PREPARATION AND CRYSTALLOGRAPHIC STUDIES OF STRONTIUM PLUTONATE

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Although complex oxide systems of plutonium with divalent metal ions have been found to be possible in number of cases (Russell *et al* 1960; Chackraburtty *et al* 1963), yet so far no difinite crystallographic studies have been reported about the complex oxide system of plutonium with strontium ion.

Specpure strontium carbonate was heated to its oxide, which was mixed with freshly prepared plutonium dioxide in the ratio necessary for the formation of SrPuO_a and finally was heated to 1300°C-1500°C in tantalum crucible in a resistance furnace similar to that described by Drummond et al (1957). The diffraction patterns of the samples were taken in a 19 cm. Unicam camora in copper radiation. In addition to diffraction lines due to unreacted plutonium dioxide, extra lines were noticed which could be partly indexed by a cubic cell. By assuming simple shear of the cubic cell leaving 'a' and 'c' axis equal but 'b' axis slightly different, a monoclinic cell was obtained which could explain the data with a $a = 4.280 \pm 0.006$ Å, $b = 4.276 \pm 0.006$ Å, $c = 4.280 \pm 0.006$ Å and $\beta = 92^{\circ} 28'$, having one formula unit per cell. The substance was found to be isostructural with CaTiO₃ (Megaw 1946, Naray Szabo 1943). Geometrically, the above lattice so obtained could have ortho-rhombic symmetry and could be referred to a new a and c axes which were the diagonals of the (010) face of the monoclinic cell. The orthorhombic cell, derived from this consideration, has the following values: $a = 5.980 \pm 0.006$ Å, $b = 4.276 \pm 0.006$ Å and $c = 6.114 \pm 0.006$ Å. The 'b' face, in this case, appeared to be face-centred. Indexing of the lines could be done on this basis, and from the consideration of symmetrical lattice obtained, the present (orthorhombic) indexing seems to be more preferable. For comparison, indexed data on monoclinic and orthorhombic cells are presented in Table I. Spectrophotometric studies indicated the valency of plutonium in IV state, hence it was concluded that strontium plutonate with a molecular formula SrPuO₃ was a complex oxide system in the group of perovskite compounds.

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| TABLE I | | | | | | | | | | |
|--------------|--------|---------|----------------------------|-----------------|---|--|--|--|--|--|
| Dat | te for | SrPu(| $D_3 \ (\lambda = 1.5418)$ | 3Å) | | | | | | |
| Orthorhombic | unit | cell is | derived from | n monoclinic ce | n | | | | | |

| dÅ* | q ₀ ² × 10 ⁻⁴ | qc ² ×10 ⁻⁴ | Monoclinic indexing** hkl | Orthorhombic indexing*** hkl | Intensity |
|-------|--|-----------------------------------|---------------------------------|------------------------------------|---------------|
| 4.278 | 325 | 3 25 | 100 | 010, 101 | |
| 3.046 | 641 | 636 | 101 | 002 | v. w . |
| 3.015 | 645 | 650 | 011 | 111 | V.8. |
| 2.982 | 668 | 664 | 101 | 200 | w * |
| 2.498 | 954 | 961 | 111 | 012 | ₩ |
| 2.461 | 981 | 989 | 111 | 210 | ₩. |
| 2.133 | 1306 | 1300 | 200 | 020 | m+ |
| 1.756 | 1926 | 1922 | 211 | 113 | m. |
| 1.739 | 1977 | 1978 | 211 | 311 | m+ |
| 1.536 | 2536 | 2544 | 202 | 004 | ₩. |
| 1.512 | 2601 | 2600 | 022 | 212 | m.w. |
| 1.497 | 2656 | 2653 | 202 | 400 | m.w |
| 1.350 | 3260 | 3250 | 031 | 131, 313 | m+ |
| 1.281 | 3619 | 3617 | 311 | 412 | v.w . |
| 1.186 | 4224 | 4225 | 032 | 323 | ₩. |
| 1.137 | 4598 | 4592 | 321 | 422 | w. |
| | | | | | |

*For unreacted plutonium dioxide the following $d(\text{\AA})$ values are obtained (in brackets estimated intensities are given): $3.112(m^+)$; 2.698 (w); $1.910(m^+)$; 1.628 (m); $1.558(w^-)$; 1.239 (w); 1.208 (w); 1.104 (w); 1.039 (w⁻); $0.913\alpha_1$, (w⁺); $0.855\alpha_1$, (w); $0.824\alpha_1$ (w). These lines could be indexed with cubic cell a = 5.40 Å (fluorite type).

**For monoclinic indexing, as $a^*=b^*=c^*$, by equivalence number of hkl indices are possible for many of the indexing planes.

***From the indexed data in orthorhombic case, the possible conditions limiting the reflections are, for hkl planes, h+1=2n present; hoo planes, h=2n present and 001 planes, l=2n present. This could indicate a B centred lattice.

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