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Bond valence analysis of the cubic perovskite $SnTaO_3$: confirmation of its existence

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The existence of the cubic perovskite phase $SnTaO_3$ has been confirmed by using the bond valence model. The bond valence analysis of the crystal structure of $SnTaO_3$ involved (i) evaluating the reliability of the bond valence parameters reported earlier for Sn(II)—O bonds; (ii) determining the hitherto unreported bond valence parameters for Ta(IV)—O bonds; (iii) calculating the bond valence sums for all the crystallographically different atoms in the structure; and (iv) calculating the "global instability index" of the structure. The values of the bond valence sums and "global instability index" calculated for the structure of $SnTaO_3$ indicate the stability of this ternary phase and the plausibility of the stoichiometric perovskite structural model proposed for $SnTaO_3$.

Perovskites / Crystal structure / Bond valence model

M. Gasperin has reported two cubic tin-tantalum-oxygen perovskite phases: $SnTaO_3$ in 1955 [1] and $Sn_{0.25}TaO_3$ in 1960 [2]. Surprisingly, both $SnTaO_3$ and $Sn_{0.25}TaO_3$ were reported to have the same lattice parameter $a = 3.880(4)$ Å; taking into account this inconsistency, the existence of the stoichiometric cubic $SnTaO_3$ phase was considered doubtful for a long time.

Based on the effective ionic radii by Shannon [3], Jiang *et al.* [4] and Moreira and Dias [5] recently proposed empirical equations reproducing lattice parameters in cubic perovskites, including $SnTaO_3$. As the lattice parameter of the stoichiometric cubic $SnTaO_3$ phase is reproduced reasonably well by the aforementioned empirical equations, one might take this fact as an indirect confirmation of the existence of the cubic $SnTaO_3$ phase reported by Gasperin in 1955 [1]. However, because of the extreme distortions typically observed for the coordination shells $[Sn^{+2}O_x]$ and $[Sn^{+2}F_x]$, Shannon [3] considered it meaningless to quote effective ionic radii for the cation Sn^{+2}; so the ionic radii used by Jiang *et al.* [4] and Moreira and Dias [5] for Sn^{+2} are actually *ad hoc* radii, which cannot be regarded as reliable without careful tests.

Another confirmation of the existence of the stoichiometric cubic $SnTaO_3$ phase has been proposed by Ali *et al.* [6] based on *ab initio* calculations; however, the lattice parameter $a \approx 4.00$ Å, obtained in [6] for $SnTaO_3$, significantly deviates from the experimental value of 3.880 Å [1].

Being interested in perovskite and related structures [7-12], the author decided to check the structure reported for the stoichiometric cubic $SnTaO_3$ phase by using the bond valence model [13,14] in order to confirm or refute the stoichiometric composition of this phase.

The bond valence model (BVM) in its modern form is a powerful and convenient tool for detecting errors in crystal structure determinations and for predicting bond lengths in structures of known chemical composition and presupposed bond network topology [13,14]. The bond valence (BV) s is defined as the part of the "classical" atomic valence shared with each cation—anion bond. According to the bond valence sum (BVS) rule, the oxidation state (or atomic valence) V_A of the central atom of the $[AX_j]$ coordination shell can be calculated from the sum of the individual bond valences s_{AX}, as given by equation (1) [15].

$$V_A = \sum_j s_{AX} \tag{1}$$

The valence of a bond (measured in valence units, *vu*) is considered to be a unique function of the bond length; and the most commonly adopted empirical expression for the relationship between the bond valences s_{AX} and the bond lengths r_{AX} is equation (2), where r_0 and b are empirically determined constants (BV parameters) for a given type of A—X chemical bond, r_0 being the length of a conceptual bond of unit valence with $s_{AX} = 1$ [13,14].

$$s_{AX} = \exp[(r_0 - r_{AX})/b] \qquad (2)$$

The b parameter in equation (2) is commonly taken to be a "universal constant" equal to 0.37 Å, and r_0 parameters have been determined for ~1000 types of A—X chemical bond, assuming $b = 0.37$ Å [16,17]. In the BVM literature, the BV parameters determined using the above "universal constant" are often referred to as the conventional BV parameters.

In well-determined stable ordered crystal structures investigated under ambient conditions, the BVS values calculated from reliable BV parameters for all the crystallographically distinct atoms are typically very close to the expected V_A values; therefore, large deviations between the BVS and V_A values can really indicate that the structural model at hand is incorrect.

It must be noted, however, that the efficiency of the BVM in detecting errors in crystal structures and in predicting bond lengths is critically dependent on the quality of the BV parameters: high-quality BV parameters are expected to give close approximations of the real (observed) "s_{AX} *versus* r_{AX}" curves over the whole ranges of observed bond lengths [18-22].

In most cases, the flexibility of the curves defined with the conventional BV parameters (*i.e.* with the preset value $b = 0.37$ Å) is sufficient to obtain a good approximation of the real "s_{AX} *versus* r_{AX}" correlation curves; but for certain ion pairs (especially for those having a wide range of coordination numbers, CN's) good approximations of the real "s_{AX} *versus* r_{AX}" curves are possible only by simultaneous fitting of both r_0 and b.

The results of a BV analysis obtained from poorly determined BV parameters can lead to serious misinterpretations of the peculiarities of the chemical bonding observed in certain crystal structures (see *e.g.* two different interpretations made by Krivovichev [23] and later by Krivovichev and Brown [24] for the chemical bonding in $[OPb_4]$ coordination tetrahedra); hence, the BV analysis of any crystal structure should include preliminary examination of the quality of the BV parameters r_0 and b reported in the literature.

The BV analysis of the crystal structure of $SnTaO_3$ [1] involved (i) evaluating the reliability of the BV parameters reported earlier for Sn(II)—O bonds; (ii) determining the BV parameters for Ta(IV)—O bonds; (iii) calculating the BVS's for all the crystallographically independent atoms in the structure; and (iv) calculating the "global instability index" G [13,14] for the structure of the title compound by using equation (3).

$$G = \langle(\mathrm{BVS} - V_A)^2\rangle^{0.5} \qquad (3)$$

The G value (*i.e.* the root-mean-square deviation of the bond valence sums from the oxidation state averaged over all the atoms in the formula unit) is a useful measure of the failure of the BVS rule. Provided that the BV parameters are of high quality, accurately determined stable structures are rarely found with G greater than 0.2 *vu* [13,14]; so a larger G value can usually be attributed to a poorly determined structural model and/or to the instability of the structure.

In the BVM literature, four different sets (r_0; b) of BV parameters have been reported for Sn(II)—O bonds: $r_0 = 1.984$ Å and $b = 0.37$ Å by Brese and O'Keeffe [17], $r_0 = 1.849$ Å and $b = 0.50$ Å by Sidey [20], $r_0 = 1.859$ Å and $b = 0.55$ Å by Brown [25], $r_0 = 1.956$ Å and $b = 0.37$ Å by Hu *et al.* [26] (in chronological order).

The performances of the BV parameters available for Sn(II)—O bonds have been compared using the corrected (for misprints) and slightly extended (by inclusion of the accurately determined structure of $SnSO_4$ [38] with a $[Sn^{+2}O_{12}]$ coordination shell) collection of inorganic structures [27-38] selected for illustrative purposes in the article by Hu *et al.* [26] (Table 1). All the interatomic distances considered in the present work have been calculated/checked by using the program *PLATON* [39]. The precision of the interatomic distances used for calculations of the BVS values was ±0.001 Å.

As seen from Table 1, only the BV parameters for Sn(II)—O bonds reported by the author of the present work steadily show BVS values close to $V_A = 2$; so these BV parameters ($r_0 = 1.849$ Å; $b = 0.50$ Å [20]) were selected for the BV analysis of the structure of the stoichiometric cubic $SnTaO_3$ phase. The conventional BV parameters reported for Sn(II)—O bonds by Brese and O'Keeffe [17] and by Hu *et al.* [26] demonstrate systematic α variations [21] of the BVS values (*i.e.* too large and too small BVS's for lower and higher CN's, respectively), clearly indicating that the b constant must have a larger value [21]; while the BV parameters reported by Brown [25] demonstrate systematic "overbonding" for all the CN's of the $[Sn^{+2}O_x]$ coordination shells considered here.

For Ta(IV)—O bonds, no BV parameters have been reported in the BVM literature. Unlike $[Sn^{+2}O_x]$ coordination shells, $[Ta^{+4}O_x]$ shells with an integer value of the oxidation state +4 are rather rare to occur, so the structural data available for Ta(IV)—O bonds are definitely insufficient to determine reliable BV parameters for this type of chemical bond. Taking into account the paucity of relevant structural data, it was decided not to adjust both r_0 and b, but to obtain a tentative conventional set (r_0; $b = 0.37$ Å) of BV parameters for Ta(IV)—O bonds.

Table 1 Comparison of BVS values calculated for $[Sn^{+2}O_x]$ coordination shells from different Sn(II)—O BV parameters.

Structure	Shell	Sn(II)—O distances (Å)	BVS (*vu*)[a]			
			a	*b*	*c*	*d*
Na_4SnO_3 [27]	$[SnO_3]$	2.005; 2.015; 2.036	2.733	2.137	2.245	2.534
$K_2Sn_2O_3$ [28]	$[SnO_3]$	2.027 × 3	2.671	2.101	2.210	2.476
$Rb_2Sn_2O_3$ [29]	$[SnO_3]$	2.038 × 3	2.593	2.056	2.167	2.404
$Cs_2Sn_2O_3$ [30]	$[SnO_3]$	2.022; 2.046 × 2	2.594	2.056	2.167	2.405
	$[SnO_3]'$	2.077 × 2; 2.104	2.279	1.868	1.986	2.112
K_4SnO_3 [31]	$[SnO_3]$	2.041; 2.049; 2.051	2.530	2.019	2.131	2.346
SnO [32]	$[SnO_4]$	2.224 × 4	2.091	1.889	2.060	1.939
$NH_4Sn(PO_4)$ [33]	$[SnO_6]$	2.079; 2.100; 2.150; 2.989; 3.266; 3.307	2.268	2.000	2.182	2.103
$Na_2Sn(C_2O_4)_2$ [34]	$[SnO_8]$	2.245 × 2; 2.357 × 2; 2.909 × 2; 3.411 × 2	1.924	1.958	2.216	1.784
$SnNb_2O_6$ [35]	$[SnO_8]$	2.177 × 2; 2.420 × 2; 3.007 × 2; 3.216 × 2	2.000	2.003	2.261	1.854
α-$SnWO_4$ [36]	$[SnO_8]$	2.184 × 2; 2.392 × 2; 2.826 × 2; 3.444 × 2	2.073	2.064	2.323	1.922
β-$SnWO_4$ [37]	$[SnO_9]$	2.214 × 3; 2.810 × 3; 3.523 × 3	1.980	1.990	2.251	1.836
$SnSO_4$ [38]	$[SnO_{12}]$	2.247; 2.273 × 2; 2.949; 3.079 × 2; 3.109 × 2; 3.181 × 2; 3.336 × 2	1.811	1.992	2.315	1.679

[a] BVS values calculated from the BV parameters: (*a*) $r_0 = 1.984$ Å and $b = 0.37$ Å by Brese and O'Keeffe [17]; (*b*) $r_0 = 1.849$ Å and $b = 0.50$ Å by Sidey [20]; (*c*) $r_0 = 1.859$ Å and $b = 0.55$ Å by Brown [25]; (*d*) $r_0 = 1.956$ Å and $b = 0.37$ Å by Hu *et al.* [26].

Analysis of the Ta(IV)—O bonds in the crystal structures of $Fe_{0.3}Mn_{0.7}TaO_4$ [40] and $Ba_3Si_4Ta_6O_{23}$ [41] resulted in a conventional r_0 value of 1.805 Å. Due to the small number of available structures (which, additionally, have been determined rather poorly), the above conventional r_0 parameter must be used cautiously. Moreover, it appears that the ion Ta^{+4} may exist in quite different electronic states, resulting in a wide spread of average bond lengths observed in chemically equivalent coordination shells $[Ta^{+4}O_x]$. Hence, in order to analyze the Ta(IV)—O bonds in terms of the BVM, a distinct set of BV parameters might be required for every electronic state of the ion Ta^{+4}. However, any sound conclusion about the BV parameters for Ta(IV)—O bonds and about the electronic states of the ion Ta^{+4} in the coordination shells $[Ta^{+4}O_x]$ will be possible only after accumulation of sufficient experimental data. Nevertheless, the quality of the BV parameters calculated here for Ta(IV)—O bonds has been considered acceptable for the BV analysis of the crystal structure of $SnTaO_3$.

The cubic perovskite phase $SnTaO_3$ is characterized by the following interatomic distances: Ta(IV)—O of 1.940(2) Å in the $[Ta^{+4}O_6]$ coordination octahedron and Sn(II)—O of 2.744(3) Å in the $[Sn^{+2}O_{12}]$ coordination cube-octahedron. From these interatomic distances, and using the aforementioned BV parameters for Sn(II)—O and Ta(IV)—O bonds, the BVS values have been calculated for all the symmetrically independent atoms in the crystal structure of $SnTaO_3$ [1]. Then, from the obtained BVS values, the *G* value [13,14] has been calculated for the whole structure of the title compound by using equation (3). The results of the BV analysis of the crystal structure of $SnTaO_3$ are summarized in Table 2.

As seen from Table 2, the BVS values calculated for the atoms of the crystal structure of $SnTaO_3$ are reasonably close to the expected V_A values, and the *G* value calculated for the whole structure of $SnTaO_3$ is far below 0.2 *vu*, considered as the critical limit for stable and accurately determined structures.

Taking into account the good agreement between the BVS and V_A values and the fairly small *G* value calculated for the structure of the title compound (see Table 2), one may conclude that the stoichiometric cubic perovskite phase $SnTaO_3$ does exist and its crystal structure reported by Gasperin [1] has been determined with no serious systematic errors.

Table 2 Bond valence analysis of the crystal structure of $SnTaO_3$.

Atom	Coordination shell	BVS (*vu*)
Sn(II)	$[SnO_{12}]$	2.004 (+0%)
Ta(IV)	$[TaO_6]$	4.166 (+4%)
O	$[OTa_2Sn_4]$	2.056 (+3%)

Global instability index: *G* = 0.10 *vu*.

As the phase $Sn_{0.25}TaO_3$ has never been synthesized again after Gasperin's report in 1960 [2], and since the structures with disorder and/or partial occupancy factors cannot be reliably examined with the BVM, the existence of the cubic perovskite phase $Sn_{0.25}TaO_3$ still needs to be confirmed.

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