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As part of a continuing program at this laboratory to investigate the chemical and physical properties of the heavy actinide elements and their compounds, a study of element 97 has been undertaken.

To date these investigations have included solution absorption studies of the tripositive berkelium ion and the preparation and crystallographic characterization of the berkelium oxides, trichloride, oxychloride, and fluorides.

The most successful absorption experiments were carried out using a newly-developed microabsorption cell, consisting of two small (100 μ diameter) quartz rods between which was placed a small volume of Bk⁺³ (aq) solution (3-5 nanoliters containing 4 μ g Bk²⁴⁹). A suitably-modified Cary Model 14 Recording Spectro-photometer served as the measuring device, yielding spectra with 15 peaks between 320 and 700 m μ . The two strongest peaks observed were at 417 and 474 m μ . The observed spectral features are in excellent agreement with those seen by Gutmacher et al. $\frac{1}{2}$ at the Livermore branch of the Lawrence Radiation Laboratory.

An attempt to observe the tetrapositive berkelium solution absorption spectrum by electrolytically oxidizing the Bk^{+3} (aq) solution while loaded on the cell was unsuccessful. It was concluded that the failure resulted from the bulk

solution acting as a reducing medium upon the tetrapositive berkelium ions formed locally at the anode.

About 16 μ g of Bk²⁴⁹ were recovered and purified by extraction from an aqueous nitrate solution with di-(2-ethylhexyl)orthophosphoric acid, followed by stripping of the organic phase with a peroxide in nitric acid solution. The aqueous berkelium solution was then further purified by standard ion-exchange techniques. Mass analysis determined total cerium and neodymium content to be 0.27 and 0.06 atom per cent, respectively.

This purified material was absorbed on Dowex 50 (ca. 10 ppm ash) resin beads of about 200 nanogram capacity each. Employing the techniques described by Cunningham² and Green,³ the following series of reactions was performed to prepare the indicated berkelium compounds:

Bk loaded air resin bead
$$\frac{\text{BkO}_2}{1200^{\circ}\text{C}}$$
 BkO₂ $\frac{\text{H}_2}{600^{\circ}\text{C}}$ BkCl₃ $\frac{\text{HCl/H}_2\text{O}}{520^{\circ}\text{C}}$ BkCl₃ $\frac{\text{N}_2 \text{ carrier}}{500^{\circ}\text{C}}$ BkOCl

The fluorides were prepared from the oxides by reaction with $\rm H_2/HF$ mixtures and $\rm F_2$ gas. Several independent samples (all containing \geq 95 atom per cent $\rm Bk^{249}$) of these compounds were characterized by use of x-ray powder techniques. $\rm BkO_2$ exhibited the face-centered cubic (fluorite) structure; $\rm Bk_2O_3$, the $\rm Mn_2O_3$ -type body-centered cubic structure; $\rm BkCl_3$, the UCl₃-type hexagonal structure; $\rm BkOCl$, the PbFCl-type tetragonal structure; and $\rm BkF_3$ appeared to exhibit two stable modifications, the YF₃-type orthorhombic structure and the LaF₃-type trigonal structure, the latter one being the high temperature form.

Comparisons between the lattice parameters of these berkelium compounds and other similar actinide compounds consistently show evidence of the so-called "actinide contraction." Similar comparisons to corresponding lanthanide compounds and the behavior of the berkelium-fluorine system provide additional important evidence for the continuing rare-earth-like character of the actinide elements beyond the point of the half-filled 5f subshell.

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