X-ray powder diffraction studies and bond-valence analysis of $Hg_2Sb_2O_7$

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Abstract

The crystal structure of $Hg_2Sb_2O_7$ has been refined using X-ray powder diffraction technique. $Hg_2Sb_2O_7$ crystallizes in the cubic pyrochlore structure type, space group $Fd\bar{3}m$, with the lattice parameter $a = 10.3525(5)$ Å, $Z = 8$, $D_c = 9.060(1)$ g/cm^3. The Rietveld refinement procedure was stopped when the intensity residual $R_B = 3.25\%$ had been reached.

In the bond-valence analysis of the crystal structure of $Hg_2Sb_2O_7$, the values of the bond-valence parameters reported for the Sb^{5+}/O^{2-} ion pair have been found to be doubtful. Using the new calculation scheme, the improved bond-valence parameters for the Sb^{5+}/O^{2-} ion pair ($r_0 = 1.908$ Å and $b = 0.409$ Å) have been derived from the crystal structure of Sb_2O_5.

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1. Introduction

This work is a part of our ongoing systematic studies of the ternary systems Hg(Pb)–Sb–O [1–3].

For the first time, existence of the ternary oxide $Hg_2Sb_2O_7$ crystallizing in the cubic pyrochlore structure type [4] was reported by Sleight [5]. Being solved correctly, the crystal structure of $Hg_2Sb_2O_7$ reported by Sleight was not refined but *deduced* from the presupposed Sb–O interatomic distances and from the observed unit-cell parameter a. In the present work, we report the crystal structure of $Hg_2Sb_2O_7$ obtained in the Rietveld refinement [6] procedures.

Although the primary aim of this work was to report the structure of $Hg_2Sb_2O_7$, here we also present the new reliable and physically meaningful bond-valence [7–9] parameters for the Sb^{5+}/O^{2-} ion pair. The reliability of the values $r_0 = 1.908$ Å and $b = 0.409$ Å derived in this work for the Sb^{5+}/O^{2-} ion pair from the crystal structure of Sb_2O_5 is illustrated in a series of examples.

2. Experimental procedures and results

The chemical synthesis of the title compound has been carried out in an open quartz container. All reactants used in the chemical synthesis were of a purity of 99.99 wt.% or better.

Dimercury diantimony (V) oxide $Hg_2Sb_2O_7$ has been synthesized by heating the stoichiometric mixture of the binary oxides HgO and Sb_2O_5 (molar 2:1 ratio) at 480 ± 5 °C in the oxygen atmosphere for 30 h. After the chemical reaction, the sample was slowly cooled to the temperature of 250 ± 5 °C and then annealed at this temperature for 14 days in the oxygen atmosphere. The stoichiometric composition of the obtained sample was confirmed by the standard analytical techniques (found: 52.94 wt.% Hg, 32.04 wt.% Sb, 14.64 wt.% O; calculated: 53.02 wt.% Hg, 32.18 wt.% Sb, 14.80 wt.% O).

The experimental density of the compound $Hg_2Sb_2O_7$ was determined by pycnometry measurements, using toluene as the working liquid.

The main difference between the synthesis carried out by Sleight [5] to obtain $Hg_2Sb_2O_7$ and the synthesis reported here is the use of Sb_2O_3 and Sb_2O_5, respectively, as a starting component.

Polycrystalline $Hg_2Sb_2O_7$ was reground to a fine powder in an agate mortar and then investigated using X-ray powder diffraction technique (XRD). X-ray powder diffraction data for $Hg_2Sb_2O_7$ were collected with a conventional Bragg–Brentano diffractometer DRON-3M in the step scan mode (Cu Kα radiation [10], $10 \le 2\theta \le 120°$, step size 0.05°, counting time 10 s per step, room temperature).

The Rietveld refinement [6] procedures have been performed using the program DBWS-9807a, an upgraded version of the classical program of Wiles and Young [11,12]. The Pearson VII [13] 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 the refinable fifth-order polynomial. Peaks below 35° (2θ) were

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Table 1
Experimental details and crystallographic data for $Hg_2Sb_2O_7$

Crystal system; space group	Cubic; $Fd\bar{3}m$ (No. 227)
Lattice parameter	$a = 10.3525(5)$ Å
Cell volume	$V = 1109.5(1)$ Å^3
Chemical formula weight	FW = 756.70
Formula units per cell	$Z = 8$
Calculated density	$D_c = 9.060(1)$ g/cm^3
Measured density	$D_m = 9.02(4)$ g/cm^3
Temperature of data collection	$T = 293(2)$ K
Radiation type; wavelength	Cu Kα; $\lambda = 1.5419$ Å
Powder diffractometer; geometry	DRON-3M; Bragg–Brentano
2θ scan range; step	10–$120°$; $0.05°$
Scan speed	10 s/step
Refinement program	DBWS-9807a
Peak shape function	Pearson VII
Peak asymmetry function	Riello–Canton–Fagherazzi
Background model	5th order polynomial
Number of atom sites	4
Number of free structural parameters	5
Total number of free parameters	18
Profile R-factors	$R_p = 6.94\%$; $R_{wp} = 8.35\%$
Bragg R-factor	$R_B = 3.25\%$
Goodness of fit	$S = 2.63$

Table 2
Atomic coordinates and isotropic displacement parameters for the crystal structure of $Hg_2Sb_2O_7$

Atom	Position	x/a	y/b	z/c	B_{iso} (Å^2)
Hg	16d	1/2	1/2	1/2	0.4(1)
Sb	16c	0	0	0	0.5(1)
O1	48f	0.323(2)	1/8	1/8	2.2(8)
O2	8b	3/8	3/8	3/8	2.2(8)

corrected for the asymmetry effects by using the Riello–Canton–Fagherazzi model [14]. The atomic scattering factor for O^{2-} used in the Rietveld refinement was taken from the paper of Hovestreydt [15]; the atomic scattering factors for Hg^{2+} and Sb^{5+} are internally tabulated in the program DBWS-9807a.

Attempts to refine atomic displacement ("thermal") parameters independently for both crystallographically non-equivalent O atoms were unsuccessful, and these parameters were constrained to be equal.

Application of the corrections for preferred orientation and surface roughness did not improve the structural model of $Hg_2Sb_2O_7$, and these corrections were not used in the final Rietveld refinement.

The refinement converged with the profile residuals $R_p = 6.94\%$ and $R_{wp} = 8.35\%$, and with the intensity residual $R_B = 3.25\%$. It should be noted that the low values of the profile residuals indicate the high background level rather than the real profile agreement [16], but the low R_B value (which is not affected by the background level) show the reasonable agreement between the experimental and theoretical structural models.

The experimental details and crystallographic data for the compound $Hg_2Sb_2O_7$ are collected in Table 1. Positional and isotropic displacement ("thermal") parameters of the crystal structure of $Hg_2Sb_2O_7$ are given in Table 2, and selected interatomic distances are given in Table 3. Fig. 1 illustrates the final Rietveld plot for the title compound.

Table 3
Selected interatomic distances for the crystal structure of $Hg_2Sb_2O_7$

Sb–O1 ($\times 6$)	1.980(8) Å
Hg–O1 ($\times 6$)	2.590(15) Å
Hg–O2 ($\times 2$)	2.2414(1) Å

As can be seen from Table 2, the precision of the positional and "thermal" parameters for the oxygen atoms is quite poor because of the relatively weak scattering of X-rays by O atoms in presence of the "heavy" atoms Hg and Sb. For this reason, the refined crystal structure of the title compound has been critically analyzed using the bond-valence model [9] (see below).

The crystal structure of $Hg_2Sb_2O_7$ is formed by two interpenetrating frameworks, $\{SbO_3\}$ and $\{Hg_2O\}$ (see Fig. 2). The $[SbO_6]$ coordination octahedra are connected by apices with six neighboring octahedra of the same kind. The O atoms that do not belong to the coordination environment of the Sb atoms (i.e. O2 atoms in Table 2) are tetrahedrally coordinated by the Hg atoms; and each $[OHg_4]$ tetrahedron shares its apices with four neighboring tetrahedra of the same kind.

The Hg atoms in the structure of $Hg_2Sb_2O_7$ are coordinated by eight oxygen atoms, forming two shorter (Hg–O2) and six longer (Hg–O1) bonds. Such coordination of the Hg atoms is typical for other mercury compounds of the pyrochlore structure type ($Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$ [5]).

Further information about the pyrochlore structure type can be found in the articles of Aleshin and Roy [17], Sleight [5], in the review of Subramanian et al. [4], or in any modern textbook on inorganic crystal chemistry.

3. Bond-valence analysis of the crystal structure of $Hg_2Sb_2O_7$

The bond valence model (BVM) has recently found wide use in mineralogy and structural inorganic chemistry as a valuable tool for detecting errors in crystal structure determination and for predicting interatomic distances in the crystal structures of known chemical composition and presupposed topology [7–9].

Bond valence (BV) s is defined as the classical valence shared with each bond. According to the bond-valence sum rule, the oxidation state V_i can be calculated from the sum of the individual bond valences s_{ij}:

$$V_i = \sum_j s_{ij}$$

where i denotes an atom bonded to j. Atom i is usually chosen as an electropositive atom (cation or Lewis acid) and atom j as an electronegative atom (anion or Lewis base).

Individual bond valences s_{ij} (in "valence units", v.u.) can be calculated from the observed bond lengths r_{ij} using the Brown–Altermatt formula:

$$s_{ij} = \exp\left[\frac{r_0 - r_{ij}}{b}\right]$$

where r_0 and b are the empirically determined parameters [18].

The b parameter is commonly taken to be the "universal constant" equal to 0.37 Å, and the r_0 parameters have been directly calculated [18,19] or extrapolated [19] for a large number of ion (atom) pairs, assuming $b = 0.37$ Å.

In order to check the crystal structure of $Hg_2Sb_2O_7$ for possible errors, this structure has been analyzed using the BVM.

The BV analysis of $Hg_2Sb_2O_7$ involved (i) critical analysis of the reliability of the BV parameters reported for the Hg^{2+}/O^{2-} and Sb^{5+}/O^{2-} ion pairs; (ii) determining the new BV parameters for the Sb^{5+}/O^{2-} ion pair; (iii) calculation of the bond-valence sums (BVSs) for every crystallographically different atom in the crystal structure of the title compound, and calculation of the global instability index (GII) [7,20] for this structure.

The BV parameters reported for a given ion pair were regarded as reliable if they closely approximate the *real* "bond
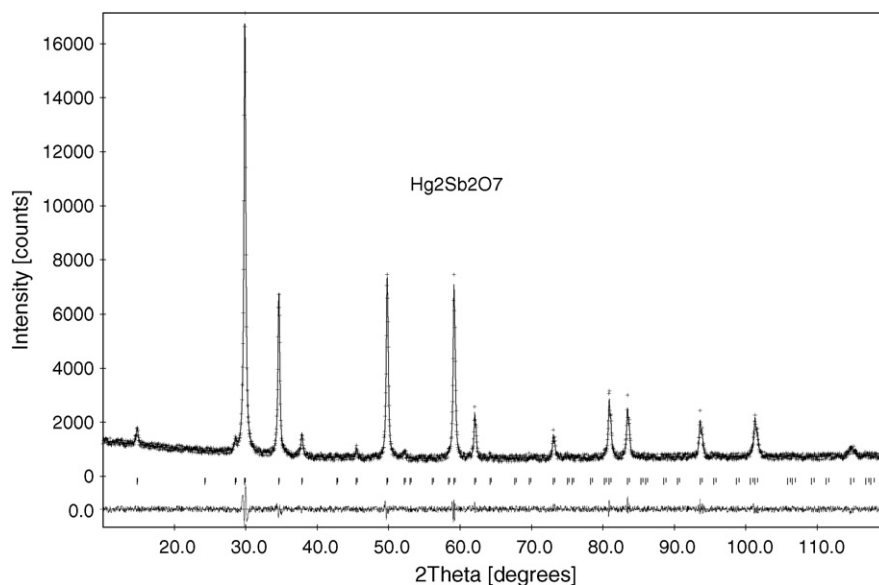
Fig. 1. Experimental (crosses), theoretical (solid line), and difference (solid line at the bottom) powder XRD patterns for $Hg_2Sb_2O_7$; reflection positions are marked by vertical bars.

length–bond valence" curve within the range of interest, i.e. if they are able to reproduce the typical interatomic distances in different coordination polyhedra formed by these ions.

In this respect, the BV parameters reported by Brown and Altermatt [18] for the Hg^{2+}/O^{2-} ion pair ($r_0 = 1.972$ Å and $b = 0.37$ Å) have been found to be fairly reliable. Thus, the interatomic distances calculated from these BV parameters for the $[HgO_8]$ and $[OHg_4]$ coordination polyhedra (2.49 Å and 2.23 Å,

respectively) reproduce the observed Hg–O interatomic distances ($[HgO_8]$: 2.50 Å in $K_2Hg(BrO_3)_2(NO_3)_2$ [21], 2.49 Å in $HgAg_6O_8(NO_3)$ [22]; $[OHg_4]$: 2.24 Å in $Hg_2Ni_2F_6O$ and $Hg_2Zn_2F_6O$ [23]) reasonably well.

However, the reliability of the BV parameters reported by Brown and Altermatt for the Sb^{5+}/O^{2-} ion pair [18] has been found to be doubtful. Thus, the bond length calculated for the ideal $[SbO_6]$ polyhedron (with $s_{ij} = 5/6$ v.u. for every Sb–O

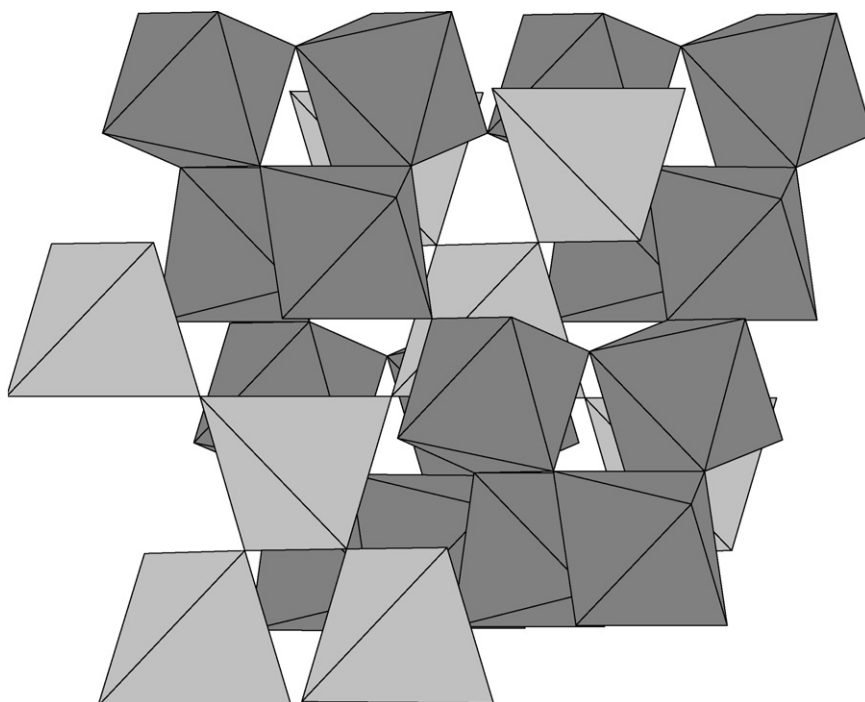Fig. 2. Fragment of the crystal structure of $Hg_2Sb_2O_7$: two interpenetrating frameworks formed by the $[SbO_6]$ coordination octahedra (dark gray) and by the $[OHg_4]$ tetrahedra (light gray).

Table 4
Reliability of the BV parameters obtained for the Sb^{5+}/O^{2-} ion pair by different procedures

Compound	Bond-valence sum (v.u.) for Sb^{5+}	
	Brown and Altermatt [18]	This work
KSb_2PO_8 [29]	5.627 (+13%)	5.207 (+4%)
	5.499 (+10%)	5.100 (+2%)
	5.441 (+9%)	5.052 (+1%)
	5.476 (+10%)	5.078 (+2%)
	Mean: 5.511 (+10%)	Mean: 5.109 (+2%)
$Sr_2Sb_2O_7$ [30]	5.385 (+8%)	5.007 (+0%)
	5.342 (+7%)	4.967 (−1%)
	Mean: 5.364 (+7%)	Mean: 4.987 (–0%)
$Li_3Zn_2(SbO_6)$ [31]	5.125 (+3%)	4.788 (−4%)
$Na(SbO)(SiO_4)$ [32]	5.753 (+15%)	5.314 (+6%)
	5.644 (+13%)	5.224 (+4%)
	Mean: 5.699 (+14%)	Mean: 5.269 (+5%)
$CuSb_2O_6$ [33]	5.302 (+6%)	4.936 (−1%)
$PbSb_2O_6$ [34]	5.270 (+5%)	4.910 (−2%)
$MnSb_2O_6$ [35][a]	5.242 (+5%) [×3]	4.885 (−2%) [×3]
	5.435 (+9%)	5.049 (+1%)
	5.586 (+12%)	5.175 (+4%)
	5.408 (+8%)	5.026 (+1%)
	Mean: 5.359 (+7%)[a]	Mean: 4.984 (–0%)[a]
Li_3SbO_4 [36]	5.273 (+5%)	4.909 (−2%)
Average BVS value	5.363 (+7%) [$\sigma = 0.163$]	4.987 (–0%) [$\sigma = 0.136$]

[a] For this compound, positions of the crystallographically non-equivalent Sb^{5+} ions have different multiplicities, and the mean BVS values were calculated taking into account this fact.

bond) from the BV parameters $r_0 = 1.942$ Å and $b = 0.37$ Å [18] is 2.01 Å, i.e. even slightly longer than the sum of the effective ionic radii [24] of the six-coordinated Sb^{5+} (0.60 Å) and six-coordinated O^{2-} (1.40 Å), 2.00 Å.

Since the coordination number (CN) of Sb^{5+} in oxides is *always* 6, and since the *average* effective ionic radius of O^{2-} is 1.38 Å [24], the expected and plausible value of the mean Sb–O bond distance can be estimated as ∼1.98 Å (i.e. considerably less than 2.01 Å, as calculated from the reported "classical" BV parameters [18]).

As a result of the above disagreement, the bond-valence sums (BVSs) calculated for the usual $[Sb^{5+}O_6]$ coordination polyhedra from the "classical" BV parameters [18] show significant "overbonding" (see Table 4).

Bearing in mind the implausibility of the "classical" values of the BV parameters reported by Brown and Altermatt for the Sb^{5+}/O^{2-} ion pair [18], and taking into account the deficiencies of the traditional procedure of direct determining the BV parameters (as recently pointed out by one of the authors of the present work [25]), we decided to derive the improved values of the BV parameters for the Sb^{5+}/O^{2-} ion pair.

In accordance with the recent paper of Sidey [25], the particular problem of determining the reliable and physically meaningful BV parameters for the Sb^{5+}/O^{2-} ion pair has been solved using only two basic assumptions: (i) the term "bond valence" (or "bond order") is strictly considered as the exact fraction (or number) of the Lewis electron pair(s) contributing

to the bond; and (ii) for Sb_2O_5 the bond-valence sum rule [7–9] is fulfilled *exactly* (i.e. BVS = 5 v.u. for Sb^{5+}).

Indeed, in the crystal structure of Sb_2O_5 [26,27] all the valence electrons are shared exclusively between the Sb^{5+} and O^{2-} ions and are not influenced by the additional ("third-party") ions. Since Sb_2O_5 is stoichiometric, it can be assumed that the *exact* number of the Lewis electron pairs used by the Sb^{5+} ion for bonding in this structure (in other words, BVS) is 5.

In the crystal structure of Sb_2O_5, two of three crystallographically non-equivalent oxygen ions are clearly two-coordinated by the ions Sb^{5+} [26,27], and for these oxygen ions the lengths of the O–Sb bonds are equal within the experimental error. Bearing in mind the fact that the physical meaning of the r_0 parameter is the length of the bond of unit valence for a given ion pair, the mean value of the O–Sb bond lengths observed for the above two-coordinated oxygen ions, 1.908 Å, has been taken as the value of the r_0 parameter for the Sb^{5+}/O^{2-} ion pair. Taking $r_0 = 1.908$ Å, the b parameter has been adjusted to give BVS = 5 for the Sb^{5+} ions in the crystal structure of Sb_2O_5; and the value of the b parameter determined in this way for the Sb^{5+}/O^{2-} ion pair is 0.409 Å.

In order to illustrate the reliability of the new BV parameters for the Sb^{5+}/O^{2-} ion pair, the most accurate crystal structures (with $R \leq 0.02$) containing the $[SbO_6]$ coordination polyhedra have been selected from the Inorganic Crystal Structure Database (2005) [28]. The crystal structures investigated at non-ambient conditions, and the structures with disorder and/or with partial occupancy were not considered. For every independent coordination sphere $[SbO_6]$ of the selected crystal structures, the BVS values were calculated using the new and "classical" [18] BV parameters obtained for the Sb^{5+}/O^{2-} ion pair (see Table 4). One can see that the new BV parameters derived in this work show much higher performance: so, the average BVS value calculated using these parameters (4.987 v.u.) is very close to the ideal value of 5 v.u., while the average BVS value calculated using the "classical" [18] BV parameters (5.363 v.u.) is considerably larger.

Being based on the physically measured r_0 value, the BV parameters obtained in this work for the Sb^{5+}/O^{2-} ion pair can be recommended for both routine BV analyses and theoretical BVM studies.

The results of the BV analysis of the title compound are given in Table 5. At the first step, only the "classical" BV parameters

Table 5
The bond-valence analysis of the crystal structures of $Hg_2Sb_2O_7$

Atom	Coordination shell	Bond-valence sum (v.u.)[a]	
		(i)	(ii)
Hg	$[HgO1_6O2_2]$	2.094 (+5%)	2.094 (+5%)
Sb	$[SbO1_6]$	5.412 (+8%)	5.034 (+1%)
O1	$[O1Sb_2Hg_2]$	2.180 (+9%)	2.054 (+3%)
O2	$[O2Hg_4]$	1.932 (−3%)	1.932 (−3%)
		GII = 0.23 v.u.	GII = 0.07 v.u.

[a] The BVS values were calculated (i) using the "classical" BV parameters [18] for both ion pairs (Hg^{2+}/O^{2-} and Sb^{5+}/O^{2-}) and (ii) using the "classical" and new BV parameters for the ion pairs Hg^{2+}/O^{2-} and Sb^{5+}/O^{2-}, respectively.

were used to calculate the BVS values for all atoms of the structure; at the second step, the "classical" and new BV parameters were used for the ion pairs Hg^{2+}/O^{2-} and Sb^{5+}/O^{2-}, respectively. In the first case, the high value of GII (0.23 v.u.) indicates high instability of the crystal structure of $Hg_2Sb_2O_7$; but in the latter case, GII is equal to 0.07 v.u. and indicates the reasonably high stability of the crystal structure of the title compound [7,20]. Our thermographic and thermogravimetric experiments confirmed the high stability of the crystal structure of $Hg_2Sb_2O_7$; and, therefore, one can conclude that the BV parameters calculated in this work for the Sb^{5+}/O^{2-} ion pair give the reasonable approximation of the *real* "bond length–bond valence" curve for these ions.

4. Concluding remarks

It must be clearly noted that the BVM should be considered only as a *supplemental* tool for the crystal structure determinations, and the results of the bond-valence analyses should always be taken with the great care. However, the results of the bond-valence analysis carried out for the title compound are in good agreement with the results of other approaches. Thus, the crystal structure of $Hg_2Sb_2O_7$ reported here is characterized by the reasonably low value of the Bragg R-factor (Table 1); the Sb–O interatomic distances in the structure of the title compound (Table 3) are in excellent agreement with the sum of the effective ionic radii of the six-coordinated Sb^{5+} and four-coordinated O^{2-}, 1.98 Å [24]; the quite low GII value (Table 5) is in good agreement with the thermal stability of $Hg_2Sb_2O_7$. Taking all the aforementioned facts into account, one may state that the refined crystal structure reported here for the title compound has been determined without serious errors.

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