ABSORPTION SPECTROPHOTOMETRIC STUDY OF BERKELIUM(III) AND (IV) FLUORIDES IN THE SOLID STATE[†]

D. D. ENSOR[‡] and J. R. PETERSON Department of Chemistry, University of Tennessee, Knoxville. TN 37916, U.S.A.

and

Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN 37830, U.S.A.

and

R. G. HAIRE and J. P. YOUNG§

Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN 37830, U.S.A.

(Received 11 February 1980; received for publication 13 July 1980)

Abstract—Absorption spectrophotometry has been used to study the dimorphic BkF_3 system and BkF_4 in the solid state. LaF₃-type trigonal BkF_3 can be distinguished from YF₃-type orthorhombic BkF_3 by subtle, but reproducible, differences in their corresponding absorption spectra. This ability emphasizes the sensitivity of absorption spectrophotometric analysis, since both crystal modifications of BkF_3 have the same metal ion coordination number of nine. The absorption spectrum of BkF_4 (UF₄-type monoclinic structure) is reported for the first time.

INTRODUCTION

Previous investigations of berkelium(III) halides in the solid state have shown the utility of absorption spectrophotometry in identifying the dimorphism exhibited by tribromide trichloride compounds the and of berkelium [1, 2]. In the BkBr₃ work it was shown that the absorption spectrum of the six-coordinate (AlCl₃-type monoclinic) BkBr₃ differed from that of the eight-coordinate (PuBr₃-type orthormbic) BkBr₃ in both intensity and shape of the Bk(III) absorption peaks[1]. A similar result was obtained in the BkCl₃ case, where eight coordinate (PuBr₃-type orthorhombic) BkCl₃ was distinguished from nine coordinate (UCl₃-type hexagonal) BkCl₃[2]. The BkF₃ system provides another and more difficult test of the sensitivity of absorption spectrophotometry in that both known crystallographic forms exhibit a metal ion coordination number of nine[3]. We report here the absorption spectra of the LaF₃-type trigonal and YF₃-type orthorhombic forms of BkF₃, as well as that of UF₄-type monoclinic BkF₄.

EXPERIMENTAL

The ²⁴⁹Bk used in this work was produced and made available as part of the U.S. Dept. of Energy's program of transplutonium element production and research. The Bk(III) solution was purified in accord with standard procedures [4]. The starting materials for the preparation of BkF₃ and BkF₄ were BkO₂ and/or BkF₃. The dioxide was prepared by calcination of berkelium oxalate (air, 1000°C) precipitated from aqueous solution with oxalic acid. The trifluoride starting material resulted from drying in air BkF₃ precipitated from aqueous solution with hydrofluoric acid.

Samples of BkO₂ and BkF₃ between 10 and 20 μ g were placed in platinum vessels and treated with anhydrous HF in a Monel tube furnace which opened into a helium atmosphere gloved box. Samples of BkF₃ exhibiting the orthorhombic crystal structure were obtained when either starting material was heated to 540-600°C in 1-2 atm total pressure of an HF/Ar mixture (HF ≥ 0.5 atm) for 18-24 hr and then quickly cooled to room temperature. Samples of BkF₃ in the trigonal crystal form were prepared by heating BkO₂ at 300-400°C in 1-2 atm of an HF/Ar mixture for 12-24 hr.

Samples of BkF₄ were prepared by treatment of the precipitated BkF₃ with either F_2 or ClF₃ at 2-3 atm pressure. A reaction temperature of 400-500°C for 48 hr followed by slow cooling to room temperature was found to produce the most crystalline samples. During the BkF₄ synthesis the F_2 or ClF₃ gas was evacuated at least once and fresh fluorinating gas was introduced into the system.

After cooling to ambient temperature, each berkelium fluoride sample was transferred to a quartz capillary tube which was flame sealed under a partial helium atmosphere. This sample-containing capillary tube allowed both X-ray powder diffraction and absorption spectrophotometric analyses to be carried out on the sample[2].

RESULTS AND DISCUSSION

X-Ray diffraction

The trigonal and orthorhombic crystal forms of BkF₃ were confirmed by the results of X-ray powder diffraction analysis. In Fig. 1 are calculated powder patterns[5] based on $\lambda = 1.54178$ Å and the previously reported lattice parameters[3], assuming the atomic coordinates of LaF₃[6] for those of trigonal BkF₃, the atomic coordinates of YF₃[7] for those of orthorhombic BkF₃, and including no corrections for sample absorption. Based on the identification of the 15 observed lines in one of the best powder patterns, the precipitated BkF₃ samples

[†]Presented in part at the 30th Southeastern Regional Meeting of the American Chemical Society, Savannah, GA, 8–10 November 1978. Research sponsored by the Divisions of Nuclear and Chemical Sciences, U.S. Dept. of Energy under Contracts DE-AS05-76ER04447 with the University of Tennessee (Knoxville) and W-7405-eng-26 with the Union Carbide Corp.

ville) and W-7405-eng-26 with the Union Carbide Corp. ‡Present address: Department of Chemistry, Tennessee Technological University, Cookeville, TN 38501, U.S.A.

^{\$}Analytical Chemistry Division, Oak Ridge National Laboratory.



Fig. 1. Calculated X-ray powder diffraction patterns for YF₃- type orthorhombic BkF₃, LaF₃-type trigonal BkF₃ and UF₄-type monoclinic BkF₄.

were found to exhibit the LaF₃-type trigonal structure. No evidence of the orthorhombic form was found in this powder pattern based on the absence of its strongest lines at $2\theta = 27.2$ and 29.4° . Treatment of such BkF₃ samples with anhydrous HF at temperatures below 450°C failed to convert them into the orthorhombic form.

Samples of BkF₃ exhibiting the YF₃-type orthorhombic structure were obtained from high-temperature hydrofluorination and were identified by comparing their powder diffraction patterns with the calculated one in Fig. 1. Even the best pattern identified as the orthorhombic structure exhibited a weak line (<5% of the intensity of the strongest line in the orthorhombic pattern) at $2\theta = 28.4^{\circ}$, which corresponds to the strongest line in the trigonal pattern. The presence of a small amount of the trigonal form in the chiefly orthorhombic modification is consistent with previous observations [3].

The synthesis of BkF₄ was also confirmed by the results of X-ray powder diffraction analysis. The lattice parameters calculated from the X-ray data obtained were $a_0 = 12.46 \pm 0.01$ Å, $b_0 = 10.48 \pm 0.01$ Å, $c_0 = 8.14 \pm 0.01$ Å, and $\beta = 126.02 \pm 0.06^\circ$. These values are in agreement with previously reported values [8, 9].

Absorption spectrophotometry

The room-temperature spectra of the trigonal and orthorhombic forms of BkF₃ are reproduced in Fig. 2. The spectrum of the orthorhombic form contains two peaks centered at 13.5×10^5 and 12×10^5 m⁻¹, which are attributed to Cf(III)[10] present as the result of the β^- decay of ²⁴⁹Bk (²⁴⁹Cf grows in at an initial rate of 0.22%/d). The features which distinguish between the



Fig. 2. Absorption spectra of the trigonal and orthorhombic forms of BkF_3 at room temperature.

spectra of the two forms are found in their relative peak heights and peak shapes. The trigonal form of BkF₃ has an absorption band at $16 \times 10^5 \text{ m}^{-1}$ that displays symmetric splitting in contrast to the more asymmetric splitting observed in the absorption of orthorhombic BkF₃ at the same wave number. The absorption peaks at 21.5×10^5 and $23.5 \times 10^5 \text{ m}^{-1}$ in the trigonal BkF₃ spectrum exhibit asymmetric character, whereas the analogous absorption peaks in the orthorhombic BkF₃ spectrum are more nearly symmetric. Based on the observation of several spectra from different BkF₃ samples, we have concluded that these differences are real and are not merely due to differences in sample crystallinity.

Absolute comparisons between the two spectra are precluded on the basis of the irregular shapes of the various trifluoride samples which lead to uncertainty in the path length of the sample. Also, the microscope spectrophotometer is a single beam instrument, so that a final sample spectrum is produced only by subtracting a non-exact background or reference spectrum from the observed sample spectrum [2]. Qualitatively, however, the most easily distinguishable spectral characteristics are found in the absorption peaks at 21.5×10^5 and $23.5 \times$ 10^s m⁻¹. In orthorhombic BkF₃ these peaks have similar relative absorbances, whereas in trigonal BkF₃ the peak at 21.5×10^5 m⁻¹ has a greater relative absorbance. The BkF₃ absorption peaks at 9.8×10^5 and 16×10^5 m⁻¹ exhibit small, but reproducible, changes in relative absorbance in the two crystal modifications. In trigonal BkF₃ these two peaks have comparable intensities, but in orthorhombic BkF₃ the peak at 16×10^5 m⁻¹ is the more intense one. Apparently the weak (forbidden) f-f transitions in Bk(III) are sensitive to changes in the metal ion's environment, even though there is no difference in the metal ion's coordination number in the two crystal modifications. By weight averaging the nine Bk-F bond distances in each structural form, one finds average Bk-F distances of 2.368 Å in the orthorhombic form and 2.375 Å in the trigonal form[3]. The fact that these structural changes are clearly reflected by absorption spectral



Fig. 3. Absorption spectrum of monoclinic BkF₄ at room temperature.

changes underscores the sensitivity of spectrophotometric analysis. The enhanced Bk(III) absorption observed in orthorhombic BkF_3 over that observed in trigonal BkF_3 (see Fig. 2) might suggest a less centrosymmetric position for Bk(III) in the former structure than that in the latter structure.

The absorption spectrum of BkF₄ is shown in Fig. 3. Absence of characteristic Bk(III) absorption peaks at 9.8×10^5 and 21.5×10^5 m⁻¹ confirms the oxidation of Bk(III) to Bk(IV) as verified by the X-ray data. The BkF₄ spectrum is characterized by major absorption bands at $16.2-16.9 \times 10^5$, 17.8×10^5 and four sharp peaks between 22×10^5 and 25×10^5 m⁻¹. This absorption spectrum of BkF₄ in the solid state is similar to the one obtained earlier in phosphate media[11], although the spectral resolution in the present case is much improved. The steeply rising baseline in the spectrum (Fig. 3) can be attributed to a very intense electron transfer band in Bk(IV) at ~ 35.7×10^5 m⁻¹[11].

The absorption spectrum of a BkF₄ sample was followed as a function of time. After 6 month's (\sim 33% Cf ingrowth) storage at ambient temperature, the BkF₄ sample spectrum exhibited new absorption peaks which matched those found in the absorption spectrum of directly synthesized CfF₄[12]. Maintenance of the metal ion's oxidation state through β^- decay is consistent with the results of a recent study of the chemical consequences of the β^- decay of ²⁴⁹BkBr₃[13].

Acknowledgement—One of us (D.D.E.) gratefully acknowledges financial support from the faculty research participation program (travel contract) administered by the Oak Ridge Associated Universities for the U.S. Dept. of Energy.

REFERENCES

- J. R. Peterson, R. L. Fellows, J. P. Young and R. G. Haire, Proc. 2nd Int. Conf. on the Electronic Structure of the Actinides, Wrockaw, Poland, 13-16 September 1976 (Edited by J. Mulak, W. Suski and R. Troć), p. 111. Ossolineum (1977).
- J. P. Young, R. G. Haire, R. L. Fellows and J. R. Peterson, J. Radioanal. Chem. 43, 479 (1978).
- J. R. Peterson and B. B. Cunningham, J. Inorg. Nucl. Chem. 30, 1775 (1968).
- R. D. Baybarz, J. B. Knauer and P. B. Orr, Oak Ridge National Laboratory Document ORNL-4672 (1973).
- D. K. Smith, University of California, Lawrence Radiation Laboratory Document UCRL-7196 (1963).
- A. Zalkin, D. H. Templeton and T. E. Hopkins, *Inorg. Chem.* 5, 1466 (1966).
- 7. A. Zalkin and D. H. Templeton, J. Am. Chem. Soc. 75, 2453 (1953).
- L. B. Asprey and R. G. Haire, *Inorg. Nucl. Chem. Lett.* 9, 1121 (1973).
- 9. H. O. Haug and R. D. Baybarz, Inorg. Nucl. Chem. Lett. 11, 847 (1975).
- J. P. Young, K. L. Vander Sluis, G. K. Werner, J. R. Peterson and M. Noé, *J. Inorg. Nucl. Chem.* 37, 2497 (1975).
- R. D. Baybarz, J. R. Stokely and J. R. Peterson, J. Inorg. Nucl. Chem. 34, 739 (1972).
- 12. D. D. Ensor, J. R. Peterson, R. G. Haire and J. P. Young, Unpublished work.
- J. P. Young, R. G. Haire, J. R. Peterson, D. D. Ensor and R. L. Fellows, *Inorg. Chem.* 19, 2209 (1980).