

## X-ray Rietveld structure refinement and bond-valence analysis of Cs<sub>2</sub>TeI<sub>6</sub>

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The crystal structure of the ternary iodide Cs<sub>2</sub>TeI<sub>6</sub> has been refined by Rietveld analysis of X-ray powder diffraction data. The refinement procedure was stopped when the intensity residual  $R_B = 3.7\%$  had been reached. Cs<sub>2</sub>TeI<sub>6</sub> crystallizes in the cubic K<sub>2</sub>PtCl<sub>6</sub> structure type, space group *Fm-3m* (No. 225), with the lattice parameter  $a = 11.6939(8)$  Å,  $Z = 4$ ,  $D_c = 4.797(1)$  g/cm<sup>3</sup>. The reliability of the structural model obtained for Cs<sub>2</sub>TeI<sub>6</sub> in the Rietveld refinement was confirmed by a bond-valence analysis of the structure. For the first time, the bond-valence parameters ( $r_0 = 2.782$  Å and  $b = 0.37$  Å) have been determined for the Te<sup>4+</sup>/I<sup>-</sup> ion pair, from a set of 14 well-determined coordination shells [TeI<sub>n</sub>]. These parameters show a reasonably high performance and can be recommended for routine bond-valence analyses of structures containing Te<sup>4+</sup>-I<sup>-</sup> chemical bonds.

Ternary halides / Crystal structure / Bond-valence model

### Introduction

This work is part of an ongoing systematic physico-chemical investigation of quasibinary halide systems AX-BX<sub>4</sub> (where A = K, Rb, Cs, Tl; B = Se, Te; X = Br, I) [1-5]. Most of the aforementioned quasibinary systems are characterized by the formation of A<sub>2</sub>BX<sub>6</sub> intermediate phases, which melt congruently and have interesting optical and electrical properties.

For the first time, the crystal structure of Cs<sub>2</sub>TeI<sub>6</sub> crystallizing in the cubic K<sub>2</sub>PtCl<sub>6</sub> structure type [6] was reported in 1956 [7,8]. The structure of Cs<sub>2</sub>TeI<sub>6</sub> was determined by using X-ray powder diffraction techniques available in the mid 1950's, and the structural model obtained clearly suffers from some deficiencies: the free positional parameter of the iodine atom in the structure of Cs<sub>2</sub>TeI<sub>6</sub> was preset but not refined, and the atomic displacement ("thermal") parameters were not determined at all (*i.e.* the values of these parameters were assumed to be zero). To our knowledge, there have been no further attempts to investigate the crystal structure of Cs<sub>2</sub>TeI<sub>6</sub>, so we decided to refine this structure by using the Rietveld analysis, which was developed in 1969 and is a much more powerful method for crystal structure refinement from powder diffraction data [9].

### Experimental procedures and results

The title compound and precursors were synthesized in accordance with procedures developed and described by us in earlier works [1,2]. The sample for this investigation was prepared from CsI and TeI<sub>4</sub>. CsI was synthesized by reacting Cs<sub>2</sub>CO<sub>3</sub> with HI; after the synthesis, CsI was homogenized in a resistance furnace at 930±5 K for 72 h. TeI<sub>4</sub> was synthesized from commercially available reagent-grade tellurium and extra-pure-grade iodine, by direct iodination of tellurium powder in a two-compartment ampoule [1]. The resultant material was then homogenized at 550±5 K for 72 h. The melting points of the obtained binary iodides agreed well with those reported earlier [2].

Cs<sub>2</sub>TeI<sub>6</sub> was synthesized by melting a stoichiometric mixture of CsI and TeI<sub>4</sub> (molar ratio 2:1) in a pretreated and outgassed silica ampoule (12 mm I.D., 14 mm O.D., L ≈ 120 mm) sealed under a vacuum of 0.133 Pa or less. After the chemical reaction, the sample was slowly cooled to, and annealed for one month at 475±5 K in the sealed ampoule.

The experimental density of the compound Cs<sub>2</sub>TeI<sub>6</sub> [4.81(3) g/cm<sup>3</sup>] was determined by pycnometry measurements, using toluene as the working liquid.

**Table 1** Experimental details and crystallographic data for Cs<sub>2</sub>TeI<sub>6</sub>.

Crystal system; space group	Cubic; <i>Fm-3m</i> (No. 225)
Lattice parameter	$a = 11.6939(8) \text{ \AA}$
Cell volume	$V = 1599.1(2) \text{ \AA}^3$
Chemical formula weight	FW = 1154.82
Formula units per cell	$Z = 4$
Calculated density	$D_c = 4.797(1) \text{ g/cm}^3$
Measured density	$D_m = 4.81(3) \text{ g/cm}^3$
Temperature of data collection	$T = 293(2) \text{ K}$
Radiation type; wavelength	Cu K $\alpha$ ; $\lambda = 1.5419 \text{ \AA}$
Powder diffractometer; geometry	DRON-3M; Bragg–Brentano
$2\theta$ scan range; step	$10\div 100^\circ$ ; $0.05^\circ$
Scan speed	10 s/step
Refinement program	DBWS-9807a
Peak shape function	Pearson VII
Peak asymmetry function	Riello-Canton-Fagherazzi
Background model	5 <sup>th</sup> order polynomial
Number of atom sites	3
Number of free structural parameters	5
Total number of free parameters	19
Profile R-factors	$R_p = 6.4 \%$ ; $R_{wp} = 7.8 \%$
Bragg R-factor	$R_B = 3.7 \%$
Goodness of fit	$S = 0.64$

**Table 2** Atomic coordinates and isotropic displacement parameters for the crystal structure of Cs<sub>2</sub>TeI<sub>6</sub>.

Atom	Position	$x/a$	$y/b$	$z/c$	$B_{\text{iso}} (\text{\AA}^2)$
Cs	8c	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	3.5(3)
Te	4a	0	0	0	0.7(4)
I	24e	0.2498(4)	0	0	2.0(2)

A polycrystalline ingot of Cs<sub>2</sub>TeI<sub>6</sub> was ground to a fine powder in an agate mortar and then investigated by the X-ray powder diffraction technique (XRD). X-ray powder diffraction data for Cs<sub>2</sub>TeI<sub>6</sub> were collected on a conventional Bragg-Brentano diffractometer in the step-scan mode (DRON-3M, Cu K $\alpha$  radiation [10],  $10 \leq 2\theta \leq 100^\circ$ , step size  $0.05^\circ$ , counting time 10 s per step, room temperature).

The Rietveld refinement [9] procedures were performed using the program DBWS-9807a [11], an upgraded version of the classical program by Wiles and Young [12,13]. The Pearson VII [14] function was used for the simulation of the peak shape. Intensities within 32 times of the full-width-at-half-maximum (FWHM) were considered to contribute to the reflection. The background was modeled using a refinable fifth-order polynomial. Peaks below  $45^\circ$  ( $2\theta$ ) were corrected for asymmetry effects by using the Riello-Canton-Fagherazzi model [15]. Application of corrections for preferred orientation and surface roughness did not improve the structural model of Cs<sub>2</sub>TeI<sub>6</sub>, so these corrections were not used in the final Rietveld refinement.

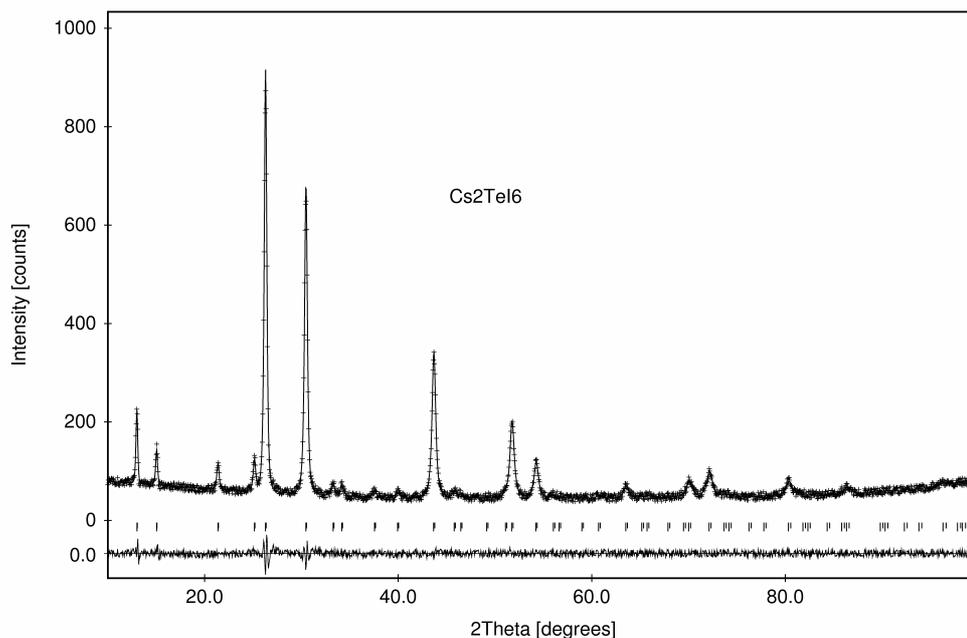
The refinement converged with the profile residuals  $R_p = 6.4\%$  and  $R_{wp} = 7.8\%$ , and with the

intensity residual (so-called “Bragg R-factor”)  $R_B = 3.7\%$ . It should be noted that the low values of the profile residuals can indicate a high background level rather than the actual profile agreement [16], but the fairly low  $R_B$  value (which is not affected by the background level) obtained in the present work indicates reasonable agreement between the experimental data and the theoretical structural model for the title compound.

Experimental details and crystallographic data for the compound Cs<sub>2</sub>TeI<sub>6</sub> are collected in Table 1. Positional and isotropic displacement (“thermal”) parameters of the crystal structure of Cs<sub>2</sub>TeI<sub>6</sub> are given in Table 2, and selected interatomic distances calculated by using the program PLATON [17] are given in Table 3. Fig. 1 illustrates the final Rietveld plot for the title compound.

**Table 3** Selected interatomic distances ( $\text{\AA}$ ) for the crystal structure of Cs<sub>2</sub>TeI<sub>6</sub>.

Te–I ( $\times 6$ )	2.921(5)
Cs–I ( $\times 12$ )	4.1344(3)
I–I ( $\times 8$ )	4.138(5)



**Fig. 1** Experimental (crosses), theoretical (solid line), and difference (solid line at the bottom) powder XRD patterns for Cs<sub>2</sub>TeI<sub>6</sub>; reflection positions are marked by vertical bars.

The crystal structure of Cs<sub>2</sub>TeI<sub>6</sub> belongs to the well-known cubic K<sub>2</sub>PtCl<sub>6</sub> structure type [6]. The structure of K<sub>2</sub>PtCl<sub>6</sub> (Fig. 2) can be conveniently derived from that of perovskite (ABX<sub>3</sub>) by removing one half of the B-type cations so that every transition metal–halogen octahedron in the structure of K<sub>2</sub>PtCl<sub>6</sub> is isolated from other octahedra of the same kind. More detailed information about the cubic K<sub>2</sub>PtCl<sub>6</sub> structure type can be found in [3] or in any textbook on inorganic crystal chemistry.

### Bond-valence analysis of the crystal structure of Cs<sub>2</sub>TeI<sub>6</sub>

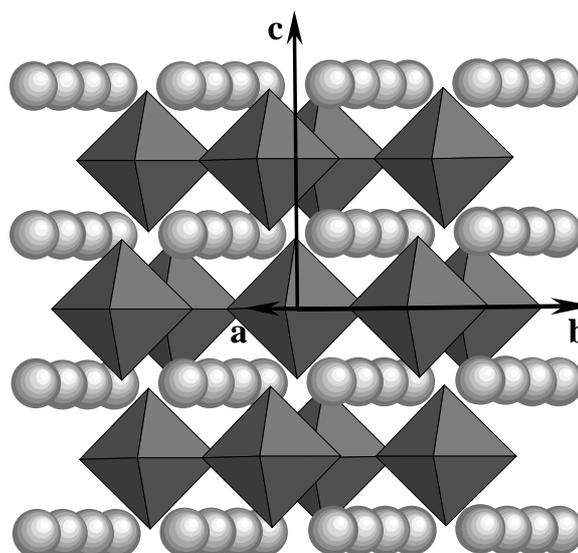
In order to check the reliability of the structural model obtained for the title compound in the present work, we employed the bond-valence analysis procedure [18,19].

The bond-valence model (BVM) in its modern form is a powerful and convenient tool for validation of newly determined crystal structures and for predicting bond lengths in structures of known chemical composition and presupposed bond-network topology [18,19]. The bond valence (BV)  $s$  is defined as the part of the “classical” atomic valence shared with each bond. According to the bond-valence sum (BVS) rule, the oxidation state (atomic valence)  $V_A$  of the central ion (atom) of the [AX<sub>*n*</sub>] coordination shell can be calculated from the sum of the individual bond valences  $s_{A-X}$ , as given in equation (1).

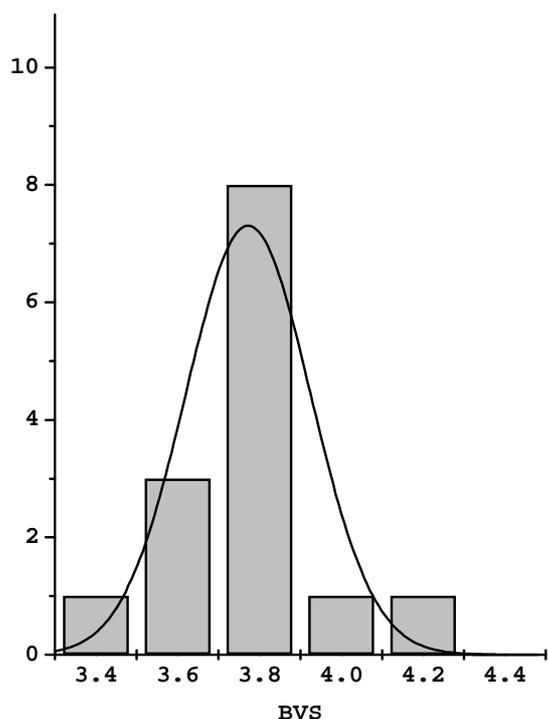
$$V_A = \sum_n s_{A-X} \quad (1)$$

The valence of a bond (measured in “valence units”, v.u.) 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  $s_{A-X}$  and the bond lengths  $r_{A-X}$  is equation (2), where  $r_0$  and  $b$  are empirically determined parameters (BV parameters) for a given ion (atom) pair,  $r_0$  being the length of a conceptual bond of unit valence,  $s_{A-X} = 1$ .

$$s_{A-X} = \exp[(r_0 - r_{A-X})/b] \quad (2)$$



**Fig. 2** Crystal structure of K<sub>2</sub>PtCl<sub>6</sub>: [PtCl<sub>6</sub>] coordination octahedra and K atoms.



**Fig. 3** Distribution of the BVS values calculated for the Te<sup>4+</sup> ions of [TeI<sub>n</sub>] coordination shells using the Brese-O’Keeffe BV parameters  $r_0 = 2.76 \text{ \AA}$  and  $b = 0.37 \text{ \AA}$  [21].

The  $b$  parameter in equation (2) is commonly taken to be a “universal constant” equal to  $0.37 \text{ \AA}$ , and the  $r_0$  parameters have been determined for a large number (~1000) of ion pairs, assuming  $b = 0.37 \text{ \AA}$  [20,21]. The BV parameters determined using the above “universal constant” are usually referred to as conventional BV parameters.

In well-determined stable ordered crystal structures, the BVS values calculated 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 be an indication of the incorrectness of a structural model.

However, as one of us (V.I.S.) has clearly illustrated in his recent works [22–25], 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) “ $s_{A-X}$  versus  $r_{A-X}$ ” curves within the *whole* ranges of observed bond lengths. In most cases, the commonly used monoparametric (with  $b = 0.37 \text{ \AA}$ ) “conventional” formula (3) can give close approximations of the real “ $s_{A-X}$  versus  $r_{A-X}$ ” curves, but for certain ion pairs (especially for those having a wide range of coordination numbers, CN’s) close approximations of the real “ $s_{A-X}$  versus  $r_{A-X}$ ”

correlations are possible only by *simultaneous* fitting of both  $r_0$  and  $b$ .

$$s_{A-X} = \exp[(r_0 - r_{A-X})/0.37] \quad (3)$$

The results of the 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 [26] and by Krivovichev and Brown [27] for the chemical bonding in [OPb<sub>4</sub>] coordination tetrahedra). Hence, the BV analysis of any crystal structure should include preliminary checking of the quality of the BV parameters  $r_0$  and  $b$  reported in the literature.

The BV analysis of Cs<sub>2</sub>TeI<sub>6</sub> involved (i) evaluating the reliability of the BV parameters reported for the Cs<sup>+</sup>/I<sup>-</sup> and Te<sup>4+</sup>/I<sup>-</sup> ion pairs; (ii) determining new BV parameters for the Te<sup>4+</sup>/I<sup>-</sup> ion pair; (iii) calculating the bond-valence sums (BVS’s) for all the crystallographically different atoms in the crystal structure of the title compound. The “global instability index”  $G$  [18,19] was calculated by using the following equation.

$$G = \langle (\text{BVS} - V_A)^2 \rangle^{0.5} \quad (4)$$

The  $G$  value [*i.e.* the square root of the 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 bond-valence sum rule. Correctly determined structures are rarely found with  $G$  greater than  $0.2 \text{ v.u.}$  [18,19]; a larger value can usually be attributed to the use of poorly determined BV parameters or to an incorrect crystal structure determination.

The BV parameters reported for a given ion pair were regarded as reliable if they closely approximate the real (observed) “ $s_{A-X}$  versus  $r_{A-X}$ ” correlation within the range of interest, *i.e.* if they are able to reproduce typical interatomic distances in different coordination polyhedra formed by these ions. In this respect, the conventional BV parameters reported by Brese and O’Keeffe [21] for the Cs<sup>+</sup>/I<sup>-</sup> ion pair ( $r_0 = 3.18 \text{ \AA}$  and  $b = 0.37 \text{ \AA}$ ) were found to be fairly reliable. Thus, the interatomic distances calculated from these BV parameters for the [CsI<sub>8</sub>] and [CsI<sub>12</sub>] coordination polyhedra (~3.95  $\text{\AA}$  and ~4.10  $\text{\AA}$ , respectively) reproduce the Cs–I distances observed in CsI (~3.96  $\text{\AA}$  [28]; CN = 8 with  $s_{A-X} = 1/8 \text{ v.u.}$ ) and in accurately determined perovskite-related structures (~4.1  $\text{\AA}$  [29–31]; CN = 12 with  $s_{A-X} \approx 1/12 \text{ v.u.}$ ) reasonably well. However, the reliability of the BV parameters reported by Brese and O’Keeffe [21] for Te–I bonds (with no oxidation state specified for Te) was found to be insufficient. The BVS values calculated from the Brese-O’Keeffe parameters ( $r_0 = 2.76 \text{ \AA}$  and  $b = 0.37 \text{ \AA}$ ) for the Te<sup>4+</sup> ions inside the [TeI<sub>n</sub>] coordination shells show systematic “underbonding” (Table 4). BV parameters for the Te<sup>4+</sup>/I<sup>-</sup> ion pair have never been reported in the literature; taking this fact into account, we decided to calculate the  $r_0$  and  $b$  parameters for this ion pair in the present work.

**Table 4** Reliability of the BV parameters obtained for the Te<sup>4+</sup>/Γ ion pair.

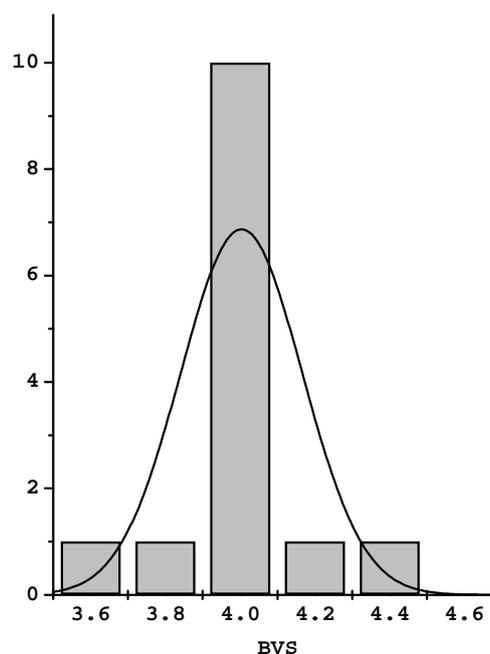
Compound	Coordination shell <sup>a</sup>	Bond-valence <sup>b</sup> sum (v.u.) for Te <sup>4+</sup>	
		Breese and O'Keeffe [21] $r_0 = 2.76 \text{ \AA}; b = 0.37 \text{ \AA}$	This work $r_0 = 2.782 \text{ \AA}; b = 0.37 \text{ \AA}$
$\delta$ -TeI <sub>4</sub> [32]	[TeI <sub>6</sub> ]	3.803 (-5%)	4.036 (+1%)
	[TeI <sub>6</sub> ] <sup>i</sup>	3.663 (-8%)	3.887 (-3%)
	[TeI <sub>6</sub> ] <sup>ii</sup>	3.700 (-8%)	3.926 (-2%)
$\beta$ -TeI <sub>4</sub> [33]	[TeI <sub>6</sub> ]	4.180 (+5%)	4.437 (+11%)
	[TeI <sub>6</sub> ] <sup>i</sup>	3.739 (-7%)	3.968 (-1%)
	[TeI <sub>6</sub> ] <sup>ii</sup>	3.486 (-13%)	3.699 (-8%)
$\gamma$ -TeI <sub>4</sub> [33]	[TeI <sub>6</sub> ]	3.690 (-8%)	3.916 (-2%)
	[TeI <sub>6</sub> ] <sup>i</sup>	3.861 (-3%)	4.097 (+2%)
	[TeI <sub>6</sub> ] <sup>ii</sup>	3.720 (-7%)	3.948 (-1%)
	[TeI <sub>6</sub> ] <sup>iii</sup>	3.763 (-6%)	3.993 (-0%)
$\epsilon$ -TeI <sub>4</sub> [33]	[TeI <sub>6</sub> ]	3.772 (-6%)	4.003 (+0%)
Rb <sub>2</sub> TeI <sub>6</sub> [34]	[TeI <sub>6</sub> ]	3.786 (-5%)	4.018 (+0%)
(NH <sub>4</sub> ) <sub>2</sub> TeI <sub>6</sub> [35]	[TeI <sub>6</sub> ]	3.746 (-6%)	3.975 (-1%)
TeI <sub>3</sub> AlI <sub>4</sub> [36]	[TeI <sub>6</sub> ]	3.907 (-2%)	4.147 (+4%)
Average BVS		3.77(15) (-6%)	4.00(16) (+0%)

<sup>a</sup> the shortest distance from the central cation to another cation in a given crystal structure was assumed to be the physical limit of the coordination sphere under consideration;

<sup>b</sup> the precision of the interatomic distances used for calculations of the BVS's was  $\pm 0.001 \text{ \AA}$ .

Although the conventional BV parameters can sometimes fail, the first step in determining the BV parameters for a given ion pair should always be calculation and evaluation of the  $r_0$  value based on the above "universal constant"  $b = 0.37 \text{ \AA}$ . It is necessary to determine "non-conventional" BV parameters only if the conventional parameters show significant systematic variations of the BVS values calculated for different CN's of a given ion pair [25]. As shown in Table 4 and in Fig. 4, the conventional BV parameters determined in the present work for the Te<sup>4+</sup>/Γ ion pair demonstrate reasonably high performance and, therefore, calculation of "non-conventional" BV parameters was senseless.

From the literature, we selected seven ordered stoichiometric inorganic structures accurately determined (with  $R \leq 0.1$ ) in single-crystal studies at ambient conditions [32-36]; these structures contain 14 symmetrically independent coordination shells [TeI<sub>*n*</sub>] with no ligands other than Γ. The  $b$  value was set to  $0.37 \text{ \AA}$ , and the  $r_0$  value was adjusted (with a step of  $0.001 \text{ \AA}$ ) to give BVS  $\approx 4$  v.u. for the above set of selected coordination shells on the average. The optimum conventional BV parameter  $r_0 = 2.782 \text{ \AA}$  determined in the present work gives  $\langle \text{BVS} \rangle = 4.00(16)$  v.u. for the above set, while the Brese-O'Keeffe parameter  $r_0 = 2.76 \text{ \AA}$  gives a considerably smaller value,  $\langle \text{BVS} \rangle = 3.77(15)$  v.u.



**Fig. 4** Distribution of the BVS values calculated for the Te<sup>4+</sup> ions of [TeI<sub>*n*</sub>] coordination shells from the BV parameters  $r_0 = 2.782 \text{ \AA}$  and  $b = 0.37 \text{ \AA}$  determined in this work.

**Table 5** Bond-valence analysis of the crystal structure of Cs<sub>2</sub>TeI<sub>6</sub>.

Ion	Coordination shell	Bond-valence sum (v.u.)
Cs <sup>+</sup>	[CsI <sub>12</sub> ]	0.911 (−9%)
Te <sup>4+</sup>	[TeI <sub>6</sub> ]	4.121 (+3%)
I <sup>−</sup>	[ITeCs <sub>4</sub> ]	0.990 (−1%)

Global instability index:  $G = 0.09$  v.u.

Fig. 3 and Fig. 4 show, respectively, the distributions of the BVS values calculated for the Te<sup>4+</sup> ions of the [TeI<sub>n</sub>] coordination shells from the above Brese-O'Keeffe parameters and from the conventional BV parameters determined here. Table 4 illustrates the performance of the BV parameters reported here for the Te<sup>4+</sup>/I<sup>−</sup> ion pair. One can see that the quality of the BV parameters determined in the present work is reasonably high, and, therefore, these BV parameters can be recommended for routine BV analyses of structures containing Te<sup>4+</sup>–I<sup>−</sup> chemical bonds.

The BVS values calculated for the symmetrically independent atoms of the crystal structure of Cs<sub>2</sub>TeI<sub>6</sub> from the Brese-O'Keeffe parameters ( $r_0 = 3.18$  Å and  $b = 0.37$  Å) reported for the Cs<sup>+</sup>/I<sup>−</sup> ion pair [21] and from the BV parameters determined here for the Te<sup>4+</sup>/I<sup>−</sup> ion pair ( $r_0 = 2.782$  Å and  $b = 0.37$  Å) are given in Table 5. The  $G$  value calculated for the crystal structure refined in this work for Cs<sub>2</sub>TeI<sub>6</sub> is also given in Table 5.

One can see that the BVS values calculated for the atoms of the crystal structure of Cs<sub>2</sub>TeI<sub>6</sub> are reasonably close to the expected  $V_A$  values. As the performances of the BV parameters used here for the BVS calculations have been found to be acceptable (see above), the fairly small  $G$  value calculated for the structure of Cs<sub>2</sub>TeI<sub>6</sub> indicates a reasonably high reliability of the structural model obtained in the present work.

Taking into account the reasonably low  $R_B$  value obtained in the Rietveld refinement (Table 1), the quite smooth difference plot (Fig. 1) and the fairly small  $G$  value calculated for the structure of Cs<sub>2</sub>TeI<sub>6</sub> (Table 5), one may conclude that the crystal structure reported here for the title compound has been determined with no serious systematic errors.

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