2X_4$ stoichiometry (X = any anion) which would accommodate both cations in tetrahedral environments seem to be the phenacite and $Ag_2HgI_4$ structures (*25*). The phenacite structure, which is well-represented among oxides, $AB_2O_4$, has never been found for X = S, Se, Te, and the $Ag_2HgI_4$ structure is favored by high values of $r_A/r_B$.

The compounds $SiZn_2S_4$, $SiZn_2Se_4$, $SiCr_2S_4$, $SiCr_2Se_4$, $SiFe_2S_4$, $GeCr_2S_4$, and $SnMn_2S_4$ for which the olivine structure was predicted could not be prepared, and only the corresponding binary chalcogenides were observed after thermal treatment.

The olivine structure has been observed for X = O, S, Se, and F (*25*, *27*). It is interesting to note that for divalent anions, the A–B cation combination, $A^{IV}B_2^{II}X_4$, seems to be the only one which is observed, the exception being the case of the mineral chrysoberyl $BeAl_2O_4$. This structure is, however predicted for a large number of combinations of the type $A^{II}B_2^{III}X_4$, none of which appears to have been successfully synthesized.

Among the possible combinations $A^{II}B_2^{III}X_4$ for which the olivine structure is predicted are:

(a) $Be^{II}$ and all trivalent cations except rare earth metals, $In^{III}$ and $Sc^{III}$;

(b) $Mg^{II}$, $Mn^{II}$, $Fe^{II}$, $Zn^{II}$, $Ge^{II}$, $Cr^{II}$ and trivalent rare earth metals from La to Gd;

(c) $Pd^{II}$, $Pt^{II}$ and practically all trivalent rare earth metals.

Some of the compounds in (b) fall in an intermediate region between those of olivine and $MnY_2S_4$, but others, like $FeLa_2S_4$, are uniquely predicted to be olivines.

The synthesis of all the compounds in (b) except those involving $Ge^{II}$ and $Zn^{II}$ have been attempted (*1*), and in most cases no single phase could be obtained. The synthesis was successful for $FeLa_2S_4$, $CrLa_2S_4$, $FeCe_2S_4$, and $MnLa_2S_4$, all of which were found to be isostructural and whose structure-type is still unknown. For the cases (a) and (c), no compounds have been reported.

No reason can be offered here to explain why the configuration $A^{IV}B_2^{II}X_4$ is so prevalent, but perhaps detailed calculations of the corresponding Madelung constants would clarify this point.

The compounds $SnMg_2S_4$ and $SnMg_2Se_4$, which should be spinels according to our prediction, are observed to have the olivine structure. The reason for this discrepancy seems to be that the value of the ionic radius of $Mg^{II}$ employed in this calculation (0.66 Å) is inappropriate for the combinations of Mg with S, Se, or Te. Thus Flahaut and colleagues (*1*) find that in most chalcogenide systems $Mg^{II}$ exhibits a radius of 0.77 Å, very close to that of $Mn^{II}$. In agreement with this, $SnMn_2S_4$ (as yet unreported) falls exactly on the boundary between the olivine and spinel regions, and hence either one of these two structures could have been predicted for $SnMgS_4$ and $SnMg_2Se_4$.

### *Spinel and $Cr_3Se_4$ Types*

As previously stated this approach does not distinguish between the spinel and $Cr_3Se_4$ structure-types. The spinel structure is based on a cubic close-packing of the anions with the cations located in the interstices. In the so-called normal configuration, the A cation occupies the tetrahedral voids and the B cation goes to the octahedral ones. Radius ratio requirements are not very restrictive because of the possibility of formation of inverse spinels, with one-half of the B cations occupying the tetrahedral sites and the other half as well as the A cations the octahedral ones. In the $Cr_3Se_4$ structure (*28*), all the Cr atoms are in octahedral coordination and the structure consists of a network of face and edge-sharing octahedra. In the $AB_2X_4$ compounds which exhibit this structure, the A and B cations are randomly distributed over the metallic sites, although some evidence of ordering has been found in some cases (*7*, *8*). The failure of the map to distinguish between these two types points to the naïveté of the approach used when applied to subtle situations. Some observations, however, can be made:

(a) The $Cr_3Se_4$ structure has only been reported for compounds in which both A and B are first-row transition metals (the only exception is Rh).

(b) Selenides and tellurides are much better represented than sulfides, while oxides are not represented at all.

The hypothesis can be advanced that as the electrostatic energy diminishes because of increasing size of the anions, crystal field-stabilization energies (or $\pi$-bond formation) may become important when transition metals are present. This may explain, for instance, that $NiCr_2O_4$ is a spinel while $NiCr_2S_4$ has the $Cr_3Se_4$ structure, since both $Ni^{II}$ and $Cr^{III}$ have high values for the octahedral site preference energy (*29*). Similarly, $FeCr_2S_4$ is a spinel while $FeCr_2Se_4$ is reported to have the $Cr_3Se_4$ structure, and $Fe_3O_4$ and $Fe_3S_4$ are spinels while $Fe_3Se_4$ has the $Cr_3Se_4$ structure. The concept that the tendency of some ions to prefer octahedral coordination can stabilize a structure by lowering the Madelung energy (e.g., the relative stability of normal and inverse spinels) is well documented (*26*). The above interpretation is proposed using the values of the octahedral site preference energies in oxide fields, and should be regarded only as a plausibility argument.

### *$Ag_2HgI_4$ Type*

This structure is based on the cubic close packing of the anions, with all the cations occupying $\frac{3}{4}$ of the tetrahedral metal positions which are occupied by Zn in the zinc blende structure. The structure has been reported for $AB_2X_4$ when A = Zn, Cd, Hg; B = Al, Ga, In and X = S, Se, Te.

$In^{III}$ appears to be too big for tetrahedral coordination and consequently only the tellurides having this structure are observed when $B = In^{III}$. The corresponding sulfides and selenides usually display the spinel structure. $Cd^{II}$ and $Hg^{II}$ are also too big for tetrahedral coordination so the bond is unlikely to be ionic. The minimum distance Hg–S in cinnabar is 2.35 Å and Cd–S is about 2.50 Å in the cubic modification of CdS. If these distances are used to estimate the radii of these two elements in chalcogenide compounds the points representing reported compounds with the $Ag_2HgI_4$ structure tend to move towards the spinel region. Thus the map does not resolve this structure from the spinel type.

### *Monoclinic Structure Types*

At very low values of the radius ratio and at a high value of $K_{AB}$, a region characterized by monoclinic structures is found in the map. The only four compounds which fall in this region are $GePb_2S_4$, $GeSr_2S_4$, $SiPb_2S_4$, and $SiPb_2Se_4$.

$GePb_2S_4$ has been studied by Susa and Steinfink (*11*) and reported to be monoclinic $P2_1/c$ with a structure related to the $K_2SO_4$ type. The similarity with the $K_2SO_4$ type was assessed from the fact that the unit-cell volume and the sum of the ionic radii $r_A$, $r_B$, and $r_X$ when plotted together with the corresponding values from compounds having the $K_2SO_4$ structure give a straight line. This was not the case for $SiPb_2S_4$ and $SiPb_2Se_4$ for which the unit-cell volume is too big to fit on that plot.

The structures of $SiPb_2S_4$ and $SiPb_2Se_4$ (*22*) are extremely similar and from the point of view of this discussion these compounds can be considered as isostructural. A closely related structure has been reported for $GeSr_2S_4$ (*30*).

It appears that the stringent requirements on the radius ratio and electronegativity necessary to produce this structure are only satisfied by column IVA elements. However, this structure is predicted for combinations of $Be^{II}$ with relatively big cations with high electronegativity like $In^{III}$ and $Sc^{III}$ and rare earths from $Er^{III}$ to $Lu^{III}$, while the combinations of $Be^{II}$ with light rare-earth metals are expected to have the $K_2SO_4$ structure. None of these compounds has been reported.

The combinations of Si with divalent rare earths fall on the borderline between the $K_2SO_4$ structure-type region and the monoclinic region, while the combination of Ge with the divalent rare earths lie in the transition between the olivine and the monoclinic regions. The syntheses of $SiYb_2S_4$, $SiYb_2Se_4$, $GeYb_2S_4$, and $GeYb_2Se_4$ were attempted, but only $SiYb_2Se_4$ appeared to give a homogeneous phase. The powder pattern could not, however, be indexed in terms of the lattice parameters of any of the expected structures.

### *$Yb_3S_4$ Structure Type*

This type is exhibited only by the low-temperature modifications of $CaLn_2S_4$ (Ln = Y, Er, Tm, Yb, Lu) and $YbLn_2X_4$ (Ln = Y, Ho, Er, Tm, Yb, Lu; X = S, Se). These compounds undergo a polymorphic transformation at high temperatures giving the $MnY_2S_4$ type for the calcium compounds and the $Th_3P_4$ type for some of the $Yb^{II}$ compounds. For all these compounds, the $Th_3P_4$ structure is predicted, and it should be noted that $CaLn_2S_4$ compounds are the only ones which do not have this structure at any temperature.

### *$MnY_2S_4$ Type*

The region occupied by this structure in the map corresponds approximately to that of the $K_2MgF_4$ type in the oxide map (*17*). The structure type is still unknown. This structure is observed for combinations $AB_2S_4$, where *B* is a rare earth metal (from Dy to Tm) and *A* is either a divalent transition metal or Mg, Ca, or Yb. The reasons why $Ca^{II}$ and $Yb^{II}$ with big ionic radii follow the same crystal chemistry as $Mg^{II}$, $Mn^{II}$, $Fe^{II}$, or $Cr^{II}$ are not very clear.

The structure is predicted for similar compounds involving other small divalent ions like $Co^{II}$, $Ni^{II}$, $Cu^{II}$, and $Zn^{II}$. Of those, only $ZnY_2S_4$ seems to have been prepared (*1*), but this structure does not appear to be the $MnY_2S_4$ type.

### *Other Structure Types*

Compounds with the formula $CaLn_2Se_4$ (*1*) (Ln = Dy–Lu) show a rhombohedral distortion of a NaCl-type structure with voids. The corresponding points fall in the $Th_3P_4$ region of the map.

Several compounds with general formula $MNb_2S_4$, where M = Ni, Mn, Fe, Co, Cu, have been reported to have the berthierite structure (*31*), but later the powder patterns have been indexed in terms of a hexagonal cell (*32*). The structure-type remains unknown. The points representing these compounds would fall in the spinel region and given that both metals are transition metals, the $Cr_3Se_4$ structure could have been expected.

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