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$Re_4As_6S_3$, a thio-spinel-related cluster system

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Abstract

We have synthesized a new compound with formula $Re_4As_6S_3$ and characterized its crystal structure by Rietveld powder diffraction methods. $Re_4As_6S_3$ crystallizes in an face-centered cubic unit cell, space group $F\bar{4}3m$ (no. 216), with lattice constant $a = 9.8608(1)$ Å and $Z = 4$. The rhenium atoms form tetrahedral clusters linked via tetrahedral arsenic clusters to produce an NaCl-type arrangement. The oxidation state of rhenium is IV and the number of electrons shared by the rhenium atoms in the cluster is 12. The structure is based on an ordered defect thio-spinel $A_{(1-x)}B_2X_4$ where the B-type atoms form tetrahedral clusters.

Keywords: Rhenium compounds; Tetrahedral clusters; Arsenic clusters; Thio-spinels

1. Introduction

Transition metal clusters show interesting physical properties in thio-spinel-type structures. For instance, a large iridium cluster has been observed in $CuIr_2S_4$, where spin dimerization is observed at low temperature [1]. Other transition metal clusters have been observed in chalcogenides and halides, in particular Chevrel-type cluster systems showing superconductivity at high temperatures [2].

Rhenium clusters occur in numerous compounds, mainly halides and chalcogenides [3]. A large number of them are Chevrel-type octahedral clusters, as for instance in $Re_6Se_8Cl_2$ [4] or Re_2Te_5 [5]. Tetrahedral rhenium clusters occur for example in the compound $Re_4S_4Te_4$, [6] where Re_4S_4 moieties are linked by bridging Te groups. Introducing halogens into such rhenium–chalcogenide systems, related compounds, such as $Re_4Te_4(TeBr_2)_4Br_8$ [7] are obtained. Here, tetrahedral Re–chalcogenide clusters are still present and the structure accommodates the additional electrons by forming $TeBr_2$ molecules linking the clusters with bromide atoms. In both cases, the rhenium valence is IV.

$Re_4S_4Te_4$ has the same defect thio-spinel structure as $GaMo_4S_8$ [8] and $AlMo_4S_8$ [9], with the Ga (or Al) position not occupied. In these compounds, similar tetrahedral transition metal clusters capped by chalcogen atoms are found.

Moving from the chalcogenides to the pnictides, using $Re_4S_4Te_4$ as a starting point, the change in the electron count allows probing the stability of the structure, with Re_3As_7 as a possible end member of the system. Here, we report on a new phase in the Re–As–S system.

2. Experimental part

2.1. Synthesis

The compound $Re_4As_6S_3$ was synthesized by heating the elements in evacuated quartz tubes sealed under a vacuum of 10^{-5} bar in the stoichiometric proportions 4:6:3. The ampoules were placed in a tube furnace at 500°C for 2 days, then shaken and reheated at 850°C for at least 1 week. The resulting powder was black. Care was taken to minimize the reaction with the quartz walls by adjusting the temperature profile and the quartz quality. Unfortunately, no crystals suitable for single crystal analysis were obtained, even after prolonged heating, warranting the use of the Rietveld method to characterize the structure.

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Phase formation was checked by X-ray diffraction. Varying the stoichiometry toward rhenium rich or sulfur rich areas resulted in the presence of metallic rhenium or ReS_2. However, reaction with the quartz walls often hampered an exact determination of the stoichiometry by the vanishing phase method. An accurate determination of the anion ratio by ICP_OES analysis (Inductively Coupled Plasma Optical Emission Spectroscopy) was obtained on samples with metallic rhenium as the only impurity, after dissolving them in nitric acid. An anion ratio As/S of 2.0(2) was confirmed. The refinement confirmed further away a ratio of 2.

2.2. X-ray diffraction

All X-ray diffraction patterns were obtained with an image foil Huber 670 Guiner camera, using either germanium monochromated $CuK\alpha_1$ radiation, or the synchrotron beam-line I711 at MAX-Lab [10], with a wavelength of 1.35 Å.

2.3. Rietveld refinement

Several refinements on powder patterns of samples from various stoichiometries in the ternary Re–As–S phase diagram were carried out. The diffraction pattern presented in Fig. 1 was collected during 32,000 s using the sealed source in the flat sample transmission geometry. Sample motion was used to get better averaging over grains to reduce texture effects.

All the peaks are indexed using a face-centered cubic lattice with unit cell parameter 9.8460(1) Å and an impurity of elemental Re. With the exception of the face-centering, no additional systematic extinctions were observed, giving the possible space groups $F23$, $Fm3$, $F432$, $F\bar{4}3m$ and $Fm3m$. Based on symmetry of the related phases $Re_4S_4Te_4$ [6] and $AlMo_4S_8$ [9], and the stoichiometry, the most likely space group was assumed to be $F\bar{4}3m$, which was confirmed by the subsequent refinements.

The Rietveld refinements were carried out using the programs WINPOW [11], a local windows version of LHMP1 [12] and PC-GSAS [13]. The final refinement presented in Fig. 1 was carried out in WINPOW using the laboratory data. The laboratory data was obtained using the flat, thin sample geometry, whereas the synchrotron measurement made use of a capillary sample. However, the absorption and texture correction for the latter hampered the refinement, but structural parameters were identical. The background, which at low-angle is due to scattering from the sample mount, was fitted with Chebyshev polynomials. The two phases present, $Re_4As_6S_3$ and elemental Re were refined simultaneously. Assignment of atom types was made according to the chemistry for the rhenium atoms and, considering Fourier maps and the anion ratio, for the other atoms.

Details of the refinement are given in Table 1, while the final atomic positions and thermal displacement parameters are shown in Table 2. Fig. 1 shows the corresponding observed diffraction pattern and the difference from the refined model. Some interatomic distances are presented in Table 3.

2.4. Tight-binding calculations

To compare the electronic band structure to the one given for $GaMo_4S_8$ [14] extended Hückel tight-binding calculations were performed for $Re_4As_6S_3$, within the extended Hückel formalism in the program YAeHMOP [15].

3. Results and discussion

The structure of $Re_4As_6S_3$ is part of a family of structures that are related to a defect thio-spinel of type $A_{(1-x)}B_2X_4$. In Fig. 3, the ideal and observed structures are shown. In this family of structures, the lowering of the symmetry from $Fd3m$ to the isomorphic subgroup $F\bar{4}3m$ splits the $32e$ anion position into two 16-fold positions. These two positions are occupied by the same atoms in the thio-spinel $A_{(1-x)}B_2X_4$, but they may also contain chemically different atoms for a more general family of compounds with formula $AA'B_4X_4Y_4$. In $Re_4As_6S_3$, one of these positions is occupied entirely by arsenic atoms (IV) whereas the other contains a random mixture of sulfur and arsenic atoms (II) in a 3:1 ratio. As a consequence, the simple close packed anion lattice in the thio-spinels now consists of two distinct sublattices, producing a distorted close packed anion lattice.

The position of atom A in the spinel-type (previously the 8a position) also splits into two different positions of multiplicity 4 each, one at (0,0,0), surrounded by four atoms from the first sublattice (in $Re_4As_6S_3$, 4 arsenic atoms), the other at $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$, surrounded by 4 atoms from the second sublattice (in $Re_4As_6S_3$ 4 As/S atoms). Once again, these two new positions allow flexibility in the chemistry of this family of compounds: they can be both unoccupied, as in $Re_4S_4Te_4$ [6], both partially occupied as in $Ga_{1.33}Cr_4S_8$ [16], or only one occupied, as in $GaMo_4S_8$ and $Re_4As_6S_3$. In the latter, a central arsenic is found in (0,0,0), producing an As_5 clusters (see Fig. 3).

The atom B, in the ideal spinel at the octahedral site $16d$ (at $\frac{3}{8},\frac{3}{8},\frac{3}{8}$), is moved out of its ideal position, shifting along the body diagonal of the unit cell (coordinates (x,x,x)). This produces different interatomic distances, allowing contacts with other atoms in symmetry-related B positions. As a consequence numerous cluster compounds are formed in the $AA'B_4X_4Y_4$ family. In $Re_4As_6S_3$, the rhenium atoms have short contacts at a

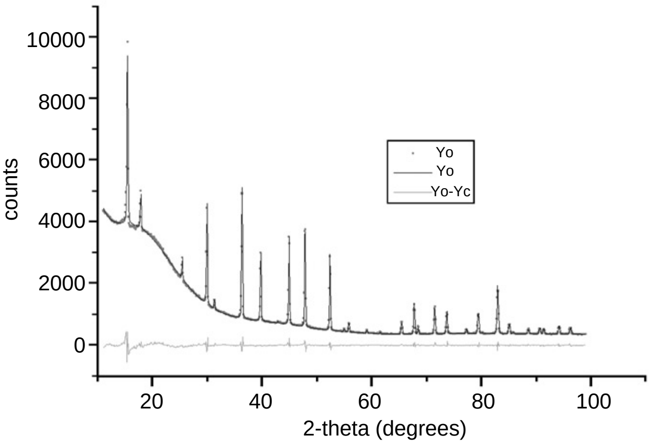

Fig. 1. Experimental and difference diffraction pattern for the Rietveld refinement.

Table 1
Structure refinement: Crystallographic data and residuals for the refinement of the $Re_4As_6S_3$ phase

Space group	$F\bar{4}3m$ (no. 216)
Lattice parameter	9.8608(1) Å
Z	4
Wavelength	1.54056 Å
Two-theta range used (deg.)	10–99
Step scan instrument	0.005
Number of reflections	40
Number of structural parameters	10
Residuals	
R_{Bragg}	0.007
R_{p}	0.018
wR_{p}	0.026
GOF	7.80

Table 2
Atomic positions and isotropic atomic temperature factors

Atom	Wyckoff	*X*	*Y*	*Z*	Occ.	Biso ($Å^2$)
Re(I)	16*e*	0.40047(5)	0.40047(5)	0.40047(5)	1	0.4(1)
S(II)	16*e*	0.6386(2)	0.6386(2)	0.6386(2)	0.74 (1)	2.1(1)
As(II)	16*e*	0.6386(2)	0.6386(2)	0.6386(2)	0.26 (1)	2.1(1)
As(III)	4*a*	0	0	0	1	0.1(1)
As(IV)	16*e*	0.1425(1)	0.1425(1)	0.1425(1)	1	0.3(1)

distance of 2.776 Å, and form tetrahedral clusters while maintaining a strongly distorted octahedral coordination. Each rhenium atom is surrounded by three sulfur/arsenic atoms from the second sublattice at 2.41 Å. These ligands, which are capping the faces of the rhenium tetrahedral cluster, are part of an outer tetrahedron, with an edge length of 3.86 Å, in which the metallic rhenium cluster is inscribed (Fig. 5). Three more arsenic atoms from the first sublattice at 2.61 Å complete the octahedral coordination of rhenium.

Since two clusters have formed in the structure of $Re_4As_6S_3$, their relative arrangements follow a simple overall rock-salt type, with Re_4AsS_3 tetrahedral clusters in the place of sodium and As_5 clusters in the place of chlorine (Fig. 4).

In the Re_4AsS_3 cluster (Fig. 5), the arsenic atom is randomly distributed, as indicated by a refined As occupancy of 0.26(1). The observed distance of 2.410 Å is found to be intermediate to the Re–S distance of 2.337 Å found in the Re_4S_4 clusters in $Re_4S_4Te_4$ [6] and the expected distance of 2.551 Å for a Re–As bond in Re_3As_7 [17].

The tetrahedral $[AsAs_4]$ or As_5 cluster shows an arsenic–arsenic distance of 2.43 Å, shorter than the As–As single bond distance of 2.48 Å found for example in Re_3As_7. The As–As distance along the edge of the tetrahedron is 3.97 Å.

The $Re_4As_6S_3$ structure is isostructural to $GaMo_4S_8$ and may be written as $AsRe_4(As_{0.25}S_{0.75})_4As_4$ according to the family of compounds $A'AB_4X_4X'_4$.

Similar to $GaMo_4S_8$, the density of states (DOS) could be separated into 3 parts (Fig. 2), the low lying bands below −14 eV with a metal–ligand bonding character, the central bands showing metal–metal character with a small gap of about 0.5 eV around –9 eV between the bonding and antibonding bands, and the upper bands produced from metal–ligand antibonding. The Fermi energy was calculated for a VEC of 12 electrons per cluster to be –9.8 eV (Fig. 2), a level that filled all the metal–metal bonding states confirming the stability of the cluster. Similar to $GaMo_4S_8$, the *d*-electrons form the bonds in the rhenium cluster. The metal–ligand bonding bands and the metal–metal bonding are not well separated, indicating a strong covalence between the ligands and rhenium.

The rhenium atoms in the tetrahedral cluster contribute a total of 28 electrons, 18 electrons come from the three face-capping sulfur ligands and a further 5 from the capping arsenic ligand, giving a total 51 electrons for the Re_4AsS_3 cluster. Of those 51 electrons, 24 are localized in the rhenium sulfur/arsenic bonding

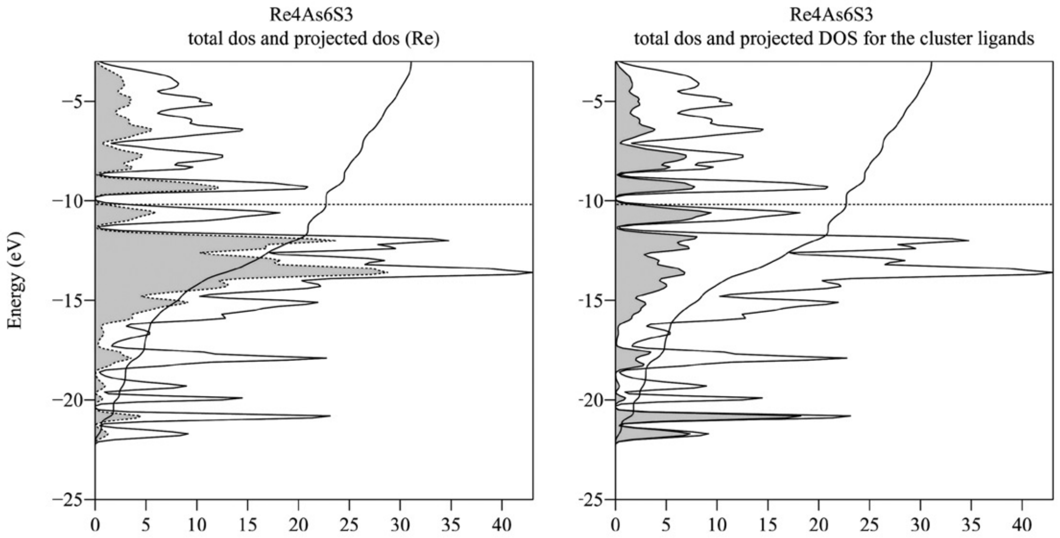

Fig 2. Calculated DOS for $Re_4As_6S_3$.

Table 3
Selected interatomic distances in Å

Re(I)–Re(I) in cluster	2.776(1)
Re(I)–S/As(II)	2.410(2)
S/As(II)–S/As(II) in the tetrahedral	3.864(3)
Re(I)–As(IV)	2.614(1)
As(III)–As(IV)	2.434(2)
As(IV)–As(IV)	3.975(3)

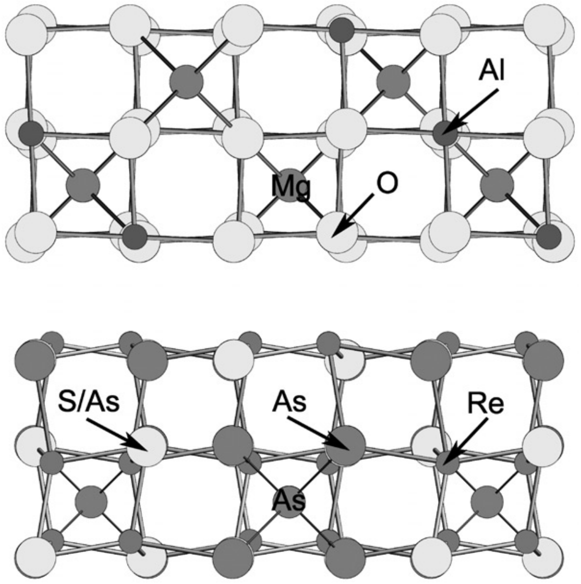

Fig. 3. The ideal spinel (up) and the distorted $AM_4X_4X'_4$ (down) structure adopted by $Re_4As_6S_3$, showing the two different sublattices. Rhenium atoms are in an octahedral site. The tetrahedral position $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$ is occupied in the spinel but vacant in $Re_4As_6S_3$.

and 8 electrons are in lone pairs belonging to the ligands (in the empty tetrahedron centered at the 4c positions $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$, resulting in 19 remaining electrons. Of those, 12 are shared in the rhenium cluster, yielding a formal valence of +7 for the Re_4AsS_3 cluster. This makes the rhenium formally Re^{4+} and is consistent with other reported clusters [3]. The As_5 unit has a formal valence of –7. If one adopts a purely ionic viewpoint, this is consistent with $(As^{5+}As_4^{3-})$. On the other hand a covalent scheme gives $(As^{+}As_4^{2-})$ also giving a formal valence of 7. The covalent description is supported by the small distance of 2.43 Å between the central and outer arsenic atoms.

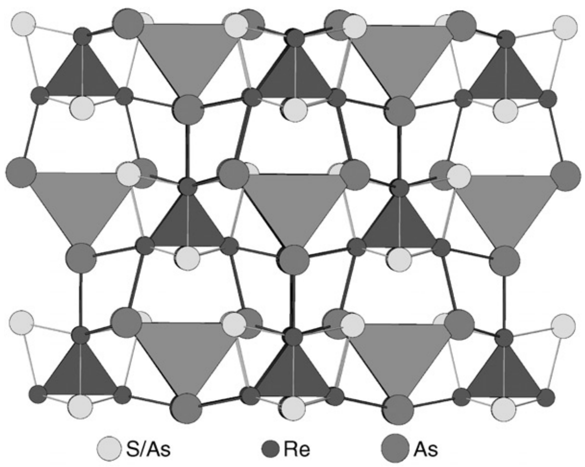

Fig. 4. View of the structure along the [110] axis showing the rock salt arrangement of the Re_4AsS_3 clusters and the As_5 clusters.

We propose that other compounds containing both arsenic (pnictogen) and chalcogen atoms might be stable. For example, since the substitution of S by Se is possible in the case of the MoS_4 tetrahedral clusters [18], the selenide analog $[(Re^{4+})_4(Se^{2-})_3(As^{3-})][(As^{5+})(As^{3-})_4]$ is expected to form. Furthermore, introduction of group IV elements should be possible, resulting in compounds such as $[(Re^{4+})_4(S^{2-})_4][(Ge^{4+})(As^{3-})_4]$ or $[Re^{4+})_4(S^{2-})_3(As^{3-})]$ $[(Si^{4+})(As^{3-})_4]$

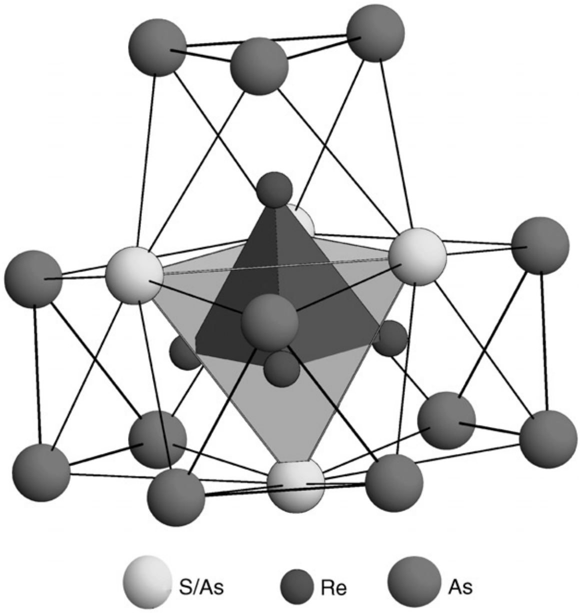

Fig. 5. The Re_4AsS_3 cluster.

where the Ge(Si) atom would restore the $SiAs_4$ fragment to an overall valence of –8, similar to the □Te4 fragment in $Re_4S_4Te_4$. Initial attempts to synthesize $Re_4S_4GeAs_4$ were carried out, however, due to the close similarities in the powder diffraction patterns and the fact that impurity phases were present, the refinement of this structure needs to be confirmed. In addition, other transition metals may substitute for rhenium [19].

4. Conclusion

We have synthesized a new compound derived from a defect thio-spinel that is rich in arsenic. The anion lattice is mixed, consisting of two different interpenetrating sublattices, one formed by arsenic, the other by sulfur with some random admixture of arsenic in a 3:1 ratio. The rhenium cations form tetrahedral clusters inscribed in a larger anion tetrahedron. Tetrahedral arsenic clusters are also present. It is interesting to note that, formally, arsenic may be considered to be present as a cation as well as an anion.

This new compound is related to the ordered defect thio-spinel structures $AA'B_4X_4Y_4$ that may be considered as a generalized version of the simple thio-spinel-type structure AB_2X_4. This structure is remarkably stable, including compounds based on a wide variety of transition metal atoms, pnictogens, chalcogens and halides. The two distinct anion sublattices allow distortions to accommodate cluster formation and produce two distinct tetrahedral interstitial sites.

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