

## CRYSTAL CHEMISTRY

*Dedicated to the 50th Anniversary of the Journal*

# Crystal Chemistry and Prediction of Compounds with a Structure of Skutterudite Type

**K. S. Aleksandrov and B. V. Beznosikov**

*Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences,  
Akademgorodok, Krasnoyarsk, 660036 Russia*

*e-mail: kaleks@iph.krasn.ru*

Received February 16, 2006

**Abstract**—Crystallochemical analysis of skutterudite-type structures in the  $BX_3$ ,  $AB_4X_{12}$ , and  $AB'_3B_4O_{12}$  compositions ( $A$  and  $B$  are metals;  $X = P, As, Sb$ ) has been performed. Probable regions of structure formation are determined, thereby indicating that more than 270 new compounds of the  $AB_4X_{12}$  composition can be synthesized.<sup>1</sup>

PACS numbers: 91.60.Ed

DOI: 10.1134/S106377450701004X

## INTRODUCTION

Skutterudite is a mineral of the basic composition  $CoAs_3$  (Fig. 1), which contains nickel and iron impurities. It was named after the region where it was first found (Skutterud, southern Norway). This mineral is formed under high-temperature hydrothermal conditions; it has a Mohs hardness of 6 and a density of  $6.8 \text{ g/cm}^3$  [2–4].

The lattice of the  $ReO_3$  type can be considered as a parent for skutterudite structures. Under high pressure, the  $ReO_3$  structure transforms into the skutterudite type with the sp. gr.  $Im\bar{3}$ ,  $Z = 8$ , in which octahedra are rotated with respect to all three previous axes of the  $ReO_3$  structure [5]. It was found that other crystals with perovskite structure can likewise be transformed into skutterudite-type ones as a result of a change in their composition. Such experiments have been performed with a limited number of crystalline oxides:  $CaCu_3Mn_4O_{12}$  [6, 7],  $CaCu_3Ti_4O_{12}$  [8–12] (Fig. 1), and  $Bi_{2/3}Cu_3Ti_4O_{12}$  [13]. In recent decades, the interest in physical properties of skutterudite crystals has been confirmed by a large number of publications, in particular, [14–16]. The purpose of this study is crystallochemical analysis of skutterudite structures.

<sup>1</sup> The results of this study were published in more detail in preprint no. 833 F [1] and are presented in the online version of the publications of the Kirensky Institute of Physics, Siberian Division of the Russian Academy of Sciences, at the website <http://www.kirensky.ru>, section “preprints.”

## ANALYSIS OF SKUTTERUDITE STRUCTURES

With respect to the type of chemical bonding, compounds of P, As, and Sb with many metals are intermediate between ionic and metallic. The larger the atomic numbers of metal elements, the more pronounced is the metallic character of a compound [17, 18].

The skutterudite unit cell is cubic, with  $a = 8.189 \text{ \AA}$  and sp. gr.  $Im\bar{3}$ . The numbers  $Z$  of formula units are 8 and 2 for  $CoAs_3$  and  $Co_4(As_4)_3$ , respectively. The atomic positions are Co 8 ( $c$ ) (000) and As 24 ( $g$ ) (0yz);  $y/b = 0.35$  and  $z/c = 0.15$  [1].

Squares formed by As atoms are located in six (from eight) octants of the unit cell; these squares are oriented in three mutually perpendicular planes. Each Co atom is surrounded by six As atoms (Fig. 2a), each As atom is surrounded by four Co atoms [2], and two octants are empty (Fig. 2b).

The general formula of structures of skutterudite type can be written as  $\square^{XII}B_4^{VI}X_{12}$ , where the symbol  $\square$  denotes a vacancy and the superscripts are coordination numbers. In the structures under consideration, these vacancies are not structural defects but unoccupied positions, i.e., empty atomic polyhedra, which can be filled by atoms of another kind with a change in the chemical composition of crystals.

This statement is confirmed by the results of investigations of the physical properties of crystals with partially or completely filled vacancies and coordination formulas  $A_2^{XII}B_4^{VI}X_{12}$  ( $A$  and  $B$  are metals (cations);  $X = P, As, Sb$ ), referred to as filled skutterudites (Fig. 1).

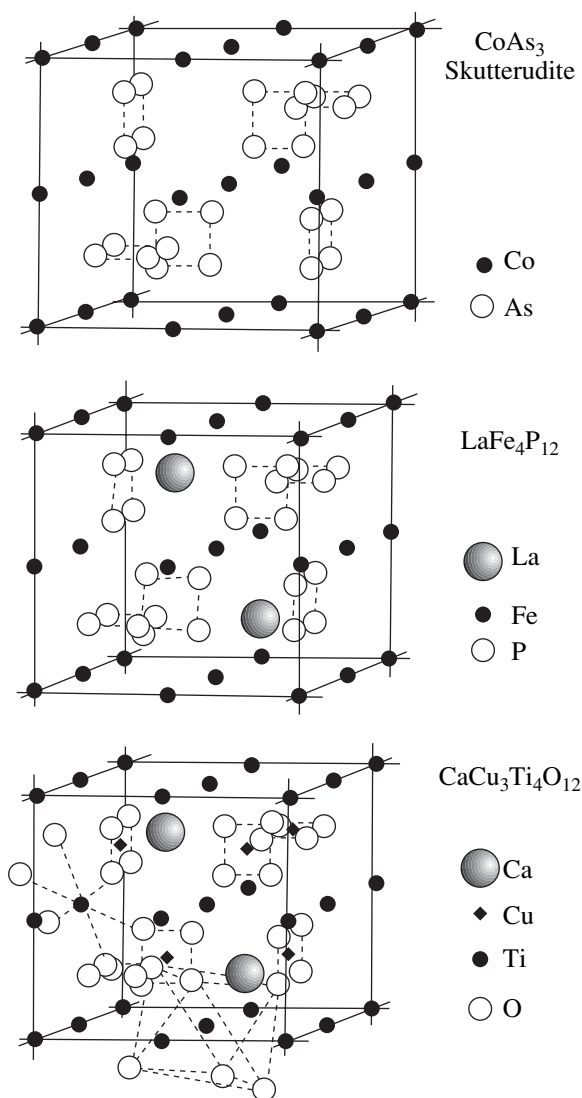


Fig. 1. Schematic image of skutterudite-type structures.

The structural parameters of empty and filled skutterudites are described in the online version of preprint [1].

In skutterudite, cobalt has an octahedral environment. The values of bond lengths are in good agreement with the sums of atomic radii (with correction to the coordination number) [19]. The bonds in atomic octahedra and in squares are moderately compressed. Analysis of skutterudite-type structures showed that they can be represented in the form of a 3D octahedral framework (Fig. 2a). Such a representation makes it possible to consider them to be related to structures of ReO<sub>3</sub> and perovskite (CaTiO<sub>3</sub>) types. The difference between CoAs<sub>3</sub> and ReO<sub>3</sub> (if we disregard rotations of octahedra) is in the types of polyhedra located between octahedra.

In the cubic structure of ReO<sub>3</sub>, the space between eight octahedra is a regular cuboctahedron. Under high pressure (~0.52 GPa), this structure is transformed into

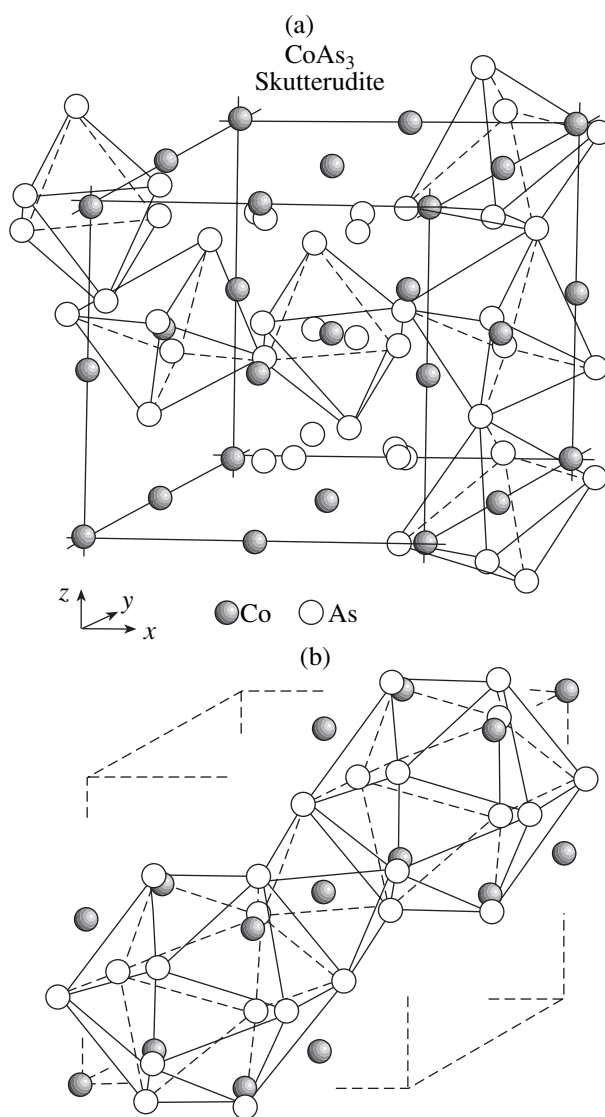
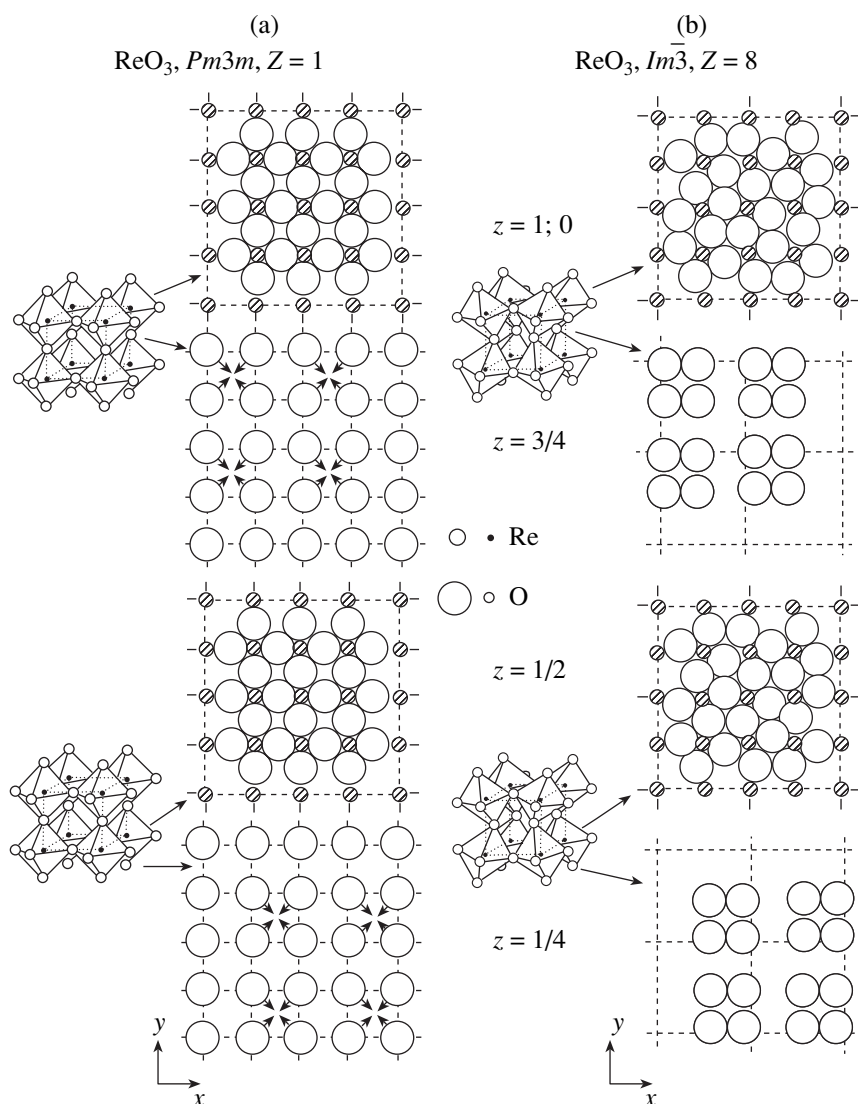


Fig. 2. Skutterudite structure: (a) packing of octahedra (not all octahedra are shown) and (b) icosahedral polyhedra in two empty octants of the structure.

the skutterudite type  $Im\bar{3}$  ( $Z=8$ ). In this case, octahedra are rotated around all three previous fourfold axes according to the scheme  $a^+a^+a^+$  (in Glazer notation [20]) by an angle of about 8°, and the packing factor (the ratio of the volume of ions to the unit-cell volume) increases from 66.8 to 89.4%. The decrease in the cell volume leads to an increase in the crystal density by 34%. The Re–O–Re valence angle is now close to 165° as a result of the rotations of the octahedra, whereas the Re–O distance in the octahedra remains almost the same.

Figure 3 shows layer-by-layer images of the structure of the cubic ( $Pm\bar{3}m$ ) and skutterudite ( $Im\bar{3}$ ) phases of ReO<sub>3</sub>.



**Fig. 3.** Layer-by-layer image of the  $\text{ReO}_3$  structure: (a) the cubic phase (16 cells are shown) and (b) the skutterudite phase (8 cells are shown).

The changes described above are not final in the reconstruction of the  $\text{ReO}_3$  structure under high pressure. With an increase in pressure to 9 GPa, the  $\text{ReO}_3$  lattice becomes hexagonal [21–23].

The structure of skutterudite  $\text{CoAs}_3$  can be represented in the form of a packing of two octahedral layers (Fig. 4). We can imagine a 3D framework of octahedra in this structure as a stack of octahedral layers with  $z = 0, 1/2$ , and 1.

Many known skutterudites have been synthesized either according to the peritectic reaction (via incongruent melting), under hydrothermal conditions, or under high pressure and temperature. The structure of these crystals is retained under normal thermodynamic conditions.

#### DETERMINATION OF THE REGIONS OF STRUCTURE FORMATION

With the use of the known structural data and principles (see [24, 25]), the following formulas were derived for calculation of the unit-cell parameters of filled skutterudites and the free parameters  $y/b$  and  $z/c$ :

$$\text{at } X = \text{P}, a_{\text{calcd}} = 0.4R_A + 2.8R_B + 3.68,$$

$$\text{at } X = \text{As}, a_{\text{calcd}} = 0.4R_A + 2.8R_B + 4.14,$$

$$\text{at } X = \text{Sb}, a_{\text{calcd}} = 0.4R_A + 2.8R_B + 4.93,$$

$$y/b = 0.103R_B/R_X + 0.255, \text{ calculation error } \pm 1.5\%;$$

$$z/c = 0.190 - 0.048R_B/R_X, \text{ calculation error } \pm 3.5\%,$$

where  $a_{\text{calcd}}$  is the calculated parameter of the cubic unit cell;  $R_A$ ,  $R_B$ , and  $R_X$  are the atomic radii of elements A, B, and X, respectively [19]; and  $y/b$  and  $z/c$  are the free

parameters of atoms  $X$  (all magnitudes are in angstroms).

It is generally accepted to characterize the stability of ionic structures by the allowable values of strengths of  $A-X$  and  $B-X$  bonds [26]. The interatomic distances  $l_{A-X}$  and  $l_{B-X}$  in the actual structure are compared with the unstrained distances, i.e., sums of ionic radii. With respect to the bonding type, the structures under consideration are closer to metallic rather than ionic compounds. Therefore, we will assume the unstrained distance to be a sum of atomic radii. The formulas for calculation of strengths  $\mu$  have the form

$$\mu_{B-X} = [(l_{B-X}/(R_B + R_X)) - 1] \times 100\%,$$

$$\mu_{A-X} = [(l_{A-X}/(R_A + R_X)) - 1] \times 100\%.$$

If the strengths  $\mu_{B-X}$  and  $\mu_{A-X}$  have negative (positive) signs, the bonds are compressed (stretched). In ionic structures, the maximum bond compression is from  $-7$  to  $-10\%$ . With a further increase in the bond compression, a structural phase transition may occur.

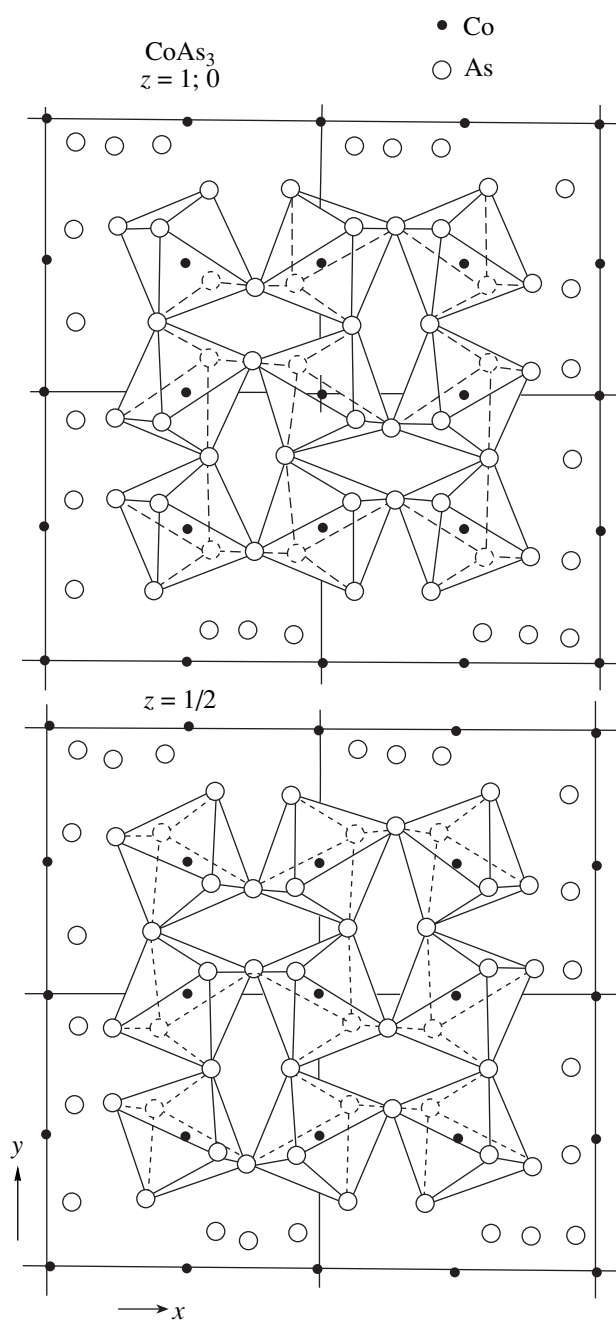
Likely regions of formation of filled skutterudites of  $AB_4X_{12}$  compositions are framed in Tables 1–3. They were determined on the basis of calculated unit-cell parameters and  $A-X$  bond strengths. The maximum allowable size of  $A$  atoms is determined by the maximum  $A-X$  bond compression (up to  $-10\%$ ). The minimum size of  $A$  atoms is determined by the absence of stretching of these bonds. The range of  $B$  atoms is limited to transition metals. All known compounds with structures of filled skutterudite type except for  $UFe_4P_{12}$ ,  $NdOs_4Sb_{12}$ , and several  $LnOs_4P_{12}$  compounds ( $Ln = Tb, Dy, Ho$ ) fall in the framed regions.

### $AB'_3B_4X_{12}$ COMPOUNDS

Some compounds are known whose structure transforms from the perovskite type into the skutterudite type as a result of a change in the chemical composition (Table 4). In these compounds, atoms occupy both octants (which are empty in  $CoAs_3$ ) and the centers of anion squares.

The parent structure for those listed in Table 4 is the four-cell structure of perovskite  $CaTiO_3$  (with the general formula  $ABX_3$ ). The transition from the perovskite structure to the structural type of skutterudite can be described as follows.

If three (of four)  $A$  atoms are replaced by copper atoms, leaving intact one unit cell, the anion cuboctahedra around the three copper atoms will be reconstructed (at rotation of octahedra) as a result the displacement of anions to copper cations. A copper cation cannot retain the cuboctahedral coordination, because it is small and has an electron shell of another type. The anions pairwise shift to copper cations to form a square. At the transition from  $CaTiO_3$  to  $CaCu_3Ti_4O_{12}$ , the  $Ca-O$  distance almost does not change. The coordination of  $Ca$  remains twelfold. The cuboctahedra are transformed




**Fig. 4.**  $CoAs_3$  structure presented in the form of two octahedral layers (four cells are shown). For informativeness, only the completely located octahedra within these four cells are shown.

into icosahedra. The structure formed is a combination of  $CaO_{12}$  icosahedra,  $TiO_6$  or  $MnO_6$  octahedra, and  $CuO_4$  squares. The closest packings are not formed on the basis of icosahedra. However, skutterudite structures in oxide compositions indicate that combinations of icosahedra with other structural elements are possible:  $CuO_4$  squares and  $BO_6$  octahedra. If copper is replaced by other elements capable of forming square oxygen coordination, synthesis of new skutterudite-

**Table 1.** Prediction of  $AB_4P_{12}$  structures ( $Im\bar{3}$ ,  $Z = 2$ )

| $X = P$                           |    |    |    |    |    |    |    |    |    |                                  |
|-----------------------------------|----|----|----|----|----|----|----|----|----|----------------------------------|
| $B \rightarrow$<br>$A \downarrow$ | Ni | Co | Fe | Rh | Ru | Pd | Ir | Os | Pt | $\leftarrow B$<br>$A \downarrow$ |
| Ba                                |    |    |    |    |    |    |    |    |    | Ba                               |
| Sr                                |    |    |    |    |    |    |    |    |    | Sr                               |
| Ca                                |    |    |    |    |    |    |    |    |    | Ca                               |
| Eu                                |    |    | ■  |    | ■  |    |    | ■  |    | Eu                               |
| Yb                                |    |    | ■  |    | ■  |    |    |    |    | Yb                               |
| La                                |    |    | ■  |    | ■  |    |    | ■  |    | La                               |
| Ce                                |    |    | ■  |    | ■  |    |    | ■  |    | Ce                               |
| Pr                                |    |    | ■  |    | ■  |    |    | ■  |    | Pr                               |
| Nd                                |    |    | ■  |    | ■  |    |    | ■  |    | Nd                               |
| Sm                                |    |    | ■  |    |    |    |    | ■  |    | Sm                               |
| Y                                 |    |    | ■  |    |    |    |    | ■  |    | Y                                |
| Th                                |    |    |    |    | ■  |    |    |    |    | Th                               |
| Gd                                |    |    |    |    |    |    |    | ■  |    | Gd                               |
| Tb                                |    |    | ■  |    |    |    |    | ■  |    | Tb                               |
| Dy                                |    |    | ■  |    |    |    |    | ■  |    | Dy                               |
| Ho                                |    |    | ■  |    |    |    |    | ■  |    | Ho                               |
| Er                                |    |    | ■  |    |    |    |    |    |    | Er                               |
| Tm                                |    |    | ■  |    |    |    |    |    |    | Tm                               |
| Lu                                |    |    | ■  |    |    |    |    |    |    | Lu                               |
| Tl                                |    |    |    |    |    |    |    |    |    | Tl                               |
| U                                 |    |    | ■  |    |    |    |    |    |    | U                                |
| $B \rightarrow$                   | Ni | Co | Fe | Rh | Ru | Pd | Ir | Os | Pt | $\leftarrow B$                   |

Note:  is the likely region of formation of skutterudite structures, and ■ are known skutterudite-type structures with filled icosahedra.

type compounds based on oxide perovskites becomes possible.

A limited number of elements can form skutterudite-type structures in simple  $BX_3$  compositions. To provide the transition from a structure containing cuboctahedra to a structure with icosahedra, an "assistant" capable of retaining a square environment around itself is required. Therefore, the choice of new compounds in  $AB_3B_4O_{12}$  compositions can be based on elements with this property.

Synthesis of known compounds is generally performed with elements in evacuated quartz ampoules at high temperatures or by the hydrothermal method. Many single crystals have been grown from solution in


tin, sulfur, and antimony melts. The corresponding data were briefly reported in the literature cited in [1].

## CONCLUSIONS

Most synthesized compounds confirm the prediction given in Tables 1 and 3; however, some compounds fall out of this prediction. Skutterudites in the  $LnOs_4P_{12}$  compositions ( $Ln = Tb, Dy, Ho$ ) [27, 29] are below the geometric boundary of the likely region of formation of skutterudites but within the calculation error (Table 1). This fact can be explained as follows: in the analysis of the region of structure formation, the geometric model was considered under normal thermodynamic conditions, whereas synthesis was carried out under high pressure; i.e., under the conditions that expand the

**Table 2.** Prediction of  $AB_4As_{12}$  structures ( $Im\bar{3}$ ,  $Z = 2$ )

| $X = As$                          |    |    |    |    |    |    |    |    |    |                                  |
|-----------------------------------|----|----|----|----|----|----|----|----|----|----------------------------------|
| $B \rightarrow$<br>$A \downarrow$ | Ni | Co | Fe | Rh | Ru | Pd | Ir | Os | Pt | $\leftarrow B$<br>$A \downarrow$ |
| Ba                                |    |    |    |    |    |    |    |    |    | Ba                               |
| Sr                                |    |    |    |    |    |    |    |    |    | Sr                               |
| Ca                                |    |    |    |    |    |    |    |    |    | Ca                               |
| Eu                                |    |    |    |    |    |    |    |    |    | Eu                               |
| Yb                                |    |    |    |    |    |    |    |    |    | Yb                               |
| La                                |    |    | ■  |    |    |    |    |    |    | La                               |
| Ce                                |    |    |    |    |    |    |    |    |    | Ce                               |
| Pr                                |    |    | ■  |    | ■  |    |    | ■  |    | Pr                               |
| Nd                                |    |    |    |    |    |    |    |    |    | Nd                               |
| Sm                                |    |    |    |    |    |    |    |    |    | Sm                               |
| Y                                 |    |    |    |    |    |    |    |    |    | Y                                |
| Gd                                |    |    |    |    |    |    |    |    |    | Gd                               |
| Tb                                |    |    |    |    |    |    |    |    |    | Tb                               |
| Dy                                |    |    |    |    |    |    |    |    |    | Dy                               |
| Ho                                |    |    |    |    |    |    |    |    |    | Ho                               |
| Er                                |    |    |    |    |    |    |    |    |    | Er                               |
| Tm                                |    |    |    |    |    |    |    |    |    | Tm                               |
| Lu                                |    |    |    |    |    |    |    |    |    | Lu                               |
| Tl                                |    |    |    |    |    |    |    |    |    | Tl                               |
| $B \rightarrow$                   | Ni | Co | Fe | Rh | Ru | Pd | Ir | Os | Pt | $\leftarrow B$                   |

Note:  is the likely region of formation of skutterudite structures, and ■ are known skutterudite-type structures with filled icosahedra.

region of structure formation. Therefore, synthesis of new compounds under pressure may increase the number of new representatives below the lower boundary with respect to the size of atoms  $A$  in Tables 1–3.

Filled skutterudites attract the attention of researchers owing to their unusual physical properties. Compounds containing elements of  $3d$  and  $4f$  groups in their structure exhibit phase transitions to the magnetically ordered state at low temperatures, and a metal–insulator phase transition has been revealed in some compositions [30, 31]. Many crystals belong to systems with heavy fermions [32, 33]. Superconductivity has been found in a number of compounds [23, 33–35]. In  $PrOs_4Sb_{12}$ , the effective heavy fermion mass was estimated to be  $m^* \sim 50m_0$  ( $m_0$  is the electron mass) [36] and, in  $NdOs_4P_{12}$ , the value of  $m^*$  is close to  $100m_0$  [37].

Some data on the specific features of physical properties of filled skutterudites are listed in Table 5.


Particular attention of the researchers of filled skutterudites is paid to the search for systems that could be used in thermoelectric coolers or thermoelectric generators. Such systems are characterized by the quality parameter  $Z = S^2\sigma/k$ , where  $S$  is the Seebeck coefficient,  $\sigma$  is the conductivity, and  $k$  is the thermal conductivity. The dimensionless quality parameter  $ZT$ , which is smaller than unity for the systems studied previously, is generally used.

To this end, attempts have been most often made to use heavily doped semiconductors, complex alloys (for example,  $Bi_2Te_3$ – $Sb_2Te_3$ ), and such skutterudites as  $CoAs_3$  and  $CoSb_3$  [46]. The history of the problem of thermoelectric materials since the 19th century is reviewed in [46].

Investigations of filled skutterudites began only in the 1980s, when these compounds were synthesized for the first time [34]. Among the specific features of their structure, along with the above-mentioned filling of

**Table 3.** Prediction of  $AB_4Sb_{12}$  structures ( $Im\bar{3}$ ,  $Z = 2$ )

| $X = Sb$                          |    |    |    |    |    |    |    |    |    |                                  |
|-----------------------------------|----|----|----|----|----|----|----|----|----|----------------------------------|
| $B \rightarrow$<br>$A \downarrow$ | Ni | Co | Fe | Rh | Ru | Pd | Ir | Os | Pt | $\leftarrow B$<br>$A \downarrow$ |
| Ba                                |    |    | ■  |    |    |    |    |    |    | Ba                               |
| Sr                                |    |    | ■  |    |    |    |    |    |    | Sr                               |
| Ca                                |    | ■  | ■  |    |    |    |    |    |    | Ca                               |
| Eu                                |    | ■  | ■  |    | ■  |    |    |    |    | Eu                               |
| Yb                                |    |    | ■  |    | ■  |    |    |    |    | Yb                               |
| La                                |    |    | ■  |    | ■  |    |    | ■  |    | La                               |
| Ce                                |    | ■  | ■  |    | ■  |    |    | ■  |    | Ce                               |
| Pr                                |    |    | ■  |    | ■  |    |    | ■  |    | Pr                               |
| Nd                                |    |    |    |    |    |    |    | ■  |    | Nd                               |
| Sm                                |    |    |    |    |    |    |    |    |    | Sm                               |
| Y                                 |    |    |    |    |    |    |    |    |    | Y                                |
| Gd                                |    |    |    |    |    |    |    |    |    | Gd                               |
| Tb                                |    |    |    |    |    |    |    |    |    | Tb                               |
| Dy                                |    |    |    |    |    |    |    |    |    | Dy                               |
| Ho                                |    |    |    |    |    |    |    |    |    | Ho                               |
| Er                                |    |    |    |    |    |    |    |    |    | Er                               |
| Tm                                |    |    |    |    |    |    |    |    |    | Tm                               |
| Lu                                |    |    |    |    |    |    |    |    |    | Lu                               |
| Tl                                |    | ■  | ■  |    |    |    |    |    |    | Tl                               |
| $B \rightarrow$                   | Ni | Co | Fe | Rh | Ru | Pd | Ir | Os | Pt | $\leftarrow B$                   |

Note:  is the likely region of formation of skutterudite structures, and ■ are known skutterudite-type structures with filled icosahedra.

two unoccupied voids of the initial skutterudite, are unusually large amplitudes of thermal vibrations of the

atoms filling these voids. Introduction of such “rattling” heavy atoms leads to strong phonon scattering, thereby decreasing the phonon contribution to the thermal conductivity by almost an order of magnitude.

**Table 4.**  $AB_3B_4O_{12}$  compounds

| Compound                          | References | $a$ , Å | $Z$ | $T$ , K          |
|-----------------------------------|------------|---------|-----|------------------|
| $CaCu_3Ti_4O_{12}$                | [28]       | 7.390   | 2   | 298              |
| $CaCu_3Ti_4O_{12}$                | [28]       | 7.384   | 2   | 35               |
| $CaCu_3Ti_4O_{12}$                | [21]       | 7.393   | 2   | room temperature |
| $Sr_{0.8}Cu_{3.2}Ti_{4.26}O_{12}$ | [21]       | 7.420   | 2   | room temperature |
| $CaCu_3Mn_4O_{12}$                | [6]        | 7.241   | 2   | room temperature |
| $CaCu_3Mn_4O_{12}$                | [7]        | ~7.24   | 2   | room temperature |
| $Bi_{2/3}Cu_3Ti_4O_{12}$          | [13, 21]   | 7.417   | 2   | room temperature |

Despite active attempts to obtain materials with large values of  $ZT \geq 2$  at room temperature, this problem has not yet been solved. The largest value known to us from the available literature,  $ZT = 0.17$  at 300 K, was obtained during investigation of the  $Eu_yFe_{4-x}Co_xSb_{12}$  compound [38]. This value increases to  $ZT = 0.9 \pm 0.2$  at 800 K for  $LaFe_3CoSb_{12}$  [47] and, as believed in [47], can be increased even more by optimization of the material composition.

The results of determination of the likely regions of formation of filled skutterudites of  $AB_4X_{12}$  compositions given in Tables 1–3 show that more than 270 new skutterudites can be synthesized. In these compositions, anion squares are not filled with cations. Therefore, a possible condition of obtainment of new com-

**Table 5.** Properties of some filled skutterudites

| Compound  | Properties and phase transitions | References |
|---|----------------------------------|------------|
| Eu <sub>0.41</sub> Co <sub>4</sub> Sb <sub>12</sub> | FM, $T_C = 8$ K                  | [38]       |
| Eu <sub>0.83</sub> Fe <sub>4</sub> Sb <sub>12</sub> | FM, $T_C = 84$ K                 | [39]       |
| EuOs <sub>4</sub> P <sub>12</sub>                   | FM, $T_C = 15$ K                 | [28]       |
| EuRu <sub>4</sub> P <sub>12</sub>                   | magnetic PT, 18 K                | [40]       |
| GdFe <sub>4</sub> P <sub>12</sub>                   | magnetic PT, 22 K                | [28]       |
| GdOs <sub>4</sub> P <sub>12</sub>                   | FM, $T_C = 22$ K                 | [28]       |
| GdRu <sub>4</sub> P <sub>12</sub>                   | AFM, $T_N = 22$ K                | [40, 41]   |
| LaFe <sub>4</sub> P <sub>12</sub>                   | SC, $T_C = 7.02$ K               | [42]       |
| LaOs <sub>4</sub> P <sub>12</sub>                   | SC, $T_C = 1.83$ K               | [42]       |
| NdFe <sub>4</sub> P <sub>12</sub>                   | FM, $T_C = 2$ K                  | [43]       |
| PrFe <sub>4</sub> P <sub>12</sub>                   | AFM, $T_N = 6.2$ K               | [43]       |
| PrOs <sub>4</sub> Sb <sub>12</sub>                  | SC, $T_C = 1.89$ K               | [43]       |
| PrRu <sub>4</sub> P <sub>12</sub>                   | metal-insulator PT, 63 K         | [44]       |
| TbRu <sub>4</sub> P <sub>12</sub>                   | magnetic PTs at 20 and 10 K      | [40, 41]   |
| UFe <sub>4</sub> P <sub>12</sub>                    | FM, $T_C = 3.15$ K               | [45]       |
| YOs <sub>4</sub> P <sub>12</sub>                    | SC, $T_C = 3$ K                  | [28]       |

Note: AFM, FM, SC, and PT denote antiferromagnet, ferromagnet, superconductor, and phase transition, respectively.

pounds of  $A^{XII}B_3^{IV}B_4^{VI}X_{12}$  compositions is filling of anion squares. Cations capable of retaining a square anionic environment are required. Likely candidates for oxide compositions are the divalent cations Pd, Co, and Cu.

The results obtained in this study open a wide field of activity for further investigations. New skutterudite-type compounds may be of interest for solving fundamental problems of condensed-matter physics and, primarily, such properties of materials as magnetoresistance, superconductivity, and thermoelectricity. Crystals of such compositions should have high hardness and density.

#### ACKNOWLEDGMENTS

The study was carried out at the Laboratory of Crystal Physics of the Kirensky Institute of Physics, Siberian Division of the Russian Academy of Sciences (SD RAS), within program no. 9.1 of the RAS Presidium and the integration project no. 88 of the SD RAS and supported by the Federal Agency for Science and Innovation (grant RI 112/001/041).

#### REFERENCES

1. B. V. Beznosikov and K. S. Aleksandrov, Preprint No. 833 F, IF SO AN SSSR (Kirensky Institute of Physics, Siberian Branch of the Academy of Sciences of the Soviet Union, Krasnoyarsk, 2005) (on-line version <http://www.kirensky.ru>, section "preprints").
2. G. B. Bokiĭ, *Introduction to Crystal Chemistry* (Mosk. Gos. Univ., Moscow, 1954) [in Russian].
3. R. Ubelt, *Guide to Minerals* (Mir, Moscow, 1978) [in Russian].
4. A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1975).
5. J. E. Schirber, B. Morosin, R. W. Alkire, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **29**, 4150 (1984).
6. H. Wu, Q. Zheng, and X.-G. Gong, *Phys. Rev. B: Condens. Matter Mater. Phys.* **61**, 5217 (2000).
7. R. Weht and W. E. Picken, *Phys. Rev. B: Condens. Matter Mater. Phys.* **65**, 014415 (2002).
8. R. Lunkenheimer, R. Fichtl, S. G. Ebbinghaus, and A. Loidl, *Phys. Rev. B: Condens. Matter Mater. Phys.* **70**, 172102 (2004).
9. L. Zhang and Z.-J. Tang, *Phys. Rev. B: Condens. Matter Mater. Phys.* **70**, 174306 (2004).
10. A. Tselev, C. M. Brooks, S. M. Angle, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **70**, 144101 (2004).
11. D. Valim, A. G. Soura Filho, P. T. C. Freire, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **70**, 132103 (2004).
12. C. McGuinness, J. E. Downes, P. Sheridan, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **71**, 195111 (2005).
13. J. Liu, C.-G. Duan, W.-G. Yin, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **70**, 144106 (2004).
14. K. S. Aleksandrov, in *Phase Transitions in Crystals of ABX<sub>3</sub> Haloid Compounds*, Ed. by A. T. Anistratov, B. V. Beznosikov, and N. V. Fedoseeva (Nauka, Novosibirsk, 1981) [in Russian].
15. K. S. Aleksandrov and B. V. Beznosikov, *Perovskite-like Crystals* (Nauka, Novosibirsk, 1997) [in Russian].
16. K. S. Aleksandrov and B. V. Beznosikov, *Perovskites: Present and Future. Variety of Parent Phases, Phase Transitions, Possibilities of Synthesis of New Compounds* (Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 2004) [in Russian].
17. I. Năray-Szabó, *Inorganic Crystal Chemistry* (Akadémiai Kiadó, Budapest, 1969).
18. *Brief Chemical Encyclopedia* (Sov. Entsiklopediya, Moscow, 1961–1967).
19. *Modern Crystallography*, Vol. 2: *Structure of Crystals*, Ed. by B. K. Väinshéin, V. M. Fridkin, and V. L. Indenbom (Nauka, Moscow, 1979) [in Russian].
20. A. M. Glazer, *Acta Crystallogr. B* **28**, 3384 (1972).
21. JCPDS: International Centre for Diffraction Data, v.1.30 (1997).
22. T. I. Dyuzheva, N. A. Bendeliani, and S. S. Kabalkina, *Dokl. Akad. Nauk SSSR* **298**, 100 (1988) [*Sov. Phys. Dokl.* **33**, 1 (1988)].
23. M. A. Measson, D. Braithwaite, J. Flouquet, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **70**, 064516 (2004).
24. B. V. Beznosikov, Preprint No. 632 F, IF SO AN SSSR (Kirensky Institute of Physics, Siberian Branch of the Academy of Sciences of the Soviet Union, Krasnoyarsk, 1990).
25. B. V. Beznosikov, *Kristallografiya* **38**, 189 (1993) [*Crystallogr. Rep.* **38**, 234 (1993)].



26. E. G. Fesenko, *Perovskite Family and Ferroelectricity* (Atomizdat, Moscow, 1972) [in Russian].
27. M. Puyet, B. Lenoir, A. Dauscher, et al., *J. Solid State Chem.* **177**, 2138 (2004).
28. H. Lixin, J. B. Neaton, M. H. Cohen, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **65**, 214112 (2002).
29. K. Kihou, I. Shirovani, Y. Shimaya, et al., *Mater. Res. Bull.* **39**, 317 (2004).
30. C. H. Lee, H. Matsuhata, H. Yamaguchi, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **70**, 153105 (2004).
31. C. Sekine, T. Uchiumi, and I. Shirovani, *Rhys. Rev. Lett.* **79**, 3218 (1997).
32. E. D. Bauer, A. Slebarski, E. J. Freeman, et al., *J. Phys.: Condens. Matter* **31**, 4495 (2004).
33. E. D. Bauer, N. A. Frederick, P. C. Ho, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **65**, 100506 (2002).
34. W. Jeitschko and D. Braun, *Acta Crystallogr. B* **33**, 3401 (1977).
35. M. S. Torikachvili, J. W. Chen, Y. Dalichaouch, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **36**, 8660 (1987).
36. M. Nishiyama, T. Kato, H. Sugawara, et al., *J. Phys. Soc. Jpn.* **74**, 1938 (2005).
37. P.-C. Ho, W. M. Yuhasz, N. P. Butch, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **72**, 094410 (2005).
38. Grytsiv, P. Rogl, St. Berger, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **66**, 094411 (2002).
39. E. Bauer, St. Berger, M. Galli, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **63**, 224414 (2001).
40. C. Sekine, M. Inoue, T. Inaba, and I. Shirovani, *Physica B* **281**, 308 (2000).
41. C. Sekine, T. Uchiumi, I. Shirovani, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **62**, 11581 (2000).
42. G. P. Meisner, *Physica B* **108**, 763 (1981).
43. M. Kobayshi, H. Sato, H. Sugawara, et al., *J. Phys. Soc. Jpn.* **74**, 1690 (2005).
44. K. Iwasa, L. Hao, K. Kuwahara, et al., *Phys. Rev. B: Condens. Matter Mater. Phys.* **72**, 024414 (2005).
45. G. P. Meisner, M. S. Torikachvili, K. N. Yang, et al., *J. Appl. Phys.* **57**, 3073 (1985).
46. G. Mahan, B. Sales, and J. Sharp, *Phys. Today*, No. 3, 42 (1997).
47. B. C. Sales, D. Mandrus, and R. K. Williams, *Science* **272**, 1325 (1996).

*Translated by Yu. Sin'kov*