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The mixed intermetallic silicide $\text{Nb}_{5-x}\text{Ta}_x\text{Si}_3$
Single crystal and electronic structure.

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Abstract

Intermetallic transition metals silicides are of particular interest because of their specific properties such as high melting point, oxidation resistance, creep resistance and toughness. Single crystals of compound $\text{Nb}_{5-x}\text{Ta}_x\text{Si}_3$ have been obtained and their X-ray structure was solved and refined in the tetragonal $I4/mcm$ space group $a = 10.0335(2)(8)$, $c = 5.0347(1)$ Å. Stability and bonding of $\text{Nb}_{5-x}\text{Ta}_x\text{Si}_3$ compound are analyzed comparatively with Nb_5Si_3 and Ta_5Si_3 parents, by means of DFT calculations.

Keywords

Intermetallics, crystal structure, X-ray diffraction, electronic band structure, enthalpy.

1. Introduction

Compounds that form between metals and silicon, known as intermetallic silicides, have attracted attention for their usefulness in a large variety of applications. Transition metal silicides are of great interest for their particular properties as excellent oxidation and corrosion resistance, creep resistance and high melting points, high hardness, high thermal conductivity... Thermal stability and chemical resistivity of refractory metal silicides enable their use as high temperature materials for advanced applications or their protective role in high temperature coatings. Generally, transition metals silicides display metal-type conduction which is an advantage in microelectronic applications devices such as Schottky barriers, ohmic contacts, gate interconnects, layers... As an example, high temperature stable Schottky contacts to GaAs have been obtained from refractory-metal-silicide/GaAs interfaces [1, 2]. Focusing on niobium and tantalum silicides, the binary diagrams available in literature [3] display analogies since they both contain three stable compounds M_3Si , M_5Si_3 and MSi_2 but they differ by the existence, only in the Ta-Si system, of compound M_2Si . The structures of these compounds established from X-ray powder data are reported in the Pearson crystal data base [4]. The compound Ta_2Si is described in the tetragonal space group $I4/mcm$ with $a = 6.16$, $c = 5.04$ Å. With the highest metal content, the isostructural compounds Ta_3Si ($a = 10.19$, $c = 5.17$ Å) and Nb_3Si ($a = 10.22$, $c = 5.19$ Å) belong to tetragonal $P4_2/n$ space group. Note that two additional cubic forms are also reported for Nb_3Si ($Pm\bar{3}n$, $a = 5.12$ Å and $Pm\bar{3}m$, $a = 4.22$ Å). The hexagonal $P6_222$ structures of $TaSi_2$ ($a = 4.78$, $c = 6.57$ Å) and $NbSi_2$ ($a = 4.82$, $c = 6.59$ Å) were more recently confirmed from single crystal studies [5]. Finally three different structures are reported for the M_5Si_3 composition. The $I4/mcm$ tetragonal Cr_5B_3 -type and W_5Si_3 -type were respectively assigned to low and high temperature forms of M_5Si_3 compound which also exists under the hexagonal Mn_5Si_3 -type.

The present work reports the single crystal X-ray structure of a (Nb,Ta)-mixed silicide obtained at high temperature. The compound $Nb_{5-x}Ta_xSi_3$ crystallizes with the W_5Si_3 -type, associated with the high temperature form of binary parents silicides. Stability, atomic site preference and bonding are discussed by means of density functional theory based calculations.

2. *Experimental section*

2.1 *Synthesis and crystal structure solution*

The compound $\text{Nb}_{5-x}\text{Ta}_x\text{Si}_3$ was serendipitously obtained as single crystals from Nb (powder, Aldrich, 99.8 %), Ta (metal, Heraeus) and Si (powder, Aldrich, 99.999 %). The niobium and silicon powders, taken as received in 1:2 proportions, were intimately mixed and then pressed into a pellet to be fused in an arc-melting furnace. The ingot was molten several times in order to improve the homogeneity of the sample. No significant weight loss was noted during the experiment. The resulting material was subsequently enclosed into a tantalum tube weld-sealed under argon and then heated in an induction furnace up to a temperature quite higher than 2000°C. At first sight, the attack of the inner surface of the tube was obvious and incorporation of some tantalum in the final product easily predictable. In fact, a large quantity of metal-grey needles can be recovered and their EDX analyses revealed the presence of the three elements in a ratio corresponding to the $\text{Nb}_{5-x}\text{Ta}_x\text{Si}_3$ ($x \sim 1.25$) stoichiometry. Several well individualized needles were selected and checked for crystallinity on the Xcalibur CCD (Oxford Diffraction) four-circle diffractometer. After collection of the diffracted intensities using $\text{MoK}\alpha$ radiation, the structure was solved and refined from several data sets of which best quality results are reported here.

The compound $\text{Nb}_{5-x}\text{Ta}_x\text{Si}_3$ displays the $I4/mcm$ tetragonal symmetry with unit cell parameters $a = 10.0335(2)$ and $c = 5.0347(1)$ Å. The structure was solved using the program SHELXS97 [6] which gave four atomic positions respectively assigned to two metal and two Si atoms, the refinement of which led to $R1 \sim 9\%$. Improvement was further obtained by considering atomic mixing at the two metal sites. The total number of reflections (including symmetry equivalent and redundant) recorded within the complete diffraction sphere (θ from 2.87 to 32.41°) were corrected for the absorption effects ($\mu = 35.37 \text{ mm}^{-1}$) using the procedure included in the CrysAlis software [7]. The final data set used for the full-matrix least-squares refinement with program SHELXL97 [8] contained 270 unique reflections of which 267 are observed according to the criterion $I > 2\sigma(I)$. A free refinement of the occupation factors showed that they did not deviate, within standard deviation limits, from the full site occupancy. Finally, atomic positions and anisotropic displacement parameters for all atoms were refined together with the Nb/Ta ratio at the two metal sites leading to $R1 =$

0.0268 (wR2 = 0.0646). Then the refined composition $\text{Nb}_{15}\text{Ta}_5\text{Si}_{12}$ was found in very good agreement with EDX analyses of the single crystals (figure 1).

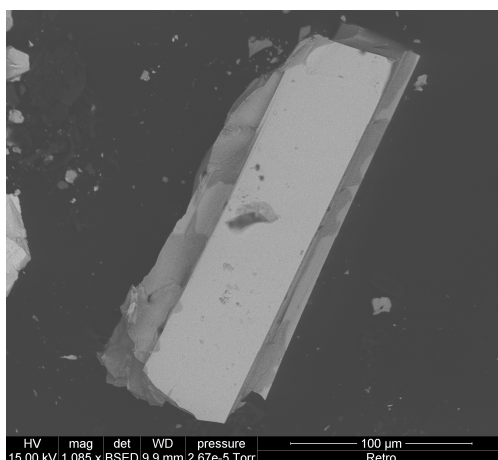


Figure 1: SEM image of a needle-shaped single crystal of $\text{Nb}_{5-x}\text{Ta}_x\text{Si}_3$

Detailed experimental parameters for data collection and structural refinements are given in table 1 and atomic positional and displacement parameters are listed in table 2. The refined compositions obtained for the different crystals remain in a narrow domain around the stoichiometry $\text{Nb}_{15}\text{Ta}_5\text{Si}_{12}$. However, compound could have a more or less wide composition range since x would theoretically vary from 0 to 5 without any structural change.

2.2 Calculation method

Calculations were performed with CASTEP program [9, 10] that employs the density functional theory plane-wave pseudo-potential method, within the gradient-corrected exchange-correlation functional GGA-PW91[11]. Ultra-soft pseudo-potentials (USPP) were taken as generated for each element according to the Vanderbilt scheme [12]. Kinetic cut-off energies for plane wave expansion of the wave functions were set to 330 eV (ultrafine quality) and, as compounds were expected to be metallic, a density-mixing scheme was chosen. A Monkhorst-Pack uniform grid of automatically generated k -points was used for numerical integration in the Brillouin zone [13]. Atomic positions have been relaxed according to the total energy and forces using the BFGS algorithm. The energy tolerance was $5 \cdot 10^{-6}$ eV/atom, the force tolerance 0.01 eV/Å and the displacement tolerance $5 \cdot 10^{-6}$ Å.

3. Results and discussion

3.1 Structural description

The tetragonal unit cell of $\text{Nb}_{5-x}\text{Ta}_x\text{Si}_3$ contains four formula units with twelve silicon atoms located at 4a and 8h crystallographic sites and twenty metal atoms distributed among 4b and 16k sites. At these two positions, Nb and Ta atoms are mixed in 87/13 and 71/29 % respective proportions. A description of the structure can be given by considering the metal shells around silicon atoms (figure 2).

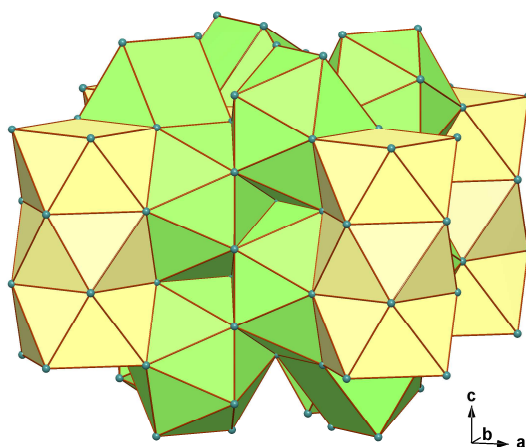


Figure 2: The tetragonal structure of $\text{Nb}_{5-x}\text{Ta}_x\text{Si}_3$ ($I4/mcm$, $a = 10.0335(2)$, $c = 5.0347(1)$ Å) viewed as a three dimensional packing of Si-centered metal polyhedra.

Atom Si2, at site 4a, is located at centre of an 8-metal-atom square antiprism which shares its square faces with two neighboring units. Consequently, Si2 atom forms with its neighbors at 2.518 Å an infinite linear silicon wire aligned along the c-axis (figure 3). Atom Si1, at site 8h, is separated by 3.5 Å from its nearest Si neighbor and is then considered as an "isolated" atom. It is enclosed in a 10-vertex metal polyhedron resulting from the condensation of an icosahedron and a cube (figure 3). The Si-centered metal polyhedral units are packed together within the three dimensional structure by sharing edges and faces. The structure of $\text{Nb}_{5-x}\text{Ta}_x\text{Si}_3$ belongs to the $W_5\text{Si}_3$ -type and is isostructural to the high temperature structures of Nb_5Si_3 and Ta_5Si_3 binary parent's silicides. Since $M_5\text{Si}_3$ compounds are known to display polymorphism (table 3), comparison of the three structural types that they adopt, tetragonal $W_5\text{Si}_3$, tetragonal Cr_5B_3 and hexagonal Mn_5Si_3 , is of interest. Although silicon atoms are

found at 4a and 8h independent crystallographic sites in the two tetragonal structures, the metal atomic arrangement highly differs in M_5Si_3 high and low temperature structural forms (W_5Si_3 and Cr_5B_3 -type).

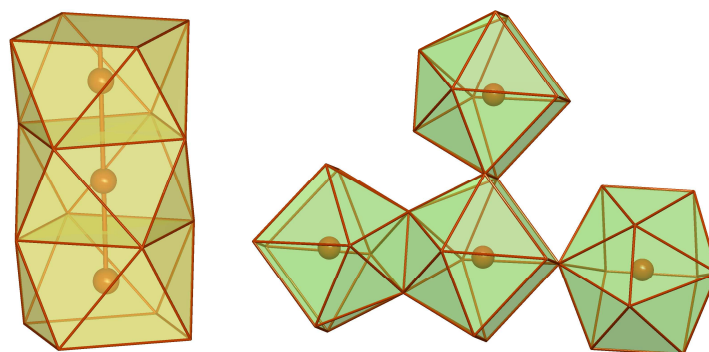


Figure 3: Metal environment around Si atoms in tetragonal W_5Si_3 -type structure. *left*: Infinite silicon wire inside its metal sheath, a consequence of packing by face sharing of Si centered metal square antiprisms. *right*: Si isolated atoms in their 10-metal-atom coordination polyhedra resulting from condensation of an icosahedron and a cube.

In tetragonal Cr_5B_3 -type, atom Si2 at site 4a is surrounded by ten metal atoms arranged at vertices of a bicapped square antiprism (figure 4) while atom Si1, at site 8h, lies inside an 8-metal-atom polyhedron, a triangular prism capped on two square faces. Actually, this latter polyhedron is joined, through square face sharing, to a nearby similar unit so that Si1 atoms separated by 2.32 Å combine into dumbbells (figure 4).

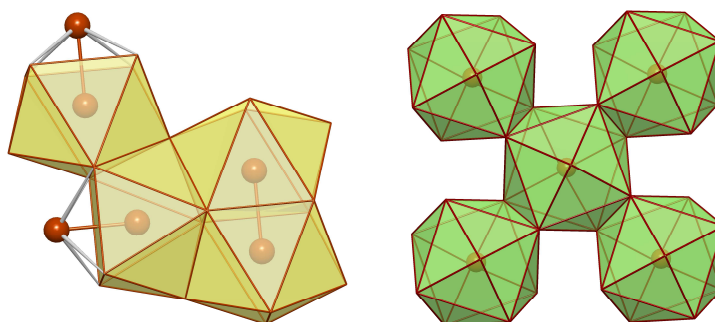


Figure 4: Metal environment around Si atoms in tetragonal Cr_5B_3 -type structure. *left*: Si atoms of dumbbells are shown in their 8-metal-atom coordination polyhedra (bicapped triangular prism). *right*: Si isolated atoms in their 10-metal-atom coordination polyhedra (bicapped square antiprism)

Silicon dumbbells are located together with Nb atoms within slices perpendicular to the c-axis at $z = 0, \frac{1}{2}$ while slices at $z = \frac{1}{4}, \frac{3}{4}$ only contain "isolated" silicon atoms. These two kinds of Si-containing slices are stacked and separated by pure niobium slices ($z = 0.15, 0.35, 0.65$ and 0.85) to build the Cr_5B_3 -type structure. By contrast, the W_5Si_3 structural type is characterized by the alternate packing along the c-axis of two kinds of mixed Nb/Si layers.

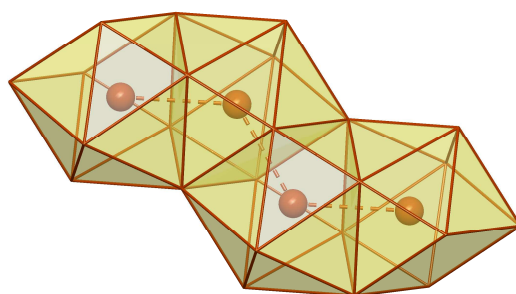


Figure 5: Metal environment around Si atoms in the hexagonal Mn_5Si_3 -type structure. Si atoms are shown inside their 9-metal-atom coordination polyhedra (capped square antiprism)

On the other hand, a mixed Nb/Si layer alternates along c-axis with a pure Nb layer in the hexagonal Mn_5Si_3 structure that displays a unique position for Si atoms lying inside a 9-metal-atom capped square antiprism (figure 5). It is worth noting that Si neighbors in the hexagonal form are separated by 3.02 \AA , a too long distance to still consider some Si-Si bonding.

3.2 *Formation enthalpy and stability of compounds*

As seen below, the electron densities calculated using first principle methods in CASTEP package will be helpful for further analysis and visualization of bonding. In a first step, the structural geometries have been optimized by minimization of the total energy. This was done, starting with experimental models, for both Nb_5Si_3 and Ta_5Si_3 polymorphs as well as for the other reported binary Nb and Ta silicides. The unit cell parameters and atomic positions were fully relaxed in these calculations and they did not deviate a lot from the experimental values. Calculated lattice parameters, total energies and formation enthalpies are given in table 4. The formation enthalpy which allows a good evaluation of the compound stability is defined as the total energy of the compound minus total energies of elements calculated in their solid state structures. Among the M-Si binary compounds of niobium and

tantalum, those having the M_5Si_3 composition are the most stable as indicated by the highest negative values of their formation enthalpies. The total energy per formula unit Nb_5Si_3 (Ta_5Si_3) was found to decrease by 0.29 eV (0.48 eV) from hexagonal Mn_5Si_3 -type to tetragonal W_5Si_3 -type and further by 0.46 eV (0.51 eV) to tetragonal Cr_5B_3 -type. Consequently the formation enthalpies decrease in the sequence Mn_5Si_3 -type - W_5Si_3 -type - Cr_5B_3 -type making the latter form the most stable for M_5Si_3 niobium and tantalum silicides. The $Nb_{15}Ta_5Si_{12}$ crystals obtained in present work belong to the little less stable W_5Si_3 structural type. With a formation enthalpy of -0.64 eV/atom, this mixed silicide takes place in the same stability range as its Nb_5Si_3 and Ta_5Si_3 parents in the W_5Si_3 -type (-0.66 and -0.59 eV/atom). It is highly likely that this compound would also crystallize with the Cr_5B_3 structural type under somewhat different conditions.

3.3 *Atomic site preference*

The structure of $Nb_{5-x}Ta_xSi_3$ ($Nb_{15}Ta_5Si_{12}$) may be viewed as derived from that of Nb_5Si_3 by partial atomic replacement of Nb by Ta. Since metal atoms occupy two non equivalent crystallographic sites, it is relevant to check the existence of an atomic site preference for substitution. For this purpose, two structural models having the $Nb_{19}TaSi_{12}$ stoichiometry were built starting from Nb_5Si_3 (W_5Si_3 -type) and replacing one Nb atom by Ta, either at 4b or at 16k position. Total energies calculated for the two models are very close, only differing by 0.08 eV per $Nb_{19}TaSi_{12}$ formula unit, indicating that Ta can be substituted for Nb without significant site preference, at least on an energetic point of view. This is confirmed by X-ray structural findings that show an equivalent repartition of tantalum atoms at the two crystallographic positions.

3.4 *Electronic structure and bonding considerations*

Band structures and densities of states (DOS) calculated for all polymorphic forms of M_5Si_3 ($M = Nb, Ta$) silicides feature metallic behavior for the compounds. Owing to close similarities between Nb and Ta compounds, total and partial densities of states are only shown for Nb representatives (figure 6). Whatever the structure-type, the low-lying energy levels between -11 and -7 eV mainly result from Si 3s states while levels comprised between -6 and 3 eV originate from Si 3p and M nd states.

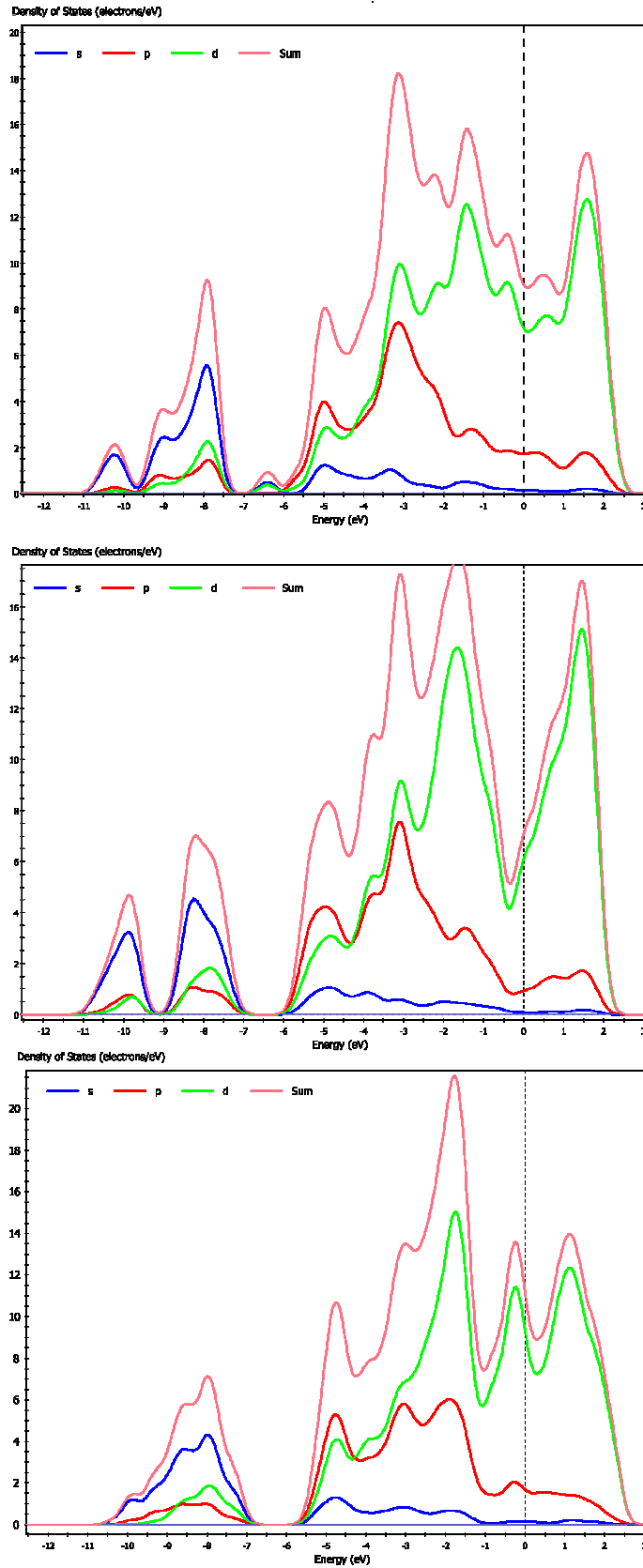


Figure 6: Castep total and partial DOS calculated for the Nb₅Si₃ polymorphs
up: W₅Si₃-type, middle: Cr₅B₃-type, down: Mn₅Si₃-type

The partial DOS point out the major contribution at Fermi level of the metal nd states. The total DOS associated with Nb₅Si₃ in Cr₅B₃-type shows a pseudo-gap, approximately 0.3 eV below the Fermi level, and a rather low density of states of 7 electrons/eV at Fermi level. For Nb₅Si₃ in W₅Si₃ and Mn₅Si₃-types, density of states values at Fermi level are 9 and 11 electrons/eV, respectively. Bearing in mind that a low density of states at Fermi level is a sign of stability, tetragonal Cr₅B₃-type is the most stable polymorph, followed by tetragonal W₅Si₃-type and then by hexagonal Mn₅Si₃-type. These results are consistent with the calculated formation enthalpies and with previous literature reports [14-16].

Owing to Nb/Ta atomic disorder at metal sites, the electronic structure of ternary compound Nb₁₅Ta₅Si₁₂ has been calculated for an ordered model in P1 symmetry in which Ta atoms are evenly distributed over the cell. The density of states (DOS) of Nb₁₅Ta₅Si₁₂ bears some resemblance with those of binary silicides. The low energy lying band (-12 to -6.5 eV) is dominated by Si 3s levels but includes weak contributions of Ta 5s, Nb 4s, Ta 5p, Nb 4p, Ta 4d and Nb 3d levels (figure 7).

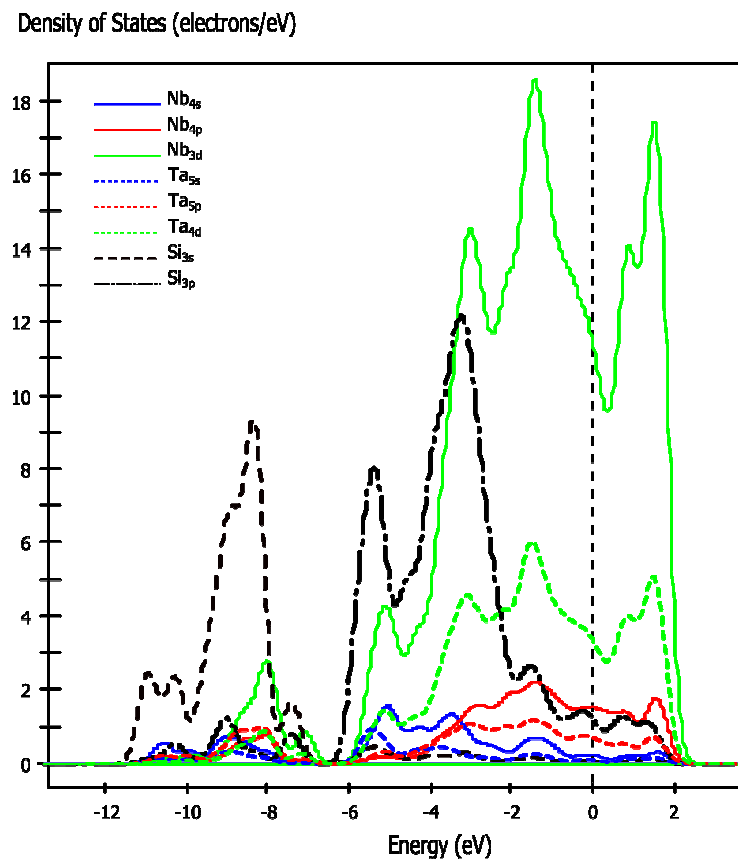


Figure 7: Castep partial DOS calculated for Nb₁₅Ta₅Si₁₂ (P1 ordered model).

From -6.5 eV to 2 eV, the second band is mostly characterized by Si 3p, Ta 4d and Nb 3d contributions. The metal states Ta 5s and Nb 4s participate up to Fermi level while the Ta 5p and Nb 4p contributions occur in the energy domain between -4 and 2 eV. It is interesting to remark the position of the pseudo gap nearly 0.4 eV above the Fermi level. Although displaying globally similar shapes, the total DOS curves calculated for Nb₅Si₃, Ta₅Si₃ and Nb₁₅Ta₅Si₁₂ (figure 8) exhibit noticeable differences in a narrow energy domain around the Fermi energy. Between -1 and +1 eV, the DOS curves of binary compounds are characterized by more or less marked waves forming three minima, the lowest density of states occurring at nearly 0.1 or 0.2 eV above the Fermi energy.

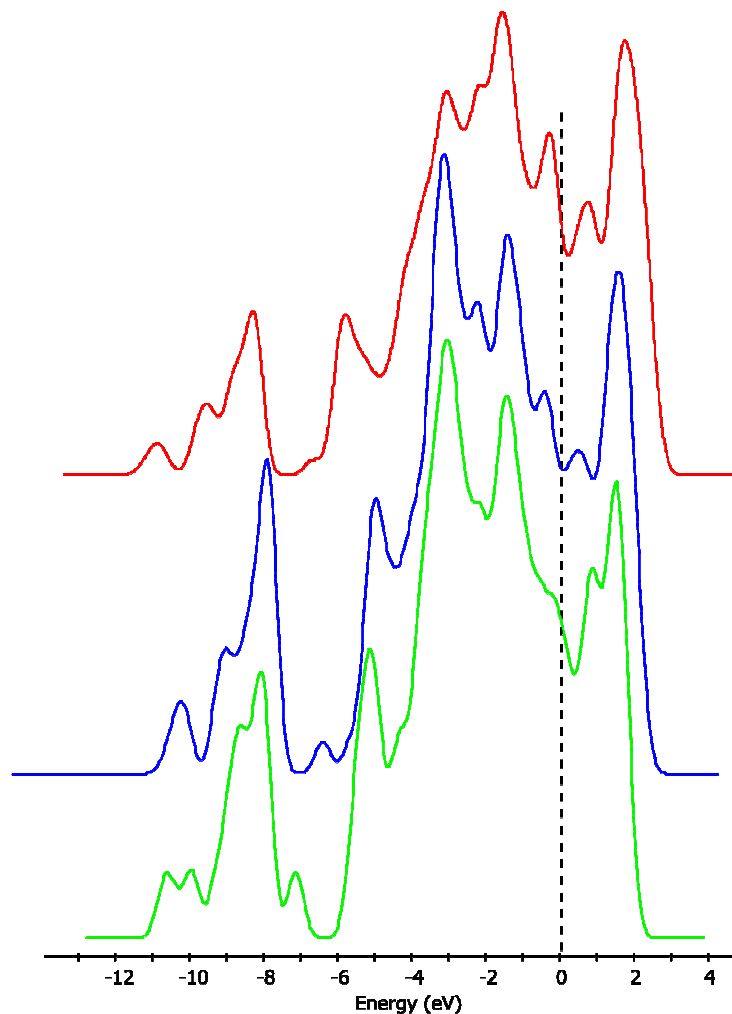


Figure 8: Castep total DOS profiles calculated for Ta₅Si₃ (*up*, red), Nb₅Si₃ (*middle*, blue) and Nb₁₅Ta₅Si₁₂ (*down*, green)

Instead, the DOS curve of the Nb₁₅Ta₅Si₁₂ mixed silicide displays a unique and deeper trough at 0.4 eV above the Fermi energy (calculation was repeated for different ordered models).

This illustrates the electronic structure perturbations induced by the Nb/Ta atomic mixing at metals sites. Atomic mixing would be of potential interest, for example to adjust the electronic properties of the compound. It has been shown recently that boron doping induces changes in the electrical and magnetic properties of Nb₅Si₃ promoting superconductivity [16]. More than the electronic density, the electron density difference is a good tool for bonding description purposes. It represents the electron redistribution due to chemical bonding and is computed by subtracting densities of isolated atoms from the total electron density. Electron density difference maps represented for the three Nb₅Si₃ polymorphs (figure 9) show positive regions indicative of bond formation while negative regions are associated with electron losses. Positive values at Si atomic pairs feature covalent interactions localized at Si dumbbells in Cr₅B₃-type and at Si wire in W₅Si₃-type while no density is found at Si-Si pairs (3.02 Å) in Mn₅Si₃-type. This well agrees with the Mulliken overlap populations calculated at the corresponding Si-Si pairs: 0.37, 0.52 and 0.01, respectively. It is generally accepted that the comparison of Mulliken overlap populations is meaningful despite the known basis set dependency of this type of analysis [17].

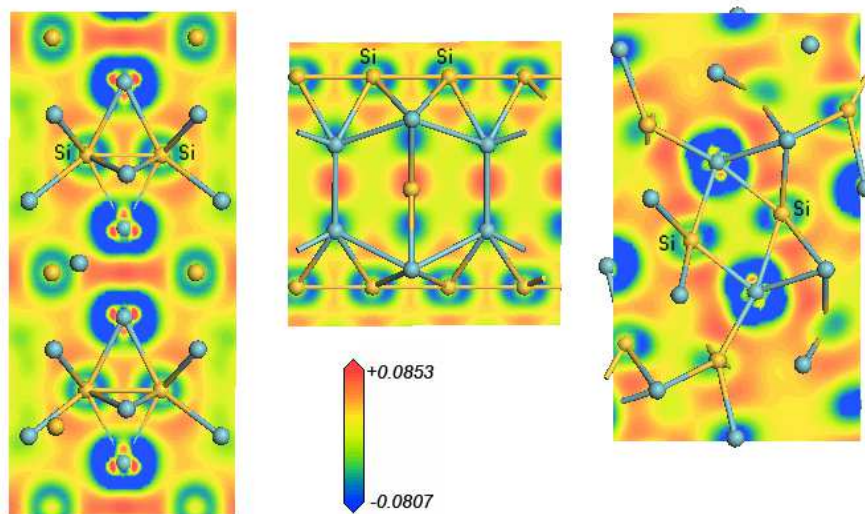


Figure 9: Electron density difference for Nb₅Si₃ polymorphs, high densities at Si-Si are indicative of bond formation. *left*: Cr₅B₃-type, *middle*: W₅Si₃-type, *right*: Mn₅Si₃-type.

Overlap population of 0.50 is calculated at Si-Si pairs in the ternary mixed compound Nb₁₅Ta₅Si₁₂ pointing out the locally covalent bonding character. On the other hand positive values of overlap populations are computed at Nb-Si and Ta-Si atomic pairs while non bonding and even antibonding interactions are found at metal pairs. Such antibonding

interactions likely result from packing geometrical strains that have the effect of moving close some atoms yet not involved in bonding. Antibonding interactions only exist in the W_5Si_3 structural type, they occur at metal pairs having distances shorter than in pure metal (Nb-Nb distance of 2.55 Å in Nb_5Si_3 compared with 2.86 Å in metal) and thus account for the lower stability of this polymorph.

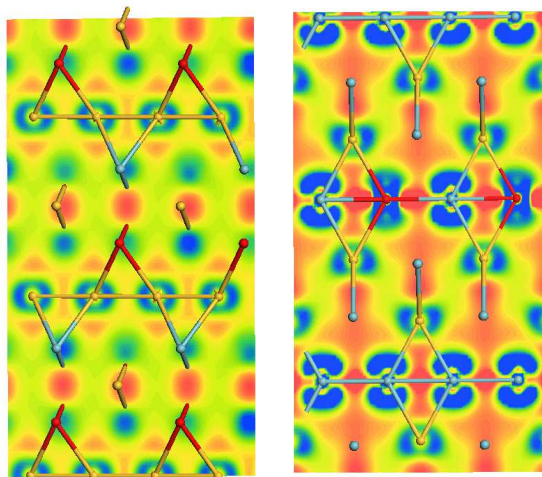


Figure 10: Electron density difference in $(\bar{1}10)$ planes for $Nb_{15}Ta_5Si_{12}$ underlining Si-Si and, to a less extent, Nb-Si and Ta-Si bonding.

Likewise for $Nb_{15}Ta_5Si_{12}$, the electron density difference represented in $(\bar{1}10)$ planes underlines the localized covalent character of the structure at Si-Si and, to a less extent, at Nb-Si and Ta-Si atomic pairs (figure 10). Highly positive values are found between metal atoms only separated by 2.52 Å, a very short distance that may cause atomic repulsions. Actually, negative overlap populations are calculated at these Nb-Ta or Nb-Nb short contacts in $Nb_{15}Ta_5Si_{12}$. The global metallic character of the compound is featured by the quite diffuse electron density over the whole structure.

4. Conclusion

The ternary mixed compound $Nb_{5-x}Ta_xSi_3$ was obtained for the first time as a single crystal. It was found to crystallize in the tetragonal W_5Si_3 structural type as do Nb_5Si_3 and Ta_5Si_3 high temperature polymorphs. Its structure is characterized by the presence of 0c-Si "isolated" atoms together with 2c-Si atoms (Si-Si bonds of 2.52 Å) that form silicon wires. The metal atoms around each Si obey particular geometric arrangements, so 0c-Si atom is located in a

10-metal-atom polyhedron (condensation of an icosahedron and a cube) while 2c-Si has a square antiprismatic environment. Stacking the antiprisms along the c-axis results in an infinite columnar polyhedron as already observed in Ta₂Si tetragonal structure characterized by metal-sheathed silicon wires aligned along the c-axis. However, in Ta₂Si, metal sheaths are directly fused by polyhedral edge sharing while, in Nb_{5-x}Ta_xSi₃, they are separated by 10-atom polyhedra with which they are fused through edge and face sharing. Note that no Nb analogue of Ta₂Si has been reported. For comparison, silicon occurs in Ta₃Si as 0c-Si lying in a Ta₉ distorted tricapped triangular prism. The Ta₅Si₃ structures also contain 0c-Si atoms which are alone in the hexagonal polymorph (Mn₅Si₃-type) but which coexist either with 1c-Si in the low temperature polymorph (Cr₅B₃-type) or with 2c-Si in the high temperature polymorph (W₅Si₃-type). Finally, TaSi₂ structure contains 5c-Si atoms involved in bonding interactions with five close neighbors as attested by positive overlap populations. Besides the local covalent character mainly at Si-Si bonds, metal to silicon interactions are mostly responsible for bonding in these compounds, a result which validates the use of Si-centered metal polyhedra to give a convenient and understandable description of the structures, particularly that of the ternary mixed silicide Nb_{5-x}Ta_xSi₃ predicted with a metallic behavior by DFT calculations.

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