Journal of Solid State Chemistry **151,** 245–252 (2000)
doi:10.1006/jssc.2000.8647, available online at http://www.idealibrary.com on IDEAL®

Bond Valence Analysis of $BaRuO_3$

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Received November 23, 1999; in revised form February 1, 2000; accepted February 3, 2000

The crystal structure of $BaRuO_3$ has been derived by the bond valence method and sphere packing geometry using only the information obtained from the indexing of a powder pattern of the compound. The structural parameters derived in this way give calculated bond distances that agree with those measured experimentally to within 0.02 Å. Since the Ba–O and Ru–O distances that completely satisfy the valence requirements of the atoms are incommensurate under the constraints imposed by the geometry of the structure, the Ba–O and Ru–O bonds of the final model are, on the average, compressed and stretched, respectively. As a result of this analysis it is found that the valences of the two crystallographically independent Ru atoms in the asymmetric unit are very nearly equal. The structure of $BaRuO_3$ is formed by units of three face-sharing RuO_6 octahedra, connected to one another by corner sharing. The oxygen atom of the shared faces in each unit are pulled together, thus providing a "shielding effect" that reduces the Ru–Ru interactions. © 2000 Academic Press

Key Words: **barium ruthenate; bond valence method; sphere packing geometry.**

INTRODUCTION

The bond valence method is based on the concept that to each bond of length d_{ij} between two atoms i and j is associated a bond valence v_{ij} which obeys the equations (1)

$$\sum_{1\,j}^{n(i)} v_{ij} = V(i), \qquad [1]$$

$$\sum_{\text{loop}} v_{ij} = 0, \qquad [2]$$

$$d_{ij} = R_{ij} - 0.37 \ln v_{ij}, \qquad [3]$$

where $n(i)$ is the number of atoms j in the coordination sphere of a central atom i of valence $V(i)$ and R_{ij} represents the length of a bond of valence $v_{ij} = 1.0$ *v.u.* The R_{ij} parameters depend on the nature and the valence of atoms i and j and their values have been tabulated for most atomic species (2, 3). Equations [1] and [3] have found application in the evaluation of a "*cost function*" used to assess the quality of initial structures, calculated by a genetic algorithm, in a program designed to predict inorganic crystal structures (4–6). Equations [1]–[3], however, can also be used to calculate the bond lengths of any atomic configuration whose bonding scheme is known or assumed. The distances calculated in this way satisfy exactly the valence requirements of the atoms and, in general, differ significantly from those determined experimentally. The discrepancies are sometimes due to the electronic behavior of particular cations which may cause distortions not accounted for by the bond valence model. In the majority of cases, however, these bond lengths are incommensurate under the constraints imposed by the crystal geometry and have to be compressed or stretched in order to fit them into a particular configuration. Since these changes introduce strains into the structure, the process of adapting the theoretical distances to the requirements of space group symmetry (sometimes called *relaxation* of the structure) must be carried out in such a way that the violations of Equations [1] and [2] are kept as small as possible. The bond valence method, therefore, can in principle be used to predict structures and/or to clarify important structural features such as oxidation states of the atoms and presence and extent of strains. Examples of its application include analysis of systems such as $YBa_2Cu_3O_x$ (7), Li_2NiO_{4+x} (1), and $TRuO_3$ (8) ($T = 0.875\text{Ba} + 0.125\text{Sr}$). In this last compound the bonding scheme of the atoms and the initial model of the structure were determined from sphere packing geometry, and the bond distances obtained after completing the relaxation process were found to agree with the experimental results to within 0.02 Å. In the case of $TRuO_3$, however, there is only one Ru atom in the asymmetric unit and consequently the valence of Ru is defined without ambiguity. This is no longer true in the case of $BaRuO_3$, whose structure is more complex and less constrained than that of $TRuO_3$. For this reason we decided to test if the bond valence method and the relaxation procedure used for $TRuO_3$ could also be

0022-4596/00 $35.00

used to predict the more complicated structure of the barium compound.

DERIVATION OF THE STRUCTURE

(1) Determination of the Sphere Packing Sequence

In our derivation of the $BaRuO_3$ structure by the bond valence method we will initially use only the information obtained from the indexing of the powder pattern, i.e., crystal system (hexagonal) and lattice parameters ($a = 5.75$, $c = 21.60$ Å), and we will ignore all other structural features determined in the experimental work (9). Since the ionic radii of Ba^{2+} and O^{2-} are similar ($Ba^{2+}(XII) = 1.61$ Å and $O^{2-}(VI) = 1.40$ Å (10)), we may expect that the structure has a configuration consistent with some packing sequence of spheres of equal radius r. This assumption is corroborated by the fact that the a-parameter calculated from the average of the ionic radii of Ba and O for the BaO_3 composition ($r = 1.45$ Å) is equal to $4r = 5.80$ Å, in reasonable agreement with the experimental value of 5.75 Å. In addition, the ionic radius of Ru ($Ru^{4+}(VI) = 0.62$ Å) is quite close to the radius of the octahedral void formed by the close packing of oxygen atoms ($(\sqrt{2} - 1) \times 1.40 = 0.58$ Å, thus making possible the presence of RuO_6 octahedra. The periodicity of the stacking sequence of the BaO_3 layers in the vertical direction is calculated from the experimental value of the c-parameter with the formula $n = c/(2r\sqrt{2/3}) = 9.1 \sim 9$. This means that $BaRuO_3$ has a 9-layer structure that may be conveniently represented by the scheme

$$\begin{array}{cccccccccccccccccc}
c & & f & & f & & c & & f & & f & & c & & f & & f & \\
0,0,0 & & \frac{2}{3},\frac{1}{3},\frac{1}{9} & & 0,0,\frac{2}{9} & & \frac{2}{3},\frac{1}{3},\frac{1}{3} & & \frac{1}{3},\frac{2}{3},\frac{4}{9} & & \frac{2}{3},\frac{1}{3},\frac{5}{9} & & \frac{1}{3},\frac{2}{3},\frac{2}{3} & & 0,0,\frac{7}{9} & & \frac{1}{3},\frac{2}{3},\frac{8}{9} & \\
X' & & Y & & X & & Y' & & Z & & Y & & Z' & & X & & Z & \\
 & B & & B' & & B & & B & & B' & & B & & B & & B' & & B \\
 & \frac{1}{3},\frac{2}{3},\frac{1}{18} & & \frac{1}{3},\frac{2}{3},\frac{3}{18} & & \frac{1}{3},\frac{2}{3},\frac{5}{18} & & 0,0,\frac{7}{18} & & 0,0,\frac{9}{18} & & 0,0,\frac{11}{18} & & \frac{2}{3},\frac{1}{3},\frac{13}{18} & & \frac{2}{3},\frac{1}{3},\frac{15}{18} & & \frac{2}{3},\frac{1}{3},\frac{17}{18}.
\end{array}$$

In this expression the symbols c and f indicate the layers on which the BO_6 octahedra share corners and faces, respectively, the symbols X, Y, Z (which replace the more conventional symbols A, B, C to avoid confusion) show in which way the BaO_3 layers are translationally related to one another, the B symbols indicate the locations of the Ru atoms, and the triplets of numbers are the coordinates of the Ba and Ru atoms referred to the hexagonal reference system formed by the sphere packing geometry. The coordinates of the oxygen atoms are easily derived from those of the zero layer ($\frac{1}{2}$, 0, 0; 0, $\frac{1}{2}$, 0; $\frac{1}{2}$, $\frac{1}{2}$, 0) by translating them with the same vector that translates the Ba atoms from one layer to the other. The coordinates of the Ru atoms clearly reveal that in this structure there are units formed by three face-sharing RuO_6 octahedra stacked on top of one another and connected to the other units by corner sharing (Fig. 1). The Ru atoms located at B' occupy the central octahedron of each unit, while those located at B are at the centers of the two end octahedra, which share corners with the octahedra of the other units. Similarly, the Ba atoms are grouped into two equivalent sets, Ba′ and Ba, located on c and f type layers, respectively. Inspection of the atomic coordinates discloses that the symmetry of this configuration is $R\bar{3}m$. The structure derived from sphere packing geometry (called the *aristotype* structure in the following sections) is reported in Table 1 and the equations of the relevant bond distances are given for convenience in Table 2.

(2) Connectivity Matrix and Evaluation of Bond Valences

The structural information obtained so far allows us to establish the coordination of all atoms, which are usually expressed with a matrix, called the *connectivity matrix* of the system (11). From the matrix the bond valence sum and loop equations can be easily derived and then solved for the bond valences (Table 3). Since there are two crystallographically independent Ru atoms in this structure, charge transfer from one to the other is possible, and consequently the valences $V(\mathrm{Ru1})$ and $V(\mathrm{Ru2})$ are not defined, except for the obvious relation $V(\mathrm{Ru1}) + 2V(\mathrm{Ru2}) = 12$ *v.u.* For this reason $V(\mathrm{Ru1})$ and $V(\mathrm{Ru2})$ are not numerically specified in the bond valence sum equations and in the bond valence solutions of Table 3.

When all atoms are located in their aristotype positions ($x = 1/6$, $z_1 = 1/9$, $z_2 = 2/9$, and $z_3 = 7/18$), all the Ba–O and all the Ru–O distances are equal. This configuration therefore requires the Ba and Ru valences to be equally divided among the bonds that these atoms form with the oxygen atoms in their respective coordination spheres. Since the valence requirements of O(1) and O(2) must also be satisfied, the equipartitioning of the cationic valences is only possible if $V(\mathrm{Ru1}) = V(\mathrm{Ru2}) = 4.0$ *v.u.* With these values, we may calculate the bond distances Ba–O and Ru–O using the bond valence parameters $R(Ba^{2+}\text{–}O) = 2.285$ Å and $R(Ru^{4+}\text{–}O) = 1.834$ Å [2, 3]. The results (Ba–O = 2.948 Å and Ru–O = 1.984 Å) should satisfy the relation $[\mathrm{Ba–O}] = [\mathrm{Ru–O}]\sqrt{2}$ required by the geometry of the aristotype structure. This, however, is not the case, since

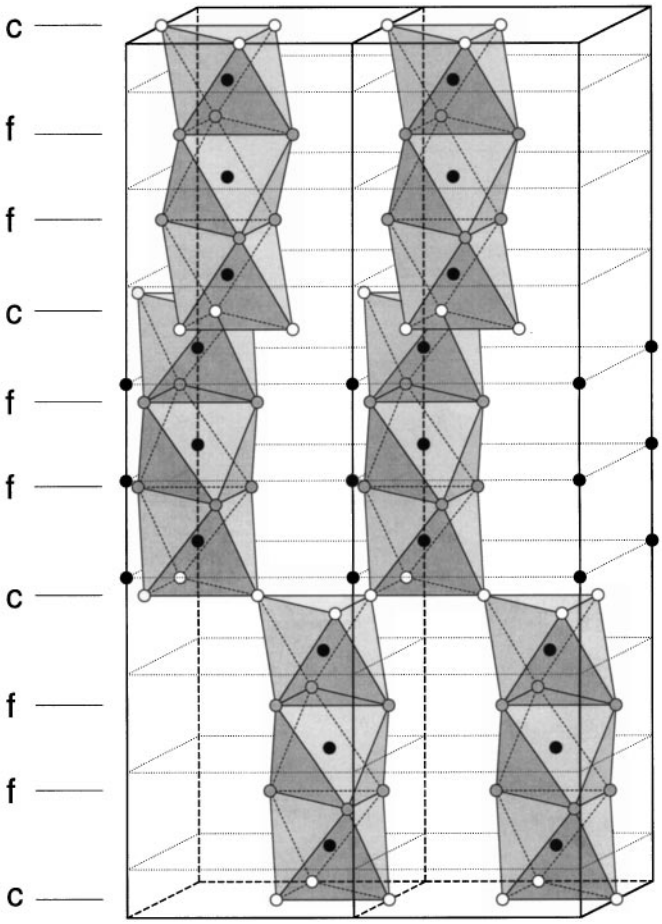

FIG. 1. The 9-layer structure of $BaRuO_3$. Full and open circles represent the Ru and O atoms, respectively. To avoid confusion, the Ba atoms have been omitted. The c and f symbols mark the layers on which the RuO_6 octahedra share corners and faces, respectively.

$1.984 \times \sqrt{2} = 2.806$ Å, a value significantly lower than the Ba–O distances of 2.948 Å. This result shows that the theoretical bond distances are incommensurate under the constraints imposed by the symmetry of the sphere packing model, and that bond distances that completely satisfy Eqs. [1] and [2] cannot exist if these constraints are to be respected. This means that the calculated distances have to be compressed or stretched in order to build the structure. These changes inevitably introduce strains in the system, and the relaxation of the calculated model has to be carried out with the idea of keeping them as small as possible.

TABLE 1
Ideal Sphere Packing Structure of $BaRuO_3$

Atom	Position	x	y	z	
Ba(1)	$3a\ \bar{3}m$	0	0	0	
Ba(2)	$6c\ 3m$	0	0	z_2	$z_2 = 2/9$
Ru(1)	$3b\ \bar{3}m$	0	0	$\frac{1}{2}$	
Ru(2)	$6c\ 3m$	0	0	z_3	$z_3 = 7/18$
O(1)	$9e\ 2/m$	$\frac{1}{2}$	0	0	
O(2)	$18h\ m$	x	$2x$	z_1	$x = 1/6$, $z_1 = 1/9$

Note. Space group $R\bar{3}m$. For $r = 1.45$, $a = 4r = 5.80$, $c = 6r\sqrt{6} = 21.31$ Å.

(3) Reliability Indices

The criteria to be followed in a relaxation procedure can be summarized by stating the two principles: (i) the violations of the valence sum rule (Eq. [1]) must be kept as small as possible; (ii) the bond valences for bonds from a central atom to others of the same chemical kind must be as nearly equal as possible (11, 12).

According to Brown (1), the root mean square

$$R = \left\{ \frac{\sum_i [(\sum_j v'_{ij}) - V(i)]^2}{m} \right\}^{1/2} \qquad [4]$$

is a measure of the extent to which Eq. [1] is violated over the whole structure. In Eq. [4], $i = 1, \ldots, m$, $j = 1, \ldots, n(i)$, m is the number of atoms in the asymmetric unit and the bond valence v'_{ij} are primed to indicate that they are associated with bonds that have been compressed or stretched as a consequence of the constraints imposed by symmetry. When $v'_{ij} = v_{ij}$ Eq. [1] is satisfied for all atoms, and $R = 0.0$ *v.u.* It has been found empirically that "well behaved" structures have $R \leq 0.1$ *v.u.* and that in cases in which $R \geq 0.2$ *v.u.* the internal strains may be large enough to cause instability of the structure at room temperature (1).

The violation of the second principle can be assessed in the following way. Consider a central atom i forming $n(i)$ bonds with atoms j of the same chemical kind. We then have $n(i)$ bond valences v_{ij} and $N = n(i)!/\{[n(i) - 2]!2!\}$ differences $\delta_{kj} = v_{ik} - v_{ij}$ $(k \neq j)$, $k = 1, \ldots, n(i)$. We may then calculate the function

$$\phi = \sum_{2j}^{n(i)} (\delta_{1j})^2 + \sum_{3j}^{n(i)} (\delta_{2j})^2 + \ldots + (\delta_{n(i)-1,n(i)})^2 \qquad [5]$$

and take the root mean square

$$r_v(i) = (\phi/N)^{1/2} \qquad [6]$$

as a measure of the violation of the bond valence equality rule. It is worth noting that the indices $r(i)$ may have values different from zero also when the bond valences v_{ij} have the theoretical values that satisfy Eqs. [1] and [2] exactly. In the case of $BaRuO_3$, for example, the v_{ij} calculated from the connectivity matrix will give $r_v(X) = 0$ only if the valences V(Ru1) and V(Ru2) are equal to 4.0 *v.u.* (X is Ba or Ru).

TABLE 2
Bond Distance Equations for the 9-Layer Structure of $BaRuO_3$

$d_1 \times 6$	Ba(1)	0	0	0	Ba(1)–O(1) $= a/2$
	O(1)	1/2	0	0	
$d_2 \times 6$	Ba(1)	0	0	0	Ba(1)–O(2) $= (3x^2a^2 + z_1^2c^2)^{1/2}$
	O(2)	x	$2x$	z_1	
$d_3 \times 3$	Ba(2)	0	0	z_2	Ba(2)–O(1) $= [a^2/12 + (1/3 - z_2)^2 c^2]^{1/2}$
	O(1)	1/6	1/3	1/3	
$d_4 \times 6$	Ba(2)	0	0	z_2	Ba(2)–O(2) $= [(3x^2 - x + 1/3)a^2 + (1/3 - z_1 - z_2)^2 c^2]^{1/2}$
	O(2)	$-x + 2/3$	$x + 1/3$	$-z_1 + 1/3$	
$d_5 \times 3$	Ba(2)	0	0	z_2	Ba(2)–O(2′) $= [3x^2a^2 + (z_1 - z_2)^2 c^2]^{1/2}$
	O(2′)	x	$2x$	z_1	
$d_6 \times 6$	Ru(1)	0	0	1/2	Ru(1)–O(2) $= [(3x^2 - 2x + 1/3)a^2 + (1/6 - z_1)^2 c^2]^{1/2}$
	O(2)	$-x + 1/3$	$x + 1/3 - 1$	$-z_1 + 2/3$	
$d_7 \times 3$	Ru(2)	0	0	z_3	Ru(2)–O(1) $= [a^2/12 + (1/3 - z_3)^2 c^2]^{1/2}$
	O(1)	1/6	1/3	1/3	
$d_8 \times 3$	Ru(2)	0	0	z_3	Ru(2)–O(2) $= [(3x^2 - 2x + 1/3)a^2 + (z_1 - z_3 + 1/3)^2 c^2]^{1/2}$
	O(2)	$x - 1/3$	$-x + 1/3$	$z_1 + 1/3$	
d_R	Ru(1)	0	0	1/2	Ru(1)–Ru(2) $= (1/2 - z_3)c$
	Ru(2)	0	0	z_3	
d_O	O(2)	$x - 1/3$	$2x + 1/3$	$z_1 + 1/3$	O(2)–O(2) $= (1 - 3x)a$
	O(2)	$x - 1/3$	$-x + 1/3$	$z_1 + 1/3$	

Since the indices $r_v(i)$ have been defined in this study for the first time, we do not know yet what their values should be for well behaved structures, and their use should therefore be limited to establishing the relative reliability of different models during the relaxation process. If the bond valences are replaced by the corresponding bond distances, new $r_d(i)$ indices may be calculated as indicated before, but with the quantities δ_{kj}, representing differences between bond distances rather than bond valences.

TABLE 3
Structural Information for the 9-Layer Structure of $BaRuO_3$

Atomic coordinations

{Ba(1)}$O(1)_6$ $O(2)_6$
{Ba(2)} $O(1)_3$ $O(2)_6$ $O(2')_3$
{Ru(1)} $O(2)_6$
{Ru(2)} $O(1)_3$ $O(2)_3$
{O(1)} $Ba(1)_2$ $Ba(2)_2$ $Ru(2)_3$
{O(2)} Ba(1) $Ba(2)_3$ Ru(1) Ru(2)

Connectivity matrix

$$\left\{\begin{array}{lll} & 3O(1) & 6O(2) \\ Ba(1) & 6v_{11} & 6v_{12} \\ 2Ba(2) & 6v_{21} & 18v_{22} \\ Ru(1) & & 6v_{32} \\ 2Ru(2) & 6v_{41} & 6v_{42} \end{array}\right\}$$

Bond valence sum and loop equations

$6v_{11} + 6v_{12} = V_{Ba(1)} = 2$
$3v_{21} + 9v_{22} = V_{Ba(2)} = 2$
$6v_{32} = V_{Ru(1)} = 12 - 2y$
$3v_{41} + 3v_{42} = V_{Ru(2)} = y$
$2v_{11} + 2v_{21} + 2v_{41} = V_{O(1)} = 2$
$v_{11} - v_{12} + v_{22} - v_{21} = 0$
$v_{21} - v_{22} + v_{42} - v_{41} = 0$

Bond valences

$v_{11} = (15 - 2y)/42$
$v_{12} = (-1 + 2y)/42$
$v_{21} = (19 - 3y)/42$
$v_{22} = (3 + y)/42$
$v_{32} = (84 - 14y)/42$
$v_{41} = (8 + 5y)/42$
$v_{42} = (-8 + 9y)/42$

In the case of compounds, such as $BaRuO_3$, in which there are only oxygen atoms in the coordination spheres of the cations, the bond valence (distance) equality rule may be extended by incorporating the maximum symmetry principle discussed by Brown (13) in relation to bond graph construction, and may be restated by saying "when the atoms in the coordination sphere of a central atom i are all of the same chemical kind, the coordination polyhedron of i will be as symmetric as possible." The symmetry violations in coordination polyhedra such as cuboctahedra and octahedra affect not only the values of the $r_d(i)$ indices, but also those of indices $r_o(i)$ calculated with Eqs. [5] and [6] taking as δ_{kj} the differences between distances separating neighboring oxygen atoms in the coordination sphere of the central atom. The values of $r_d(i)$ and $r_o(i)$ for regular cuboctahedra, octahedra, etc. are obviously equal to zero. It is worth noting that a polyhedron is distorted (with $r_o > 0$) even when the corresponding $r_d(i)$ is equal to zero, i.e., when the bond distances from the central atom to the surrounding oxygen atoms are all equal.

(4) Relaxation of the Structure

The a-parameter calculated from the theoretical Ba–O and Ru–O distances is $(2.948 \times 2) = 5.896$ Å and $(1.984 \times 2 \times \sqrt{2}) = 5.612$ Å, respectively. The average of these two values ($a = 5.754$ Å) is very close to the parameter measured experimentally ($a = 5.747$ Å). This result shows that the

TABLE 4
Relaxation of the 9-Layer Structure of $BaRuO_3$

		1	2	3	4	5	6
Lattice parameters (Å) and atomic positions							
	a	5.754	5.754	5.754	5.754	5.747	0.007
	c	21.142	21.142	21.626	21.626	21.602	0.024
	x	1/6	0.1769	0.1769	0.1769	0.1769	0.0000
	z_1	1/9	1/9	0.1087	0.1087	0.1082	0.0005
	z_2	2/9	2/9	2/9	0.2185	0.2175	0.0010
	z_3	7/18	7/18	0.3844	0.3844	0.3829	0.0015
Bond distances							
d_1	Ba(1)–O(1)	2.877	2.877	2.877	2.877	2.8733(1)	0.004
d_2	–O(2)	2.877	2.937	2.938	2.938	2.926(2)	0.012
d_3	Ba(2)–O(1)	2.877	0.877	2.922	2.988	3.002(2)	– 0.014
d_4	–O(2)	2.877	2.879	2.879	2.882	2.880(2)	0.002
d_5	–O(2′)	2.877	2.937	3.022	2.957	2.945(3)	0.012
d_6	Ru(1)–O(1)	2.034	1.952	2.001	2.001	2.005(2)	– 0.004
d_7	Ru(2)–O(1)	2.034	2.034	1.995	1.995	1.974(1)	0.021
d_8	–O(2)	2.034	1.952	1.995	1.995	2.007(2)	– 0.012
d_R	Ru–Ru	2.349	2.349	2.500	2.500	2.530(2)	– 0.030
d_O	O(2)–O(2)	2.877	2.700	2.700	2.700	2.697(3)	0.003
Bond valences							
v_{11}	Ba(1)–O(1) × 6	0.2019	0.2019	0.2019	0.2019	0.2039	
v_{12}	–O(2) × 6	0.2019	0.1717	0.1710	0.1710	0.1767	
v_{21}	Ba(2)–O(1) × 3	0.2019	0.2019	0.1790	0.1497	0.1439	
v_{22}	–O(2) × 6	0.2019	0.2009	0.2007	0.1993	0.2004	
v'_{22}	–O(2′) × 3	0.2019	0.1717	0.1364	0.1624	0.1678	
v_{32}	Ru(1)–O(2) × 6	0.5821	0.7267	0.6376	0.6376	0.6070	
v_{41}	Ru(2)–O(1) × 3	0.5821	0.5821	0.6472	0.6472	0.6980	
v_{42}	–O(1) × 3	0.5821	0.7267	0.6472	0.6472	0.6390	
	R	0.38	0.24	0.15	0.14	0.15	

Note. 1: Model calculated with the average value of the parameter a and with the positional parameters obtained from sphere packing geometry. 2: Model obtained after optimizing the positional parameter x. 3: Model calculated after determining the optimal z_1 and z_3 parameters. 4: Final model. 5: Experimental structure. 6: Differences between final model minus experimental results.

length of the a-axis of the real structure reflects a compromise between the valence requirements of Ba and Ru and that our initial assumption about the equal valence for the two Ru atoms must be very nearly correct. The structural model calculated with the average value of a ($c = a \times 3 \times \sqrt{3/2} = 21.142$ Å) and with all atoms kept in their aristotype positions is shown in column 1 of Table 4.

This structure is clearly unacceptable because: (i) the R index (0.38 *v.u.*) is far larger than the limit 0.2 *v.u.* discussed previously; (ii) the valences of the Ru atoms ($0.5821 \times 6 = 3.49$ *v.u.*) are far lower, and those of the Ba atoms ($0.2019 \times 12 = 2.42$ *v.u.*) far higher than the expected values. From inspection of the bond valence equations (Table 2) and from the geometry of the structure illustrated in Fig. 2, it is clear that the most convenient way to decrease the Ru–O distances, and thus increase the valences V(Ru1) and V(Ru2), is to increase the parameter x of O(2) from its aristotype value of 1/6. Such an increase has also the beneficial effect of increasing some Ba–O distances, thus decreasing V(Bal) and V(Ba2). However, an increase in x also causes a decrease in the nonbonded O(2)–O(2) distance, as shown by the equation of d_o in Table 2. If we assume that the O–O separation cannot be shorter than 2.7 Å, we may calculate the largest allowed value of x with the formula $x = (a - 2.7)/(3a)$, where a is the average parameter determined previously. The model with this new value of x is shown in column 2 of Table 4. The result of this change on the atomic configuration, illustrated in Fig. 2, is to pull together the O(2) atoms, interposing them between the Ru atoms located immediately above and below ("shielding effect"). Although this structure is a significant improvement compared with the previous one, it is still not acceptable because the R index is too high. Furthermore, the Ru–Ru distances d_R are too short ($d_R = 2.349$ Å) and the $Ru(2)O_6$ octahedron considerably distorted. If we assume for d_R the value 2.5 Å, equal to the Ru–Ru distance found for the 4-layer structure of $(Ba_{0.875}Sr_{0.125})$ RuO_3 (5), we may connect the c and z_3 parameters with the relation

$$c = 5.0/(1 - 2z_3). \qquad [7]$$

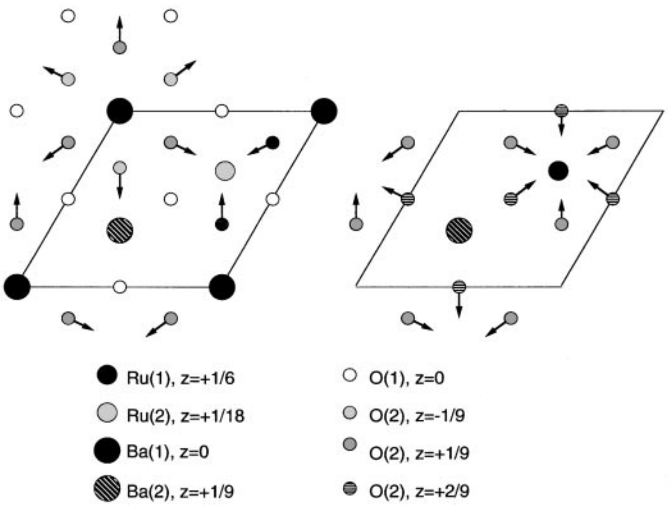

FIG. 2. Projections on the 00·1 plane of two layers of the $BaRuO_3$ structure. The heights of the atoms above and below the horizontal plane are indicated for each atom. The polyhedron around Ba(1) at $z = 0$ is formed by three O(2) atoms at $z \simeq -1/9$, three O(2) atoms at $z \approx 1/9$, and six O(1) atoms at $z = 0$ (left diagram). The polyhedron around Ba(2) at $z \simeq 1/9$ is formed by three O(1) at $z = 0$ (left diagram), three O(2) at $z \simeq 2/9$ (right diagram), and six O(2) at $z \simeq 1/9$. Atoms O(2) at $z \simeq 1/9$ and $z \simeq 2/9$ are in the coordination sphere of Ru(1) at $z = 1/6$ (right diagram), and atoms O(1) at $z = 0$ and O(2) at $z \simeq 1/9$ in the coordination sphere of Ru(2) at $z \simeq 1/18$. The arrows indicate the direction of the shifts of the O(2) atoms from their aristotype positions. These displacements have the effect of shortening the Ru–O distances and thus of providing a "shielding" to Ru–Ru interactions.

If, in addition, we satisfy the bond valence equality rule around Ru(2) by requiring Ru(2)–O(1) and Ru(2)–O(2) to be equal, we obtain from the bond distance equations of d_7 and d_8 (Table 2) the expression

$$z_1 = \{c(z_3 - 1/3) + [c^2(z_3 - 1/3)^2 + k]^{1/2}\}/c, \qquad [8]$$

where $k = a^2(2x - 3x^2 - 0.25) = 0.3284$. With the parameters z_1, z_3, and c connected in this way, the lowest R index (calculated by changing z_3 in ± 0.001 steps) is obtained for $z_3 = 0.1087$ and $c = 21.626$ Å. The model calculated with these parameters is shown in column 3 of Table 4.

A comparison of the results of columns 1 and 3 (Table 4) shows that the shifts of the x, z_1, and c parameters from their aristotype values have had the effect of increasing the Ba(2)–O(2′) distances significantly more than Ba(2)–O(1) ($\delta = 0.1$ Å), with only a marginal change of Ba(2)–O(2). The distortion introduced in the Ba(2)O$_{12}$ coordination polyhedron by these changes can be reduced by decreasing the value of z_2 from its value of 2/9. By varying this parameter in -0.0005 steps, a minimum of $R = 0.14$ *v.u.* is found for $z_2 = 0.2185$, with a corresponding decrease in r_v (Ba2) from 0.04 to 0.03 *v.u.* These changes are small, but they are probably significant since they are associated with a configuration of the Ba(2) coordination sphere that is more regular than the initial one.

No improvement of the reliability indices was obtained in attempts to change the valences of the two Ru atoms, and consequently the model shown in column 4 of Table 4 must be considered as final.

EXPERIMENTAL STRUCTURE

The sample of BaRuO$_3$ used to collect the neutron powder diffraction data was a mixture of the 9-layer majority phase (more than 90% of the sample) with small quantities of the 4-layer modification. The 9-layer structure was refined with excellent agreement between observed and calculated intensities, and the results of these calculations are shown in column 5 of Table 4.

The valences of the two crystallographically independent Ru atoms were evaluated from the experimental Ru–O distances by the method described by Brown (7). With this procedure, the bond valences v_{ij} are calculated around each Ru atom from the observed distances using the valence parameter $R(\mathrm{Ru}^{4+}\text{–O}) = 1.834$ Å (3). The bond valence sum $\sum_j v_{ij} = V_4$ is then used to determine if the oxidation state of the atom is greater or smaller than 4.0 *v.u.* If $V_4 > 4$, the proportion P_5 of Ru^{5+} is given by the formula

$$P_5 = (V_4 - 4)/(V_4 + 1 - V_5) \qquad [9]$$

and if $V_4 < 4$, the proportion P_4 of Ru^{4+} is given by

$$P_4 = (V_3 - 3)/(V_3 + 1 - V_4) \qquad [10]$$

the rest obviously being Ru^{3+}. In these formulas, V_3 and V_5 are the bond valence sums obtained using the bond valence parameters $R(\mathrm{Ru}^{3+}\text{–O})$ and $R(\mathrm{Ru}^{5+}\text{–O})$, respectively. Since these parameters are not available in the literature, their values were determined *ad hoc* using "well behaved" structures in which (i) Ru is bonded only to oxygen atoms; (ii) there is only one Ru atom in the asymmetric unit and, preferably, all other metal atoms have uniquely defined valences. The parameters R_{ij} were then evaluated with the formula

$$R_{ij} = 0.37 \ln\{V(i)/[\textstyle\sum_j \exp(-d_{ij}/0.37)]\}, \qquad [11]$$

in which all symbols are the same as those defined in Eqs. [1]–[3]. The structures used in these calculations and the values of the R_{ij} parameters obtained from each structure are listed in Table 5.

The valences V(Ru1) and V(Ru2) calculated with this procedure were found to be 3.49 and 3.84 *v.u.*, respectively. The sum $(3.84 \times 2) + 3.49 = 11.17$ *v.u.* differs significantly from 12.0 *v.u.*, expected from stoichiometry, and this difference can be attributed to the presence of strains that affect the Ru–O distances used in the evaluation of P_4 and P_5. An average correction for this effect is given by $\{12 - [3.49 + (2 \times 3.84)]\}/3 = 0.28$ *v.u.* With this correction V(Ru1) and V(Ru2) become 3.77 and 4.12 *v.u.*, respectively, and these are the values used to calculate the experimental bond valences shown in column 5 of Table 4. This result shows that some charge transfer between the two Ru atoms probably occurs in the structure. Its effect on bond valence sums, however, is very small and was not detected in the relaxation procedure described in the previous section.

TABLE 5
Determination of the Valence Parameters R_{ij} for Ru^{5+}–O and Ru^{3+}–O Bonds

Compound	$R(\mathrm{Ru}^{5+}\text{–O})$	Ref.	Compound	$R(\mathrm{Ru}^{3+}\text{–O})$	Ref.
Sr$_2$YRuO$_6$*	1.888	(14)	Ru$_2$P$_6$O$_{18}$	1.765	(19)
Nd$_3$RuO$_7$	1.890	(15)	PrRuO$_3$	1.790	(20)
Sr$_2$ErRuO$_6$*	1.895	(16)	LaRuO$_3$*	1.770	(20)
Sr$_2$LuRuO$_6$*	1.893	(17)	Average	1.775	
NaSr$_3$RuO$_6$*	1.908	(18)			
Average	1.895				

Note. In compounds marked with an asterisk the valences of all atoms are uniquely defined.

DISCUSSION

A comparison of the theoretical and experimental structures shows that the agreement between lattice and structural parameters is quite good, and that the differences between bond distances are generally less than 0.02 Å (column 6 in Table 4). This result shows that the assumptions made (including the adopted nonbonded O–O and Ru–Ru distances) are valid, and is a clear proof that, at least in favorable cases (e.g., when sphere packing geometry can be used to obtain an initial model of the structure, and when Jahn–Teller or lone-pair cations are not present), the bond valence method may yield an accurate model of the structure without requiring more information than that needed to index a powder pattern.

After establishing the space group and the Wyckoff positions of the atoms in the initial structure of $BaRuO_3$, our final model has been derived by simply minimizing the R index defined by Eq. [4], i.e., by reducing the extent to which the valence sum rule is violated over the whole structure. This result indicates that the need to satisfy the valence requirements of the atoms as much as possible is an important factor in determining the magnitude and the direction of the atomic shifts allowed by the constraints of symmetry. As we have mentioned previously, however, not only must the violation of the valence sum rule be kept as low as possible in a relaxation process, but also the configuration of the coordination polyhedra around each atom must be kept as regular as possible. These two criteria must be balanced one against the other. In fact, we have a better chance to minimize R when the number of adjustable positional parameters is large (i.e., when the symmetry of the space group is low), but, at the same time, the larger this number the more the atoms can be shifted from their symmetrically optimal positions and the more difficult it will be to contain the distortions of the coordination polyhedra within acceptable limits.

To test this conclusion, the structure of $BaRuO_3$ was also modeled with the same 4-layer sequence and the same relaxation procedure used for $TRuO_3$ (8) and similarly the structure of $TRuO_3$ was also modeled with the same 9-layer sequence and the same relaxation procedure used for $BaRuO_3$ (it is worth noting that the coordination polyhedra of Ru and Ba are identical in the $R\bar{3}m$, 9-layer and in the $P6_3/mmc$, 4-layer structures). The reliability indices R, $r_d(i)$, and $r_o(i)$ of the resulting four configurations are shown in Table 6. As expected, in both $TRuO_3$ and $BaRuO_3$ the R indices are lower in the less constrained 9-layer structure than in the 4-layer structure, while the opposite is true for the $r_d(i)$ and $r_o(i)$ indeces. In going from the 9- to the 4-layer model, the R index of $BaRuO_3$ increases from 0.14 to 0.21 *v.u.*, i.e., at the limit of stability of the structure, and therefore it seems logical to think that in this case it is the value of R that drives the compound to assume the 9-layer structure, despite the larger distortion of some of the Ba and Ru coordination polyhedra. For $TRuO_3$, on the other hand, R increases from 0.11 *v.u.* to a still acceptable value of 0.15 *v.u.*, and consequently the symmetry of the coordination polyhedra becomes more important than the value of R in determining the final configuration of the $TRuO_3$ structure.

TABLE 6
Reliability Indices for the 4-Layer and 9-Layer Models of $TRuO_3$ and $BaRuO_3$

	$TRuO_3$		$BaRuO_3$	
	4-layer	9-layer	4-layer	9-layer
r_d(BaT1)	0.06	0.06	0.05	0.05
r_d(BaT2)	0.01	0.08	0.01	0.04
r_d(Ru1)		0.00		0.00
r_d(Ru2)	0.00	0.00	0.00	0.00
r_o(BaT1)	0.11	0.10	0.12	0.13
r_o(BaT2)	0.12	0.15	0.13	0.16
r_o(Ru1)		0.18		0.19
r_o(Ru2)	0.11	0.10	0.11	0.10
R	0.15	0.11	0.21	0.14

Attempts to derive and interpret in a similar way the structures of $SrRuO_3$, $SrCoO_3$, and $BaCoO_3$ are now underway, and preliminary results look promising. We are well aware, however, that these examples, being too few in number and too restricted in generality, do not allow us to reach firm conclusions about the applicability of the method used in this work to structural types other than perovskites.

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