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Structural Trends and Chemical Bonding in Te-Doped Silicon Clathrates

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The recently discovered tellurium-doped silicon clathrates, $Te_{7+x}Si_{20-x}$ and $Te_{16}Si_{38}$, both low- and high-temperature forms (cubic and rhombohedral, respectively), exhibit original structures that are all derived from the parent type I clathrate G_8Si_{46} (G = guest atom). The similarities and differences between the structures of these compounds and that of the parent one are analyzed and discussed on the basis of charge distribution and chemical bonding considerations. Because of the particular character of the Te atom, these compounds appear to be at the border between the clathrate and polytelluride families.

Introduction

For about a decade, thermoelectric materials have attracted an increasing amount of attention because of the need for energy saving procedures, such as the recovery of heat of industrial or domestic origin, and the development of advanced refrigeration devices that would avoid the use of environmentally harmful fluorocarbons in domestic refrigerators or car air conditioners.[1] The required conditions to get good thermoelectric materials have been discussed by Slack in his concept of PGEC materials (a phonon glass and an electron crystal).[2] Slack suggests that thermoelectric materials could be found in structures having large and weakly bonded cations that can “rattle” inside oversized cages of a host lattice, independently of the phonon modes of the framework. Clathrate-like compounds of silicon, germanium, and tin appeared to be suitable candidates and have been the subject of numerous works of research.[3,4]

It was shown that the clathrate of type II, Na_xSi_{136} ($0 \leq x \leq 24$), was characterized by a high value of the Seebeck coefficient (~ −300 mV/K for Na_3Si_{136}),[5,6] and a recent work has been published on the thermal conductivity of the empty form, Si_{136}.[7] Most of these clathrate-type structures involve metallic guest atoms (Na, K, Rb, Cs, and Ba) and, consequently, have n-type conductivity, whereas compounds having p-type conductivity, which are also of prime importance in thermoelectric materials, are much less numerous.[8] Nesper et al. showed that iodide ions can enter the two types of cages of a type I clathrate of germanium, $I_8Ge_{46-x}I_x$ ($x = 8/3$), which involves a charge compensation through the disproportionation of iodine.[9] More recently, the silicon analogue, $I_8Si_{46-x}I_x$ ($x = 2$) has been synthesized by Reny et al. under high-pressure conditions.[10,11]

Given the proximity of tellurium and iodine in the periodic table and the interest in tellurium in thermoelectric materials, we have recently investigated the Te−Si system under

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Table 1. Atomic Positions Occupied by the Guests (G, Te) and Host-Forming Atoms (Te, Si)

G_8Si_{46}	$Te_{16}Si_{38}$ (i.e., $Te_8(Te_8Si_{38})$)		$Te_{7+x}Si_{20-x}$ (x~2.5)
Cubic; a~10.3 Å Pm-3n (223)	Cubic; a=10.457(1) Å P-43n (218)	Rhomb.; a=10.465(1) Å, α= 89.88° ; R3c (161)	Cubic; a= 21.136(2) Å Fd-3c (228)
G1 (2a)	Te1 (2a)	Te1 (2a)	Te1 (16a)
G2 (6d)	Te2 (6c)	Te2 (6b)	Te4 (96g)
Si1 (6c)	Si1 (6d)	Si1 (6c)	
Si2 (16i)	Te3 (8e)	Te31 (2a)	X^a2 (64e)
		Te32 (6b)	X^a3 (64e)
	Si2 (8e)	Si21 (2a)	
		Si22 (6b)	
Si3 (24k)	2/3 Si31 (24i)	Si31 (6b)	Si1 (192h)
		Si32 (6b)	
	1/3 Si32 (24i)	Si33 (6b)	
		Si34 (6b)	

[a] X stands for (0.315 Te + 0.685 Si).

ambient and high-pressure conditions of up to 5 GPa and found two new compounds, whose structures are closely related to that of a classical type I clathrate. The first one was found to correspond to the formula $Te_{7+x}Si_{20-x}$, with $x \sim 2.5$ (Te/Si = 0.543), and to crystallize in a fcc structure [$a = 21.136(2)$ Å; $Fd\bar{3}c$]. The second turned out to be $Te_{16}Si_{38}$ (Te/Si = 0.421), which exists under two forms, a cubic one [$a = 10.457(1)$ Å; $P\bar{4}3n$] and a rhombohedral one [$a = 10.465(1)$ Å; $\alpha = 89.88(1)°$; $R3c$]. The crystal structures of these new tellurium-doped silicon clathrates have been solved by powder and single-crystal XRD analyses and have been recently published in two separate papers.[12,13] However, no discussion has been given so far about the similarities and differences, from the structural viewpoint, between these new tellurium−silicon compounds and the parent type I clathrate, G_8Si_{46} (G = guest atom; G/Si = 0.174). Actually, the change in the structures of the tellurium-doped clathrates clearly appears as the result of the particular character of the tellurium atom, which not only behaves as a guest, but also participates in the formation of the framework.

The aim of this paper is to point out the similarities and differences between the structure of the parent type I clathrate and those of the new phases and to discuss the peculiar characters of these compounds, which are due to the originality of the crystal chemistry of tellurium and appear to be at the border between clathrates and polytellurides.

Because the pressure and temperature conditions for the synthesis of the new tellurium−silicon clathrates as well as the methods used for data collection and structural analyses have been reported in two previously cited papers,[12,13] no experimental part will be included in the present paper.

Results and Discussion

For a better understanding of the structural trends and the discussion on the chemical bonds in these new tellurium-doped clathrate structures, a brief description of the concerned structures is first provided.

Summary of the Structures. The results of the structural analyses of the three new tellurium-doped clathrates, that is, $Te_{7+x}Si_{20-x}$ and $Te_{16}Si_{38}$, both high- and low-temperature forms, showed an obvious relationship between them and a classical type I clathrate, G_8Si_{46}, as can be seen in Table 1, which summarizes the occupied atomic positions in these structures. It is noteworthy that the total number of atoms per unit cell is, in any case, 54 (i.e., 8 + 46 or 16 + 38) or a multiple of it (8 × 54 for the $Te_{7+x}Si_{20-x}$ cubic super cell).

The unit-cell parameter of the $Te_{7+x}Si_{20-x}$ structure is slightly higher than 2 times the expected value for a type I clathrate, which is the result of a higher Te/Si ratio. The structure corresponds to a kind of superstructure of the parent clathrate, but the space group ($Fd\bar{3}c$) is not a supergroup of that of the parent clathrate ($Pm\bar{3}n$). On the other hand, the unit-cell parameters of the cubic and pseudocubic (rhombohedral) forms of $Te_{16}Si_{38}$ are both very close to that of the parent structure, and the corresponding $P\bar{4}3n$ and $R3c$ space groups are both noncentrosymmetric subgroups of the $Pm\bar{3}n$ one, $R3c$ being itself a polar group.

The structures of the cubic and rhombohedral forms of $Te_{16}Si_{38}$, depicted in Figure 1a,b, respectively, show an increasing distortion of the fullerene-like Si_{20} and Si_{24} cages in comparison to that of the parent structure, which is due to the splitting of the Si2 and Si3 silicon atoms' positions (see Table 1). The structure of $Te_{7+x}Si_{20-x}$, although showing an XRD pattern similar to those of the above structures, is actually different (Figure 1c). The Si_{24} cages are here replaced by a new type of cage in the form of truncated octahedron, one of the filling-space Fedorov polyhedra,

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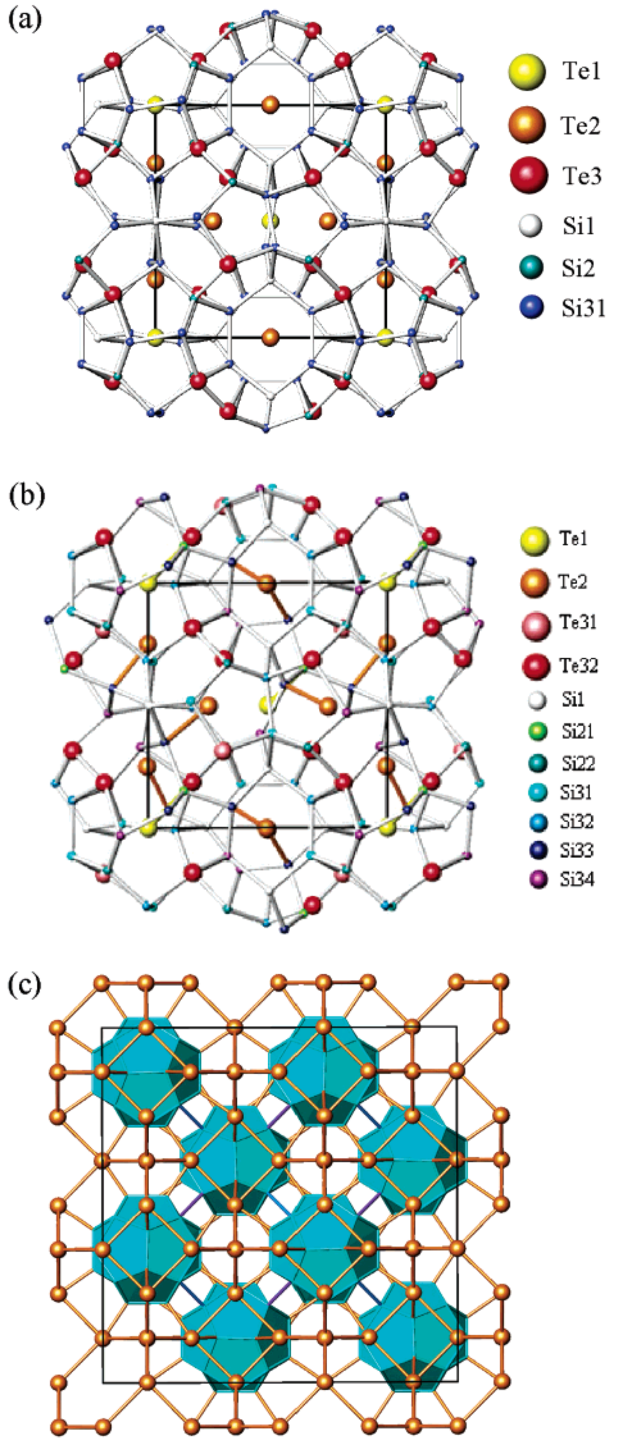

Figure 1. Structure of the Te-doped silicon clathrates: (a) cubic form of $Te_{16}Si_{38}$, showing the buckling of the pentagonal and hexagonal faces of the host cages (for the sake of clarity, the Si32 atoms are not shown and are treated as Si31; for more details, see ref 13); (b) rhombohedral form of $Te_{16}Si_{38}$, showing the more important distortion of the structure and the formation of Te1−Si21 (yellow) and Te2−Si33 (orange) bonds between the guest Te and host-forming Si atoms; (c) cubic $Te_{7+x}Si_{20-x}$, in which the $Te4_{(96g)}$ atoms form a 3-D network of truncated octahedra (orange network).

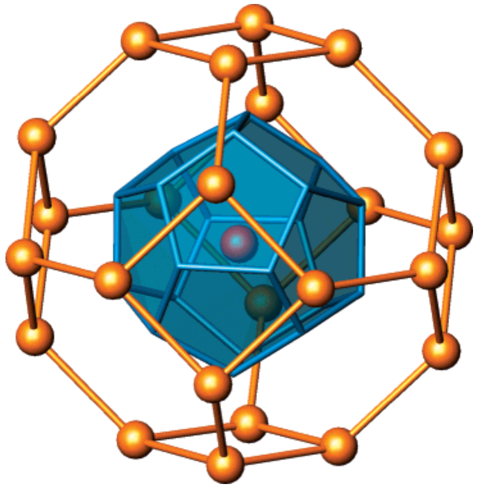

Figure 2. Close view of the double clathration in the Te_{7+x} Si_{20-x} structural unit, i.e., $[Te@(Te_xSi_{20-x})]@Te_{24/4}$.

entirely made of tellurium, which results in the merging of the 6c and 6d sites of the parent structure (96g). These polyhedra form a 3-D network, which is analogous to the water host lattice of a type VII clathrate, such as (HEF_6)-$(H_2O)_5(HF)$ (E = P, As, or Te), or to that of the Al/Si one in sodalite-type alumino-silicates, such as $(Na,K)_8(Al_6$-$Si_6O_{24})(Cl,S,SO_4)_2$.[14,15] Each cage of this network, which, unlike the Si_{20}, Si_{24}, and Si_{28} cages encountered in clathrates of types I and II, is not of the fullerene type, encloses a slightly Te-substituted Si_{20} pentagonal dodecahedron [Te/(Si + Te) = 2.5:20] with a tellurium (Te^{2-}) at its center, thus, leading to a double clathration (Figure 2).

The resulting formula unit corresponds, therefore, to $[Te@(Te_xSi_{20-x})]@Te_{24/4}$ (@ means enclosed in...), and there are 16 of these in the unit-cell, leading to a total number of 432 atoms, that is, 8 × 54 (Table 1).

Charge Distribution and Chemical Bonding. In the three above structures, the Si−Si interatomic distances are slightly higher than those in the diamond form of silicon (∼2.35 Å) and the bond angles range between 105 and 120°. A silicon atom surrounded by four Si neighbors will be assumed to bear a neutral charge. Concerning the Te−Si bonds, two different cases have to be considered. When the Te atom is located at the center of wide Si_{20} dodecahedral (2a) or Si_{24} tetrakaidecahedral (6b, 6c, or 6d) cages, it is surrounded by a large number of Si atoms at a distance higher than 3 Å, which implies that no strong ionocovalent bond can be formed. It is only submitted to the positive Coulombic potential of the silicon network and should be considered to be negatively ionized as Te^{2-}. Its electronic configuration is $...5s^25p^6$, and it has four nonbonding pairs, or lone pairs (LPs), of electrons. When the Te atom is in the substitutional position in the tetrahedrally bonded host lattice with inter atomic distances ranging from 2.45 to 2.66 Å, it has to be compared to a Te atom in an ionocovalent telluride such as CdTe, which exhibits a prominent covalent character despite the classical ionic formula $Cd^{2+}Te^{2-}$. To compare these bonds, one has to consider the values of the Coulomb integral, H_{ii}, for the atomic orbitals of Te, Cd, and Si.[16] The difference in energy between the 5p(Te) and 5s(Cd) or 3p(Si) orbitals is only of 2 eV and, therefore, limits the ionic

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character of the bond. In this case, the Te atom will be noted as Te^{II-} and will bear four bonding pairs (BPs) of electrons. In the above three structures, all of the intermediates between these two situations are encountered.

The cubic form of $Te_{16}Si_{38}$ is structurally analogous to the $I_8As_8Ge_{38}$ clathrate studied by Menke and von Schnering.[17] This latter compound corresponds to a Zintl-type phase, with a charge distribution of $I_8{}^{q-}As_8{}^{q+}Ge_{38}{}^0$ and As−Ge distances which are quite the same as the Ge−Ge ones. One could assume a similar situation in the Te analogue, involving a charge distribution of $Te_8{}^{2q-}Te_8{}^{2q+}Si_{38}{}^0$, but the observed Te−Si distances are much larger than those of the Si−Si ones and close to those observed in the Si_2Te_3 (∼2.58 Å) or Ba_2SiTe_4 (∼2.50 Å) tellurides.[18,19] Therefore, one has to reject the above hypothesis of a Zintl-phase and consider a charge distribution of $Te_8{}^{2-}Te_8{}^{II-}Si_{32}{}^{I+}Si_6{}^0$, in which 32 of the silicon atoms (8e + 24i) have 1 Te neighbor and 3 silicon ones, whereas the 6 other ones are surrounded only by Si atoms and are, thus, neutral. A similar situation is observed in the rhombohedral form of $Te_{16}Si_{38}$.

In the $Te_{7+x}Si_{20-x}$ clathrate-like structure, the $Te_{(96g)}$ atoms have two $Si_{(192h)}$ neighbors (interatomic distance = 2.58 Å) and should be ionized as Te^{II-}. However, the interatomic Te−Te distance (3.737 Å) involves noticeable Te−Te interactions. The formation of holes, h^+, at the top of the 5p band of tellurium is a well-known phenomenon, as is the case, for example, in the structure of Ta_3SiTe_6, where the ionic charge of Te has been demonstrated to be −1.833 (the average Te−Te distance is 3.73 Å).[20] Furthermore, the fact that, in the structure of $Te_{7+x}Si_{20-x}$, $^1/_3$ of the 64e sites are occupied by Te atoms supports oxidation states such as $Si^{I+}Te^{II-}Si^{I+}$. In the unit cell, the overall charge distribution is assumed to be

$$Te^{2-}{}_{(16a)}Te^{(II-\delta)-}{}_{(96g)}Si^{I+}{}_{(192h)}({}^2/_3Si^{I+}-{}^1/_3Te^{II-})_{(64e,\ 64e)}$$

which shows an overall charge equilibrium, if one considers $\delta = 0$ and neglects the sixteen Te^{2-} ions in the (16a) position. In such conditions, the thirty two electrons needed for the ionization of the Te atoms in the (16a) position must arise from the sodalite-type Te network, which results in an average ionic charge of 20/12 = 1.667, that is, $\delta = 0.333$. In fact, the substitution rate of Te for Si in the 64e position, as determined by the structural analysis, corresponds to only 31.5%. It follows a slight excess of positive charges, which increases the anionic charge of Te in the sodalite network up to −1.75. This value is quite consistent with that reported by Jobic et al. (Figure 3).[21] The substitution of Te for Si in the 16i sites is, thus, associated with the position of the Fermi level, which intercepts the top of the valence band. Figure 4 illustrates the charge transfer of two electrons from the top of the filled $5p^6$ band to the $5p^4$ electronic states of the $Te_{(16a)}$ atoms, which are more stabilized by the positive Madelung potential of the neighboring 20 − x silicon atoms, as shown in the case of an ideal 1-D system.

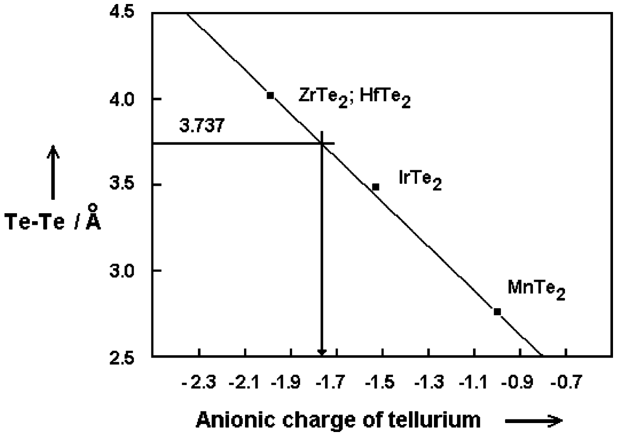

Figure 3. Variation of the Te−Te distance as a function of the anionic charge of Te (reconstructed from data in ref 21).

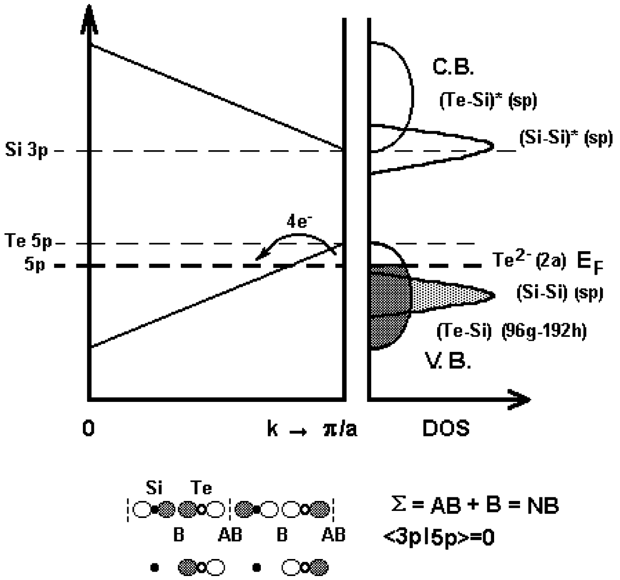

Figure 4. Formation of holes at the top of the valence band through the charge transfer from the $5p^6$ valence band of the $Te4_{(96g)}$ atoms of $Te_{7+x}Si_{20-x}$ to the 5p electronic states of $Te1_{(2a)}$, leading to Te^{2-} anions. AB, B, and NB mean antibonding, bonding, and nonbonding, respectively, the latter being the situation at $k = \pi/a$ of a schematic 1-D Brillouin zone.

One of the main characteristics of the cubic ($P\bar{4}3n$) and rhombohedral ($R3c$) forms of the $Te_{16}Si_{38}$ clathrate is the existence of strong bonds between the guest Te atoms (2a and 6c or 6b) and the silicon atoms of the partially Te-substituted cages of the host lattice, which are at the origin of the distortion of the structures. In the rhombohedral form, one of the Si atoms of the dodecahedral cage (Si21) is shifted toward the Te1 atom at the center of the cage to form a strong bond (2.716 Å). The latter Te1 atom has, therefore, one BP engaged in a bond and three LPs directed toward the pentagonal faces having the Te31 atom as a common vertex (Figure 5). A similar situation exists for the Si33 atoms, which are also shifted, even in a closer manner (2.632 Å), toward the Te2 atoms located at the center of the tetrakaidecahedral cage. In the cubic form of $Te_{16}Si_{38}$, one or

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Table 2. Nature of Te Bonding Encountered in the Te-Doped Silicon Clathrates

Clathrate	4 LPs	3 LPs + 1 BP	2 LPs + 2 BPs	1 LP + 3 BPs	4 BPs
$Te_{7+x}Si_{20-x}$ Cubic, Fd-3c	Te1 (16a)		Te4 (96g)		Te2, Te3 (64e)
$Te_{16}Si_{38}$ Cubic, P-43n	Te1 (2a)	Te2 (6c)[a]	Te2 (6c)[a]	Te3 (8e)	
$Te_{16}Si_{38}$ Rhomb., R3c		Te1, Te2 (2a), (6b)	Te32 (6b)	Te31 (2a)	
Bond character	Ionic	⟶			Covalent

[a] The Te2 atoms in the 6c position exhibit either the 3 LP + 1 BP (66%) or the 2 LP + 2 BP (33%) configuration.

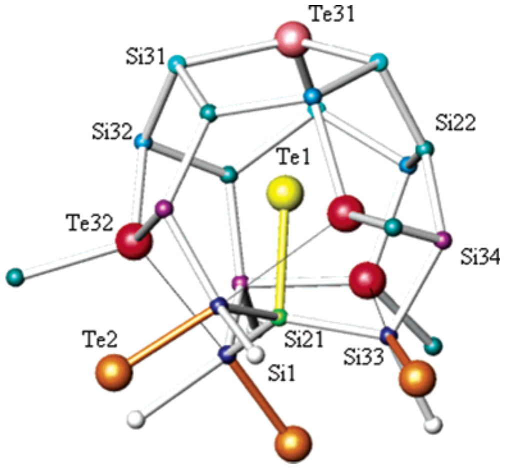

Figure 5. Close view of the Te1−Si21 (yellow) and Te2−Si33 (orange) bonds between the guest Te and host-forming Si atoms in the rhombohedral form of $Te_{16}Si_{38}$.

two silicon atoms in the Si32 position tend to come closer to the guest Te2 atoms, which can either adopt the same configuration as above (1 BP + 3 LPs) or engage two BPs with two Si32 (with a bond angle of 87.9 or 121.3°) and keep two LPs. The situation in which the Te atom has three BPs engaged in three bonds and only one LP is encountered in the Te atoms in the substitutional position. The most obvious case concerns the Te31 atoms in the rhombohedral form of $Te_{16}Si_{38}$ (Figure 5). The Te31 atoms are strongly bonded to three Si31 silicon atoms, and its fourth silicon neighbor is pushed away at a distance of more than 3 Å by its own LP. All of these distortions can be either randomly oriented or directed toward a single direction, as is the case in the rhombohedral form, which exhibits a polar character along the ternary axis. All of the possible bonding situations for the Te atoms are summarized in Table 2.

The tendency to form polyanions, $(Te)_n^{p-}$, which exist in a large number of polytellurides, is also one of the characteristics of the Te-doped silicon clathrates. In the cubic and rhombohedral forms of $Te_{16}Si_{38}$, only the Te1 atoms (2a) are surrounded by other Te atoms (four total) involving noticeable interactions. The only possible cluster is the $(Te{-}Te_4)^{n-}$ tetrahedron, but the Te−Te distances (3.35 Å) are significantly longer than those generally observed in polyanionic tellurides (3.05−3.10 Å). The Te−Te interactions are obviously weaker than those in the polytellurides.[22] These interactions, which involve the empty 5d Te orbitals, as in the square-planar $(Te{-}Te_4)^{6-}$ fragment (sp^3d^2 hybridization; 4 BP + 2 LP), could gradually increase, passing from $(TeTe_4)^{10-}$ to $(TeTe_4)^{2-} + 8e^-$. Such a cluster could also act as an electron reservoir in the same way as the $5p^{6-x}$ band in the $Te_{7+x}Si_{20-x}$ phase.

In the $Te_{7+x}Si_{20-x}$ clathrate-like phase, where a Te/Si disorder occurs in the 64e sites (about $^1/_3$ Te and $^2/_3$ Si atoms), the $Te1_{(16a)}{-}Te\mathit{i}_{(64e)}$ ($i = 2$ and 3) distances range from 3.25 to 3.40 Å. Several types of clusters may exist, involving two, three, and even four neighbors. The latter would correspond to a distorted form of the square-planar one. As in the previous case, a $(TeTe_4)^{10-} \leftrightarrow (TeTe_4)^{6-} + 4e^-$ equilibrium could explain the longer Te−Te bond, the 4 electrons of this new reservoir being compensated by the h^+ holes of the $5p^{6-x}$ band of the Te network.

Conclusion

In conclusion, the present three Te-doped clathrate-like structures of silicon have an obvious relationships with the parent one. However, it is clearly apparent that these structures, particularly that of $Te_{7+x}Si_{20-x}$, are at the border between the clathrate family and that of the ionocovalent tellurides. With an increasing Te content, an evolution occurs from a 3-D host lattice of silicon to a 3-D network of $Te^{(II-\delta)-}$ ions enclosing almost isolated fullerene-like dodecahedral $(Te_xSi_{20-x})^{n+}$ cationic units. In these structures, the Te atoms show a variety of coordination polyhedra and bonds ranging from four BPs to four LPs. Furthermore, the appearance of holes at the top of the Te 5p valence band seems likely, involving a negative oxidation state of II − δ, with $\delta \sim 0.25$. Of course, these hypotheses have to be confirmed, for example by Mössbauer spectroscopy and theoretical band structure calculations. Furthermore, the physical properties of the materials have to be studied in the scope of their thermoelectric properties, after the preparation of suitable amounts of samples.

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