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The Distorted Perovskite $Sr(Na_{1/4}Sb_{3/4})O_3$: A Novel Example of 1 : 3 *B*-Cation Ordering

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Powder neutron diffraction data (λ = 1.909 Å), have been used to refine the crystal structure of the ordered perovskite $Sr(Na_{1/4}Sb_{3/4})O_3$ at 295 K. This compound is monoclinic, **a** = 8.0913(2), **b** = 8.0871(1), **c** = 8.0918(2) Å, β = 89.953(1)°, with space group $P2_1/n$, $Z = 8$. $R_p = 4.27$, $R_{wp} = 5.43$, and $R_I = 3.44$. The fairly distorted NaO_6 and SbO_6 octahedra, ordered in a 1 : 3 three-dimensional arrangement, are tilted according to a system similar to that of the $GdFeO_3$ structure. The tilting angles for the four kinds of octahedra have been obtained from the atomic positional parameters. Sr atoms are in strongly asymmetrical environments, coordinated to 12 oxygens, in agreement with bond-valence calculations.

Introduction

The ideal perovskite structure, with general formula ABO_3 (unit-cell parameter **a** = $\mathbf{a}_0$) consists essentially of a framework of parallel BO_6 octahedra linked by their corners, with a large *A* atom occupying a void of about the same size as that of an oxygen atom. If the radius of *A* is too small, the void is reduced in size by tilting of the octahedra. Megaw (*1*), Glazer (*2*), and O'Keeffe and Hyde (*3*) analyzed these tilts in terms of regular octahedra of the same size. The effect of tilting, widely extended, is a predominant feature which determines the overall space-group symmetry of a particular perovskite.

On the other hand, when the octahedral *B* sites are occupied by two different cations, an ordered arrangement between them is to be expected if their sizes or charges are different enough. A large number of perovskites showing 1 : 1 and 1 : 2 *B* cation orderings, with stoichiometries $A(B'_{1/2}B''_{1/2})O_3$ and $A(B'_{1/3}B''_{2/3})O_3$, respectively, are well known (*4*), while the examples of 1 : 3 ordered compounds, $A(B'_{1/4}B''_{3/4})O_3$, are by far more scarce. Among them, the perovskites $Ba(M_{1/4}Sb_{3/4})O_3$ (*M* = Li, Na) (*5, 6*) show a cubic body centered structure, **a** = $2\mathbf{a}_0$, with space group $Im\bar{3}m$, in which the alkali element occupies the center and vertices of the unit cell and Sb locates at the center of the faces and the middle point of the edges.

When the *A* cation of an ordered perovskite is too small, the corresponding tilting effect is more difficult to analyze, since the tilt angles are different for the distinct octahedra contained in the framework. The precise structure determination of these oxides by X-ray diffraction is particularly difficult as the superlattice reflec-

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tions associated with the tilting of the octahedra arise from the oxygen atoms, weak scatterers if compared with the *A* and *B* atoms; hence neutron diffraction measurements are more suitable for these determinations.

A number of 1 : 1 ordered perovskites showing the tilting effect have been studied by neutron powder diffraction (*7–10*). This work aims to report the synthesis and structure of the compound $Sr(Na_{1/4}Sb_{3/4})O_3$, which simultaneously exhibits 1 : 3 *B*-cation ordering and rotation of the BO_6 octahedra.

Experimental

$Sr(Na_{1/4}Sb_{3/4})O_3$ was prepared as a white powder by solid state reaction among analytical grade $SrCO_3$, Na_2CO_3, and Sb_2O_3. The alkali carbonate was in excess (20%) so as to offset its partial volatilization in the first stages of the synthesis. The sample was ground, pelletized, and heated in air several times, in alumina crucibles, at increasing temperatures between 953 and 1213 K. After each thermal treatment (18 hr) the product was characterized by X-ray diffraction. The Na content was analyzed by emission spectrophotometry.

The X-ray powder diffraction pattern was obtained using a Siemens Kristalloflex 810 generator, Cu*Kα* radiation (λ = 1.540598 Å), a D 500 goniometer, and *W*, **a** = 3.16524(4) Å, as an internal standard. The **a** parameter of the pseudocubic unit cell was determined from the 2θ values of the last seven strong peaks of the diagram, in the range $90° < 2\theta < 156°$.

The neutron powder diffraction data were collected in the high resolution diffractometer D1A at ILL Grenoble, with the experimental conditions listed in Table 1.

TABLE I

EXPERIMENTAL CONDITIONS FOR THE COLLECTION OF THE NEUTRON POWDER DIFFRACTION DATA

Temperature: 295 K
Monochromatic beam: reflection 511 of a Ge monochromator
Wavelength: 1.909 Å
Sample container: Cylindrical vanadium can, 15 mm diameter
2θ angular range: $6° < 2\theta < 157°$, steps 0.05°
Time required: 20 hr

The neutron diffraction pattern was analyzed by the Rietveld (*11*) method, using the Young and Wiles (*12*) profile refinement program, which employs a Newton–Raphson algorithm to minimize the function $x = \Sigma w_i[y_i - (1/c)y_{ci}]^2$, where y_i and y_{ci} are the observed and calculated data points, w_i is the statistical weight ($w_i = 1/\sigma i$), and *c* is the scale factor. A Pearson VII function was chosen to generate the line shape of the diffraction peaks. The coherent scattering lengths for Sr, Na, Sb, and O were 7.02, 3.63, 5.461, and 5.804 fm, respectively (*13*).

In the final $P2_1/n$ structural model a number of 48 parameters were refined, including background coefficients; zeropoint; half-width, Pearson and asymmetry parameters for the peak shape; scale factor; positional, thermal isotropic, and unit-cell parameters; and Sr, Na, and Sb occupancy factors. Thermal and occupancy factors for the nonequivalent Sr and Sb atoms were constrained in order to reduce the total number of variable parameters. Atomic parameters marked with an asterisk in Table II were defined as $\frac{1}{4}$ or $\frac{3}{4}$ since, while refined, they converged to very close values with large standard deviations. The maximum value of Δ/σ in the final refinement cycle was 0.11.

Results

X-ray powder diffraction. All the reflections of the X-ray powder diffraction pattern of $Sr(Na_{1/4}Sb_{3/4})O_3$ could be indexed in a cubic cell with **a** = 8.0972(3) Å. A series of relatively strong superstructure reflec-

TABLE II

FINAL PARAMETERS FOR $Sr(Na_{1/4}Sb_{3/4})O_3$ AT 295 K WITH ESD'S IN PARENTHESES

Atom	Site	$x/\mathbf{a}$	$y/\mathbf{b}$	$z/\mathbf{c}$	B (Å^2)	Occ.
Sr1	4(*e*)	0.2514(13)	$\frac{1}{4}^a$	0.2401(10)	1.33(3)	0.988(4)
Sr2	4(*e*)	0.2405(10)	$\frac{3}{4}^a$	0.7678(7)	1.33(3)	0.988(4)
Na	2(*a*)	0	0	0	1.43(29)	0.972(24)
Sb1	2(*b*)	0	0	$\frac{1}{2}$	0.41(6)	0.976(8)
Sb2	2(*c*)	$\frac{1}{2}$	0	$\frac{1}{2}$	0.41(6)	0.976(8)
Sb3	2(*d*)	$\frac{1}{2}$	0	0	0.41(6)	0.976(8)
O1	4(*e*)	0.2646(14)	−0.0316(16)	0.0406(13)	1.68(15)	1
O2	4(*e*)	−0.0188(16)	−0.0259(22)	0.2645(17)	2.69(16)	1
O3	4(*e*)	0.0228(12)	0.2656(17)	0.0287(11)	1.73(11)	1
O4	4(*e*)	0.5304(15)	0.0269(26)	$\frac{1}{4}^a$	2.16(16)	1
O5	4(*e*)	0.4529(8)	$\frac{1}{4}^a$	−0.0253(11)	1.11(11)	1
O6	4(*e*)	$\frac{1}{4}^a$	0.0332(17)	0.4742(16)	0.42(14)	1

Note. $\mathbf{a} = 8.0913(2)$, $\mathbf{b} = 8.0871(1)$, $\mathbf{c} = 8.0918(2)$ Å, $\beta = 89.953(1)°$, S.G. $P2_1/n$ (No. 14), $Z = 8$. $R_p = 4.27$, $R_{wp} = 5.43$, $R_{Ex} = 2.61$, $R_I = 3.44\%$.

[a] Defined parameters: see text.

tions was observed (hkl, $h + k + l = 2n$) similar to those described for the analogous perovskite $Ba(Na_{1/4}Sb_{3/4})O_3$ (*6*), arising from the ordering between Na and Sb.

Considering a first model based on the $Ba(Na_{1/4}Sb_{3/4})O_3$ structure ($Im\bar{3}m$, $Z = 8$, Sr at 8(*c*), Sb at 6(*b*), Na at 2(*a*), O1 at 12(*d*), and O2 at 12(*e*) positions) and using X-ray scattering factors, a discrepancy factor of 4.5% was obtained for 40 integrated intensities corresponding to reflections with $h + k + l = 2n$. This result shows that Na and Sb exhibit the same kind of 1 : 3 ordering in both Sr and Ba perovskites. This ordering allows a maximum distance, $\sqrt{3}\mathbf{a}_0$, between every two Na ions.

However, a closer examination of the X-ray diagram for the Sr compound showed the existence of an additional series of very weak ($I_0 < 1\%$) superstructure peaks, which could also be indexed in the cubic $\mathbf{a} = 2\mathbf{a}_0$ unit cell, the only extinction condition being $h00$, $h \neq 2n$. This second series of extra lines was thought to be related to the tilting of BO_6 octahedra and was studied by neutron diffraction.

Neutron powder diffraction. In a first approach the neutron diffraction data were refined in a trial model based on the $GdFeO_3$ structure (*14*), in which a random distribution of Na and Sb on the *B* sites of the perovskite was supposed. The setting chosen was that which gave the space group as *Pnma*, with orthorhombic lattice parameters $\mathbf{a} \simeq \mathbf{c} \simeq \sqrt{2}\mathbf{a}_0$, $\mathbf{b} \simeq 2\mathbf{a}_0$; $Z = 4$, and atomic positions as follows: Sr at 4(*c*), Na/Sb at 4(*b*) and two kinds of oxygen atoms, O1 at 4(*c*) and O2 at 8(*d*). Good discrepancy *R* factors were obtained ($R_p = 6.60$, $R_{wp} = 8.61$, $R_I = 5.76\%$ for 161 reflections), although several observed superstructure lines are not allowed in the assumed space group (obviously those lines arising from the Na/Sb ordering, not taken into account in this simplified model). However, this result was useful in determining the kind of octahedral tilt system, $\mathbf{a}^-\mathbf{b}^+\mathbf{a}^-$ in the Glazer nomenclature (*2*).

When the 1 : 3 ordering between Na and Sb is incorporated to this tilting model the **n**, **m**, and **a** symmetry elements of the orthorhombic cell are lost. A new unit cell ($\mathbf{a} \simeq \mathbf{b} \simeq \mathbf{c} \simeq 2\mathbf{a}_0$) with double volume ($Z = 8$) must be considered, in which a new **n** plane appears. This leads to the monoclinic space group $P2_1/n$ (No. 14, unique axis **b**).

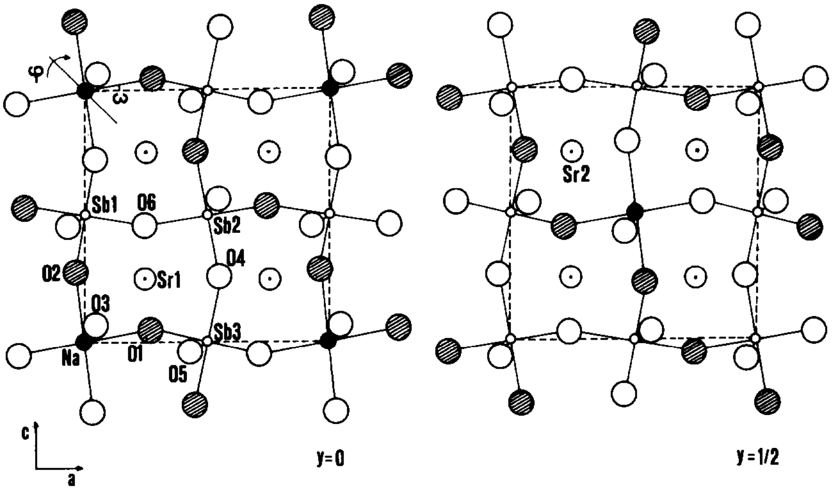

FIG. 1. Projection along [010] of the $Sr(Na_{1/4}Sb_{3/4})O_3$ structure showing the octahedra tilt system. The centers of the octahedra at the first layer are at height 0 and those of the second at height $\frac{1}{2}$. Open circles denote O atoms above the plane of the diagram while hatched circles are those below. For the first and second diagrams Sr atoms are at heights $\frac{1}{4}$ and $\frac{3}{4}$, respectively. The dashed line limits the crystallographic unit cell. ω and ϕ rotation angles are indicated for NaO_6 octahedron.

Figure 1 shows the final structural model considered in the refinement of the structure. Final atomic parameters are given in Table II, and selected interatomic distances can be found in Table III. The agreement between the observed and calculated profile of the data is shown in Fig. 2.

Discussion

The structure of $Sr(Na_{1/4}Sb_{3/4})O_3$ can be described as a perovskite constituted by fairly distorted NaO_6 and SbO_6 octahedra which share corners giving rise to a 1 : 3 three-dimensional ordered arrangement, as shown in the STRUPLO (*15*) view of Fig. 3. Sr atoms are placed in strongly asymmetrical environments between the octahedra.

SbO_6 octahedra are smaller than those of NaO_6 and show two shorter Sb–O distances (those corresponding to the Sb–O–Na bonds).

All octahedra are rotated in order to reduce the size of the void occupied by the Sr atoms. Megaw's analysis (*1*) for the $GdFeO_3$ ($CaTiO_3$)-type tilt system used two independent rotation angles, ω about [010] and ϕ about [101] of the aristotype, interactions between the two being negligibly small.

In the case of perovskites with more than one type of octahedra, different ω and ϕ angles have to be defined for each one. The expressions corresponding to perovskites of general formula $A(B'_{1/2}B''_{1/2})O_3$, showing 1 : 1 B cation ordering, were derived by Groen *et al.* (*16*). The formulae for the calculation of the rotation angles of $B'O_6$ and $B''O_6$ octahedra about [010] (ω) and [$\bar{1}$01] (ϕ) in ordered $A(B_{1/4}B_{3/4})O_3$ perovskites from the oxygen atomic positions in $P2_1/n$ are given in Table IV. Table V lists the values of ω and ϕ calculated for $Sr(Na_{1/4}Sb_{3/4})O_3$ (see also Fig. 1).

In order to compare the magnitude of the rotation of the octahedra in this perovskite with those observed in other compounds showing the same tilting system, it is useful to calculate the rotation angles corresponding to the trial *Pnma* model, in which a ran-

TABLE III

ATOMIC DISTANCES (Å) AND ANGLES (°) FOR $Sr(Na_{1/4}Sb_{3/4})O_3$ AT 295 K, WITH ESD'S IN PARENTHESES

Sr1-O1	2.79(1)	Sr2-O1	2.83(1)
-O1	2.51(1)	-O1	3.38(1)
-O2	3.13(2)	-O2	2.88(2)
-O2	2.82(2)	-O2	2.66(2)
-O3	2.52(1)	-O3	3.07(1)
-O3	3.21(1)	-O3	2.69(1)
-O4	2.89(2)	-O4	2.59(2)
-O4	3.20(2)	-O4	2.82(2)
-O5	2.70(1)	-O5	2.51(1)
-O5	3.07(1)	-O5	3.24(1)
-O6	2.58(1)	-O6	2.73(1)
-O6	2.87(1)	-O6	3.30(1)
Mean	2.86	Mean	2.89
Calculated	2.84	Calculated	2.84
Na-O1	2.18(1)×2	O1-Na-O2	84.7(4)
-O2	2.16(1)×2	O1- -O3	90.94(4)
-O3	2.17(1)×2	O2- -O3	89.8(5)
Mean	2.17		
Calculated	2.42		
Sb1-O2	1.92(1)×2	O2-Sb1-O5	90.4(6)
-O5	2.067(2)×2	O2- -O6	89.6(4)
-O6	2.051(2)×2	O5- O6	87.5(4)
Mean	2.01		
Calculated	2.00		
Sb2-O3	1.92(1)×2	O3-Sb2-O4	89.8(6)
-O4	2.049(3)×2	O3- -O6	91.3(4)
-O6	2.051(2)×2	O4- -O6	90.2(4)
Mean	2.01		
Calculated	2.00		
Sb3-O1	1.95(1)	O1-Sb3-O4	88.0(5)
-O4	2.049(3)	O1- -O5	88.0(4)
-O5	2.068(2)	O4- -O5	90.9(6)
Mean	2.02		
Calculated	2.00		

dom distribution of Na and Sb was supposed. For this space group O'Keeffe and Hyde (*3*) proposed a tilting description based on a sole rotation angle ϕ_0 about different [111] directions of the aristotype. ϕ_0 can be obtained from the y parameter of the oxygen at 8(*d*), from the formula $\phi_0 = \mathrm{arctg}[-y(O2)\sqrt{48}]$. For $Sr(Na_{1/4}Sb_{3/4})O_3$ the refinement of the neutron diffraction data in *Pnma* led to $y(O2) = -0.0263(4)$, therefore, $\phi_0 = 10.3°$. This angle, similar to that found in the mineral perovskite itself, $CaTiO_3$, is small in comparison to the value found in the majority of compounds showing this tilting system. For example, a sequence across a range of rotation angles from $\phi = 15°$ to $\phi = 23°$ was observed for the lanthanoid orthoferrites $LnFeO_3$ (*17*), from *Ln* = La to *Ln* = Lu.

On the other hand, the rotation angles can be derived not only from the atomic positional parameters but also from the unit-cell parameters, **a**, **b**, **c**, according to the expression (*3*) $\phi_0' = \arccos[\sqrt{2}c^2/(ab)]$. The difference between the calculated values of ϕ_0 and ϕ_0' for a given compound indicates the degree of distortion of the octahedra. For $Sr(Na_{1/4}Sb_{3/4})O_3$ (lattice parameters for the orthorhombic *Pnma* model: $\mathbf{a} = 5.7186(2)$, $\mathbf{b} = 8.0882(3)$, $\mathbf{c} = 5.7220(2)$ Å), the value of ϕ_0' is close to zero, owing to the strong pseudo-cubic character of the unit cell; hence, a strong distortion of the octahedra could be expected for this compound, as, in effect, it occurs.

In many perovskites with tilted octahedra the coordination polyhedron of the *A* atom can be described as a bicapped prism

TABLE IV

EXPRESSIONS FOR THE CALCULATION OF THE TILT ANGLES ω AND ϕ (DEFINED IN THE TEXT) FOR $B'O_6$ AND $B''O_6$ OCTAHEDRA IN $A(B'_{1/4}B''_{3/4})O_3$ PEROVSKITES

$$\omega(B') = \tfrac{1}{2}\,\mathrm{arctg}\left[\frac{\mathbf{z}(O1)}{\mathbf{x}(O1)}\cdot\frac{\mathbf{c}}{\mathbf{a}}\right] + \tfrac{1}{2}\,\mathrm{arctg}\left[\frac{-\mathbf{x}(O2)}{\mathbf{z}(O2)}\cdot\frac{\mathbf{a}}{\mathbf{c}}\right]$$

$$\phi(B') = \mathrm{arctg}\{[\mathbf{x}(O3)^2\mathbf{a}^2 + \mathbf{z}(O3)^2\mathbf{c}^2]^{1/2}/\mathbf{y}(O3)\mathbf{b}\}$$

$$\omega(B''1) = \tfrac{1}{2}\,\mathrm{arctg}\left[\frac{\frac{1}{2} - \mathbf{z}(O6)}{\mathbf{x}(O6)}\cdot\frac{\mathbf{c}}{\mathbf{a}}\right] + \tfrac{1}{2}\,\mathrm{arctg}\left[\frac{\mathbf{x}(O2)}{\mathbf{z}(O2) - \frac{1}{2}}\cdot\frac{\mathbf{a}}{\mathbf{c}}\right]$$

$$\phi(B''1) = \mathrm{arctg}\{[(\tfrac{1}{2} - \mathbf{x}(O5))^2\mathbf{a}^2 + \mathbf{z}(O5)^2\mathbf{c}^2]^{1/2}/(\tfrac{1}{2} - \mathbf{y}(O5))\mathbf{b}\}$$

$$\omega(B''2) = \tfrac{1}{2}\,\mathrm{arctg}\left[\frac{\frac{1}{2} - \mathbf{z}(O6)}{\frac{1}{2} - \mathbf{x}(O6)}\cdot\frac{\mathbf{c}}{\mathbf{a}}\right] + \tfrac{1}{2}\,\mathrm{arctg}\left[\frac{\mathbf{x}(O4) - \frac{1}{2}}{\frac{1}{2} - \mathbf{z}(O4)}\cdot\frac{\mathbf{c}}{\mathbf{a}}\right]$$

$$\phi(B''2) = \mathrm{arctg}\{[\mathbf{x}(O3)^2\mathbf{a}^2 + \mathbf{z}(O3)^2\mathbf{c}^2]^{1/2}/(\tfrac{1}{2} - \mathbf{y}(O3)\mathbf{b})\}$$

$$\omega(B''3) = \tfrac{1}{2}\,\mathrm{arctg}\left[\frac{\mathbf{z}(O1)}{\frac{1}{2} - \mathbf{x}(O1)}\cdot\frac{\mathbf{c}}{\mathbf{a}}\right] + \tfrac{1}{2}\,\mathrm{arctg}\left[\frac{\mathbf{x}(O4) - \frac{1}{2}}{\mathbf{z}(O4)}\cdot\frac{\mathbf{a}}{\mathbf{c}}\right]$$

$$\phi(B''3) = \mathrm{arctg}\{[\tfrac{1}{2} - \mathbf{x}(O5))^2\mathbf{a}^2 + \mathbf{z}(O5)^2\mathbf{c}^2]^{1/2}/\mathbf{y}(O5)\mathbf{b}\}$$

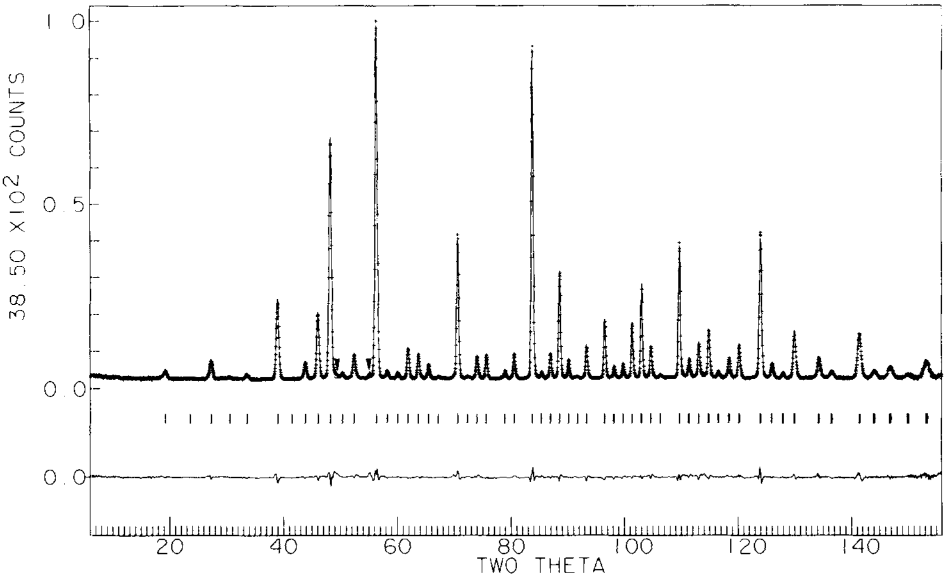

FIG. 2. Observed (crosses), calculated (full line), and difference (down) neutron powder diffraction diagrams of $Sr(Na_{1/4}Sb_{3/4})O_3$ at 295 K. Arrows indicate reflections corresponding to small amounts of $SrSb_2O_5$.

or a distorted Archimedes antiprism, in which the coordination number has changed from 12 (aristotype) to 8 (*3*, *16*). In $Sr(Na_{1/4}Sb_{3/4})O_3$ the calculation of the bond valences (*18*) of Sr–O bonds (Table VI) shows that a coordination number of 12 should be considered to obtain a sum of bond valences close to 2 (valence of Sr atoms). In this compound the rotation of the octahedra is not large enough to lower the Sr coordination number to 8.

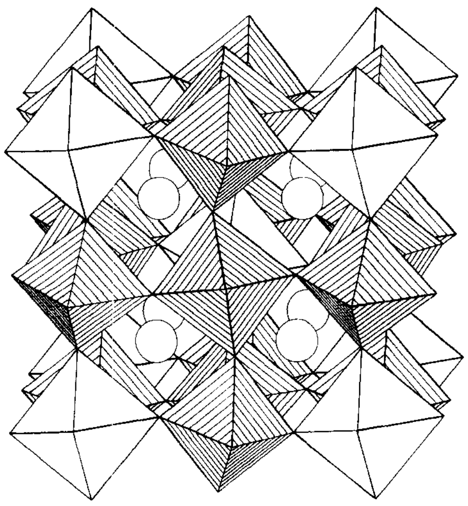

FIG. 3. STRUPLO (*15*) view of the structure. Open octahedra correspond to Na atoms, and hatched octahedra to Sb atoms. Both kinds of octahedra alternate according to a 1 : 3 ordered arrangement. Sr atoms (open circles) are in the voids formed by the octahedra.

The mean Sr–O, Na–O, and Sb–O distances (Table III) and those calculated as sums of the Shannon (*19*) ionic radii (for Sr, Sb, Na, and O coordination numbers of 12, 6, 6, and 6, respectively) compare for Sb and Sr atoms, while for Na–O bonds the observed distances are fairly shorter than those calculated. As a general fact, the

TABLE V

ROTATIONAL ANGLES (°), ω AND ϕ, FOR NaO_6 AND SbO_6 OCTAHEDRA IN $Sr(Na_{1/4}Sb_{3/4})O_3$

	NaO_6	$Sb1O_6$	$Sb2O_6$	$Sb3O_6$
ω	6.4	5.2	6.4	8.4
ϕ	7.9	12.1	8.9	12.1

TABLE VI

Bond Valence Values for Sr Calculated as $s = [\exp(r_0 - r)/B]$ ($B = 0.37$, $r_0 = 2.118$)

Sr–O1	0.163	Sr–O1	0.146
–O1	0.347	–O1	0.033
–O2	0.065	–O2	0.128
–O2	0.150	–O2	0.231
–O3	0.337	–O3	0.076
–O3	0.052	–O3	0.213
–O4	0.124	–O4	0.279
–O4	0.054	–O4	0.150
–O5	0.207	–O5	0.347
–O5	0.076	–O5	0.048
–O6	0.287	–O6	0.193
–O6	0.131	–O6	0.041
Valence (Σs)	1.993	Valence (Σs)	1.883

ionic-radii sum rule does not seem to be useful for pervoskites in which voluminous (i.r. > 1 Å) alkali, earth alkaline, or lanthanoid elements occupy the *B*-cation positions, the calculations always leading to larger values. As representative examples, the observed Na–O distance in the ordered $BaLa(NaW)O_6$ (*20*) is 2.14 Å (calculated, 2.42 Å); the mean observed Sr–O distance in Ba_2SrUO_6 (*9*) is 2.462 Å (calculated, 2.54 Å); and the observed Y–O distance in Sr_2YRuO_6 (*10*) is 2.202 Å (calculated, 2.30 Å).

On the other hand, the hypothesis of a partial inversion of the Na and Sb positions as an explanation for the abnormally short Na–O distances has to be discarded in view of the refined occupancy factors for both elements, within 1 (Na atom) and 3 (Sb atoms) standard deviations of the theoretical values. The difference of scattering lengths for Na and Sb is large enough to allow the detection of such an inversion. Hence, this result suggests that the ordering between Na and Sb is complete in this compound.

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References

1. H. D. Megaw, *J. Phys. (Paris) Suppl. (C2)* **33,** 1 (1972).
2. A. M. Glazer, *Acta Crystallogr. Sect. B* **28,** 3384 (1972).
3. M. O'Keeffe and B. Hyde, *Acta Crystallogr. Sect. B* **33,** 3802 (1977).
4. S. Nomura, "Landolt-Börnstein Zahlenwerte und Functionen aus Naturwissenchaften und Technik, Neue Series" (K. H. Hellwege and A. M. Hellwege, Eds.), Gruppe III, Band 12a, 368, Springer-Verlag, Berlin (1978).
5. A. J. Jacobson, B. M. Collins, and B. E. F. Fender, *Acta Crystallogr. Sect. B* **30,** 1705 (1974).
6. J. A. Alonso, E. Mzayek, and I. Rasines, *Mater. Res. Bull.* **22,** 69 (1987).
7. P. D. Battle and W. J. Macklin, *J. Solid State Chem.* **54,** 245 (1984).
8. H. C. Duivenboden and D. J. W. Ijdo, *Acta Crystallogr. Sect. C* **42,** 523 (1986).
9. W. A. Groen and D. J. W. Ijdo, *Acta Crystallogr. Sect. C* **43,** 1033 (1987).
10. P. D. Battle and C. W. Jones, *J. Solid State Chem.* **78,** 108 (1989).
11. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969).
12. R. A. Young and D. B. Wiles, *J. Appl. Crystallogr.* **15,** 430 (1982).
13. L. Koester, H. Rauch, M. Herkens, and K. Schröeder, Report 1755, Kernforschungsanlage, Jülich, Federal Republic of Germany (1981).
14. P. Coppens and M. Eibschütz, *Acta Crystallogr.* **19,** 524 (1965).
15. R. X. Fischer, *J. Appl. Crystallogr.* **18,** 258 (1985).
16. W. A. Groen, F. P. F. van Berkel, and D. J. W. Ijdo, *Acta Crystallogr. Sect. C* **42,** 1472 (1986).
17. M. Marezio, J. P. Remeika, and P. D. Dernier, *Acta Crystallogr. Sect. B* **26,** 2008 (1970).
18. I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B* **41,** 244 (1985).
19. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
20. P. D. Battle, *Mater. Res. Bull.* **9,** 1041 (1974).