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# $Ba_2Ce_{3/4}SbO_6$, a Rietveld Refinement of Neutron Powder Diffraction Data

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**Abstract.** Dibarium cerium antimonate, $Ba_2Ce_{3/4}SbO_6$, $M_r = 597.52$, tetragonal, $I4/mmm$. At room temperature, $a = 8.4562$ (1), $c = 17.0002$ (4) Å, $V = 1215.64$ (2) Å$^3$, $Z = 8$, $D_x = 6.5297$ (1) Mg m$^{-3}$, $\mu R = 0.15$, $\lambda = 2.5717$ (1) Å, $R_{wp} = 2.85\%$. The structure has been refined using Rietveld analysis of neutron powder diffraction data recorded for 106 reflections. The structure is a perovskite with complete order of $CeO_6$ and $SbO_6$ octahedra. Ordered vacancies in the cerium sublattice give rise to a superstructure.

**Introduction.** In a research project concerned with investigation of uranium perovskites, the structures of $A_2BUO_6$, $A$ = Ba, Sr, Ca and $B$ = Sr and Ca, were determined (Groen & IJdo, 1987; IJdo, 1993). Also, perovskites with vacancies on the $B$ site are known (Rauser & Kemmler-Sack, 1980); some examples are $Ba_2Sm_{2/3}UO_6$, $Ba_2Ce_{3/4}SbO_6$ and $Ba_2Zr_{3/4}SbO_6$. Ordering of the vacancies is indicated by the occurrence of superstructures, but details of these structures are unavailable at present. Because $Sb^{V}$ and $U^{V}$ in oxides sometimes give rise to isomorphous compounds (Cordfunke & IJdo, 1988), the study of the structure of $Ba_2Ce_{3/4}SbO_6$ is attractive in relation to the perovskite phases in nuclear fuel elements. This paper deals with the crystal structure of $Ba_2Ce_{3/4}SbO_6$.

Treiber & Kemmler-Sack (1980*a*) reported an ochre-coloured compound with a tetragonal superstructure of the perovskite type [$a = 11.954$ Å $\simeq 2a_p\sqrt{2}$, $c = 17.000$ Å $\simeq 4a_p$, $P4/mmm$, where $a_p$ is the lattice parameter of a simple cubic perovskite $ABO_3$]. A model structure was given suggested by X-ray powder diffraction data; however, the positions of the O atoms could not be determined accurately.

**Experimental.** AR starting materials $BaO_2$, $CeO_2$ and $Sb_2O_3$ were thoroughly mixed in an agate mortar in the appropriate ratios. The mixture was heated in an alumina crucible in air at 973 K for 1 d, at 1273 K for 1 d, and at 1523 K for 7 d with repeated grinding. In addition, the compound was annealed at 1273 K for 1 d and cooled in air to room temperature.

X-ray diffraction patterns were obtained at room temperature with a Philips 1050 diffractometer by step scanning in the range $5 < 2\theta < 90°$, with $\Delta(2\theta) = 0.05°$, $t = 3$ s per step. All calculations were made with the program *DBW*3.2*S* version 8804 (Young & Wiles, 1982). Electron diffraction data were collected with a Siemens Elmiskop 102 electron microscope: double tilt; lift cartridge; 100 kV. The electron diffraction patterns showed a tetragonal unit cell with $a \simeq 2a_p$ and $c \simeq 4a_p$ with systematic absences for $h + k + l = 2n + 1$, indicating the space group $I4/mmm$ or a lower one. Refinement of the X-ray powder diffrac-

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tion data using a perovskite model with ordered $CeO_6$ and $SbO_6$ octahedra and vacancies on the Ce sublattice gave $R_{wp} = 18.7\%$. Space group $I4/m$ gives no better results.

For more accurate O-atom positions, a sample of about 25 g was prepared for neutron powder diffraction data collection on the powder diffractometer at the Petten High-Flux Reactor. Experimental details are as reported earlier (Groen & IJdo, 1987). Maximum absorption correction was < 1%; $\mu R = 0.15$ (Weber, 1967). Coherent scattering lengths were: Ba 5.25, Ce 4.84, Sb 5.64 and O 5.805 fm (Koester, Rauch, Herkens & Schroeder, 1981). $\Delta/\sigma < 0.3$ in the final cycle. Some unreacted $CeO_2$ and a trace of $BaSb_2O_6$ were present and refined as separate phases. 42 parameters were included in the refinement: three scale factors for the three phases, three half-width parameters defining the Gaussian-like shape of the reflections, the counter zero error, six background parameters, unit-cell parameters, atomic positional parameters, isotropic thermal parameters (overall thermal parameters for the minority phases) and an asymmetry parameter. The largest correlation-matrix element for structural parameters was 0.35. The final $R$ values obtained were $R_p = 2.08$, $R_{wp} = 2.85\%$ ($w_i = 1/y_i$), with $R_{exp} = 1.77\%$, giving $S = 1.61$.

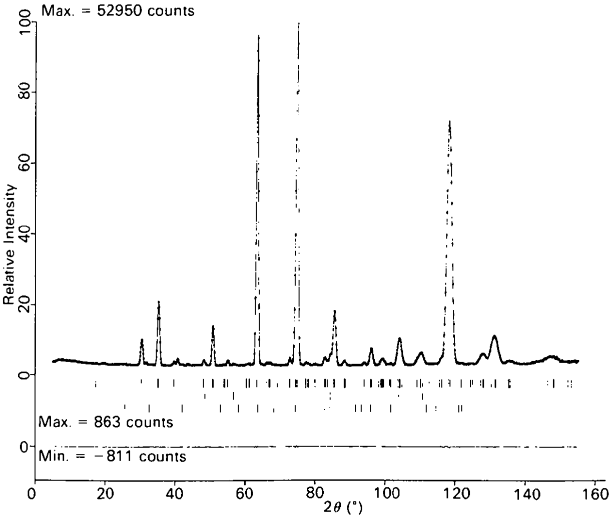

Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of $Ba_2Ce_{3/4}SbO_6$ at room temperature. A difference (observed − calculated) curve appears at the bottom of the plot. Tick marks below the profile indicate the position of the Bragg reflections included in the calculation for $Ba_2Ce_{3/4}SbO_6$, $CeO_2$ and $BaSb_2O_6$.

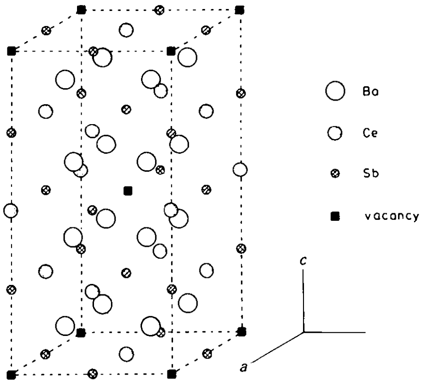

Fig. 2. The structure of $Ba_2Ce_{3/4}SbO_6$; O atoms are omitted for clarity.

Table 1. *Fractional atomic coordinates and thermal parameters* (Å$^2$) *for* $Ba_2Ce_{3/4}SbO_6$ *at room temperature*

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| Ba | 0.2306 (2) | 0.2306 (2) | 0.1167 (2) | 0.98 (4) |
| Ce1 | 0 | 0 | 0.5 | 0.45 (7) |
| Ce2 | 0.5 | 0 | 0.25 | 0.45 (7) |
| Sb1 | 0.5 | 0 | 0 | 0.09 (5) |
| Sb2 | 0 | 0 | 0.2555 (4) | 0.09 (5) |
| O1 | 0.5 | 0.2382 (6) | 0 | 1.71 (16) |
| O2 | 0 | 0 | 0.6302 (4) | 0.68 (19) |
| O3 | 0.2378 (4) | 0 | 0.2546 (1) | 0.78 (10) |
| O4 | 0.2706 (5) | 0 | 0 | 0.49 (14) |
| O5 | 0 | 0 | 0.1400 (3) | 0.87 (18) |
| O6 | 0.5 | 0 | 0.1193 (3) | 1.05 (13) |

Table 2. *Atomic distances* (Å) *and angles* (°) *in* $Ba_2Ce_{3/4}SbO_6$ *at room temperature*

| | | | |
|---|---|---|---|
| Ba—O1 | 3.022 (3) × 2 | Ba—O4 | 2.802 (3) × 2 |
| —O2 | 3.230 (2) | —O5 | 2.786 (2) |
| —O3 | 3.050 (3) × 2 | —O6 | 2.999 (2) × 2 |
| —O3 | 3.170 (3) × 2 | | |
| $CeO_6$ octahedra | | | |
| Ce1—O1 | 2.214 (5) × 4 | O3—Ce2—O3 | 175.96 (9) |
| —O2 | 2.213 (7) × 2 | O3—Ce2—O6 | 92.02 (4) |
| Ce2—O3 | 2.219 (3) × 4 | | |
| —O6 | 2.222 (5) × 2 | | |
| $SbO_6$ octahedra | | | |
| Sb1—O1 | 2.014 (5) × 2 | O2—Sb2—O3 | 90.44 (20) |
| —O4 | 1.940 (4) × 4 | O3—Sb2—O3 | 179.13 (40) |
| Sb2—O2 | 1.943 (10) | | |
| —O3 | 2.011 (3) × 4 | | |
| —O5 | 1.964 (9) | | |

**Discussion.** Atomic parameters are given in Table 1 and selected distances in Table 2. The agreement between the observed and calculated data is shown in Fig. 1.* The structure is shown in Fig. 2.

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* Primary diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55743 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0294]

The structure of $Ba_2Ce_{3/4}SbO_6$ may be described as a perovskite structure with ordering of nearly regular $CeO_6$ and $SbO_6$ octahedra. Owing to the formula there are two empty octahedra, at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ in the Ce sublattice. Each $CeO_6$ octahedron shares corners with six $SbO_6$ octahedra. The $Sb1O_6$ octahedron shares corners with five $CeO_6$ octahedra and the $Sb2O_6$ octahedron shares corners with six $CeO_6$ octahedra. There is no tilting of the octahedra as was reported for $BaCeO_3$ (Jacobson, Tofield & Fender, 1972) and $Ba_2SrUO_6$ (Groen & IJdo, 1987).

The Ba atoms are shifted from their ideal positions at $\frac{1}{4}\frac{1}{4}\frac{1}{8}$ in the direction of the vacancy, leading to short Ba—O4 and Ba—O5 distances (Table 2). The coordination of Ba to O atoms is 12 as in a regular cubic perovskite.

The Ce—O distances are in good agreement with similar distances reported for $BaCeO_3$ (Jacobson, Tofield & Fender, 1972). The Sb—O distances are in agreement with those found in $SbO_6$ octahedra in $Sr_2Sb_2O_7$ (Groen & IJdo, 1988). The model of Treiber & Kemmler-Sack (1980*a*) has been confirmed using a reduced unit cell.

Treiber & Kemmler-Sack (1980*b*) reported that $Ba_2Zr_{3/4}SbO_6$ has the same structure as $Ba_2Ce_{3/4}SbO_6$. From their X-ray diffraction data it can be derived that $Ba_2Zr_{3/4}SbO_6$ has an *I*-centred tetragonal lattice with about the same lattice parameters and intensity distribution as the title compound. In conclusion, we have for $Ba_2Zr_{3/4}SbO_6$: $a = 8.2625$ (5), $c = 16.605$ (5) Å, *I4/mmm*, $Z = 8$.

Betz, Schittenhelm & Kemmler-Sack (1982) report for low-temperature $Ba_2Ca_{1/4}Y_{1/2}UO_6$ an orthorhombic face-centred structure with $a \simeq b \simeq 2a_p\sqrt{2}$ and $c \simeq 4a_p$ with the same structure as $Ba_2Ce_{3/4}SbO_6$. Using the program *LINES*2.0 (de Graaff, 1990), their X-ray data could be refined tetragonally with $a = 8.667$ (6), $c = 17.36$ (1) Å with all reflections $h + k + l = 2n$, so it is likely that this compound has the same structure as the title compound.

The authors are indepted to Mr G. H. Renes for the collection of the electron diffraction pattern.

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# $Pb_3U_{11}O_{36}$, a Rietveld Refinement of Neutron Powder Diffraction Data

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**Abstract.** Trilead undecauranate, $Pb_3U_{11}O_{36}$, $M_r = 3815.88$, orthorhombic, *Pmmn*. At $T = 295$ K, $a = 28.459$ (1), $b = 8.3790$ (3), $c = 6.7650$ (3) Å, $V = 1613.2$ (1) Å$^3$, $Z = 2$, $D_x = 7.854$ Mg m$^{-3}$, $\mu R = 0.11$, $\lambda = 2.5700$ (1) Å, $R_p = 2.94$, $R_{wp} = 3.99\%$. The structure has been refined by Rietveld analysis of neutron powder diffraction data for 427 reflections. The structure is closely related to $\alpha$-$U_3O_8$.

**Introduction.** In the system Pb–U–O, several compounds have been reported but only the crystal structures of $Pb_3UO_6$ (Sterns, 1967) and $PbUO_4$ (Cremers, Eller, Larson & Rozenzweig, 1986) have been determined. In the system $PbO$–$UO_3$, Polunina, Kovba & Ippolitova (1973) report the existence of $Pb_{11}U_5O_{26}$ and $Pb_3U_{11}O_{36}$ in addition to the compounds already mentioned. In the present paper the

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